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PREFACE

With the Boards having a weightage (40%) for admission through JEE Main the need of a book that can help students both in JEE Main and Boards becomes more prominent. The All New "Objective Chemistry for JEE Main with Boards Score Booster" encapsulates the formula for cracking Boards & JEE Main simultaneously.

Salient features of Disha's "Objective Chemistry for JEE Main with Boards Score Booster" book are:

- Fully Solved 2015 JEE Main Question paper has been added.
- Exhaustive theory, with solved examples, explaining all fundamentals/ concepts to build a strong base.
- Illustrations to master applications of concepts & sharpen problem-solving skills.
- 4 level of graded exercises to ensure sufficient practice.
- 1200+ NCERT based Questions (Boards Score Booster) for Board exams covered in a separate exercise.
- 1500+ past Competitive Exam MCQ's of JEE Main/ AIEEE and other entrance exams to provide a better exposure covered in the exercise "Window to Competitive Exams."
- 3500+ Practice MCQ's for the JEE Main exam. Finally 2 Practice exercises at the end of each chapter – Basic and Applied.
- The book covers all variety of questions as per the format of the previous year AIEEE/ JEE Main Papers.
- The book has a very strong focus on Practical Skills as per the syllabus of JEE Main exam and the questions that have been asked in previous exams. The book covers Volumetric Analysis, Analytical Chemistry and other practical skills as per the syllabus of JEE Main.
- Covers entire syllabus as per the latest NCERT books and JEE Main syllabus. The complete book has been aligned as per the chapter flow of NCERT class 11 & 12 books. At places certain chapters have been divided into sub-chapters. For example - Equilibrium is divided into 2 parts Part A – Chemical Equilibrium; Part B – Ionic Equilibrium.

More than 25 out of the 30 JEE Main questions were directly or indirectly covered in our book and the readers must have really benefitted from it.

We are highly thankful to the Disha Publication team who continuously encouraged us to update this book. We are also thankful to the editorial team and the D.T.P. Team who worked day & night for bringing this work before you. We would like to give a special thanks to **Mr. Kulpreet Singh** (Sr. SME - Chemistry) who has really spent a lot of time in bringing this book to the present shape.

Last but not the least we would request all readers to come up with suggestions so that we can further improve the book in the next edition.

With best of luck!!

AUTHORS

DR. DALJEET SINGH
Ph.D., Delhi University
Professor of Chemistry (Retd.)
MM PG College, Meerut University,
Modinagar (U.P.)

ER. PRAMIT SINGH
B.Tech. MS
Concordia University, Montreal, Canada

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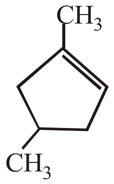
JEE MAIN 2015 CHEMISTRY

(Held on 4th April-2015)

1. Which compound would give 5 - keto - 2 - methylhexanal upon ozonolysis ?

(a)



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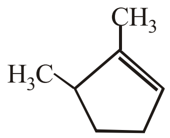

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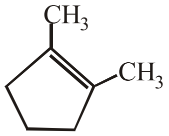
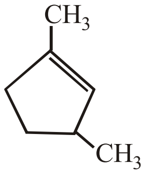


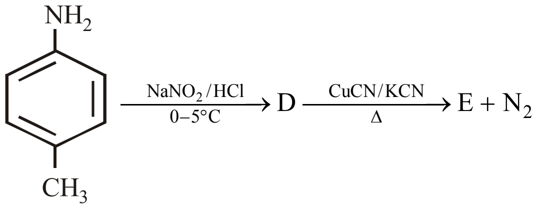
(d)



2. Which of the vitamins given below is water soluble ?
(a) Vitamin E (b) Vitamin K
(c) Vitamin C (d) Vitamin D

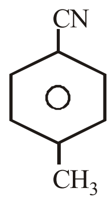
3. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy ?
(a) $BaSO_4$ (b) $SrSO_4$
(c) $CaSO_4$ (d) $BeSO_4$

4. In the reaction



the product E is :

(a)



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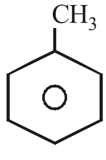
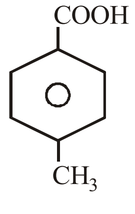


(c)



(d)

5. Sodium metal crystallizes in a body centred cubic lattice with a unit cell edge of 4.29Å. The radius of sodium atom is approximately :
(a) 5.72Å (b) 0.93Å
(c) 1.86Å (d) 3.22Å

6. Which of the following compounds is not colored yellow ?
(a) $(NH_4)_3[As(Mo_3O_{10})_4]$ (b) $BaCrO_4$
(c) $Zn_2[Fe(CN)_6]$ (d) $K_3[Co(NO_2)_6]$

7. Which of the following is the energy of a possible excited state of hydrogen ?
(a) –3.4 eV (b) +6.8 eV
(c) +13.6 eV (d) –6.8 eV

8. Which of the following compounds is not an antacid ?
(a) Phenelzine (b) Ranitidine
(c) Aluminium hydroxide (d) Cimetidine

9. The ionic radii (in Å) of N^{3-}, O^{2-} and F^- are respectively :
(a) 1.71, 1.40 and 1.36 (b) 1.71, 1.36 and 1.40
(c) 1.36, 1.40 and 1.71 (d) 1.36, 1.71 and 1.40

10. In the context of the Hall - Heroult process for the extraction of Al, which of the following statements is **false** ?
(a) Al^{3+} is reduced at the cathode to form Al
(b) Na_3AlF_6 serves as the electrolyte
(c) CO and CO_2 are produced in this process
(d) Al_2O_3 is mixed with CaF_2 which lowers the melting point of the mixture and brings conductivity

11. In the following sequence of reactions :

$$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$$

the product C is :
(a) $C_6H_5CH_2OH$ (b) C_6H_5CHO
(c) C_6H_5COOH (d) $C_6H_5CH_3$

12. Higher order (>3) reactions are rare due to :
(a) shifting of equilibrium towards reactants due to elastic collisions
(b) loss of active species on collision
(c) low probability of simultaneous collision of all the reacting species
(d) increase in entropy and activation energy as more molecules are involved

13. Which of the following compounds will exhibit geometrical isomerism ?
(a) 2 - Phenyl -1 - butene
(b) 1, 1 - Diphenyl - 1 - propene
(c) 1 - Phenyl - 2 - butene
(d) 3 - Phenyl -1 - butene

14. Match the catalysts to the correct processes :

	Catalyst		**Process**
(A)	$TiCl_4$	(i)	Wacker process
(B)	$PdCl_2$	(ii)	Ziegler - Natta polymerization
(C)	$CuCl_2$	(iii)	Contact process
(D)	V_2O_5	(iv)	Deacon's process

(a) (A) - (ii), (B) - (iii), (C) - (iv), (D) - (i)
(b) (A) - (iii), (B) - (i), (C) - (ii), (D) - (iv)
(c) (A) - (iii), (B) - (ii), (C) - (iv), (D) - (i)
(d) (A) - (ii), (B) - (i), (C) - (iv), (D) - (iii)

15. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is :

(a) London force (b) hydrogen bond

(c) ion - ion interaction (d) ion - dipole interaction

16. The molecular formula of a commercial resin used for exchanging ions in water softening is $C_8H_7SO_3^- Na^+$ (Mol. wt. 206. What would be the maximum uptake of Ca^{2+} ions by the resin when expressed in mole per gram resin ?

(a) $\frac{2}{309}$ (b) $\frac{1}{412}$

(c) $\frac{1}{103}$ (d) $\frac{1}{206}$

17. Two Faraday of electricity is passed through a solution of $CuSO_4$. The mass of copper deposited at the cathode is (at. mass of Cu = 63.5 amu)

(a) 2g (b) 127 g

(c) 0 g (d) 63.5 g

18. The number of geometric isomers that can exist for square planar complex $[Pt (Cl) (py) (NH_3) (NH_2OH)]^+$ is (py = pyridine) :

(a) 4 (b) 6

(c) 2 (d) 3

19. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is : (at. mass Ag =108; Br = 80)

(a) 48 (b) 60

(c) 24 (d) 36

20. The color of $KMnO_4$ is due to :

(a) L → M charge transfer transition

(b) σ - σ^* transition

(c) M → L charge transfer transition

(d) d – d transition

21. The synthesis of alkyl fluorides is best accomplished by :

(a) Finkelstein reaction (b) Swarts reaction

(c) Free radical fluorination (d) Sandmeyer's reaction

22. 3 g of activated charcoal was added to 50 mL of acetic acid solution (0.06N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal) is :

(a) 42 mg (b) 54 mg

(c) 18 mg (d) 36 mg

23. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass (g mol^{-1}) of the substance is :

(a) 128 (b) 488

(c) 32 (d) 64

24. Which among the following is the most reactive ?

(a) I_2 (b) ICl

(c) Cl_2 (d) Br_2

25. The standard Gibbs energy change at 300 K for the reaction $2A \rightleftharpoons B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is $[A] = \frac{1}{2}$, $[B] = 2$ and $[C] = \frac{1}{2}$. The reaction proceeds in the : [R = 8.314 J/K/mol, e = 2.718]

(a) forward direction because $Q < K_c$

(b) reverse direction because $Q < K_c$

(c) forward direction because $Q > K_c$

(d) reverse direction because $Q > K_c$

26. **Assertion:** Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.

Reason: The reaction between nitrogen and oxygen requires high temperature.

(a) The assertion is incorrect, but the reason is correct

(b) Both the assertion and reason are incorrect

(c) Both assertion and reason are correct, and the reason is the correct explanation for the assertion

(d) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion

27. Which one has the highest boiling point ?

(a) Kr (b) Xe

(c) He (d) Ne

28. Which polymer is used in the manufacture of paints and lacquers ?

(a) Polypropene (b) Polyvinyl chloride

(c) Bakelite (d) Glyptal

29. The following reaction is performed at 298 K.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The standard free energy of formation of NO(g) is 86.6 kj/mol at 298 K. What is the standard free energy of formation of $NO_2(g)$ at 298 K? ($K_p = 1.6 \times 10^{12}$)

(a) $86600 - \frac{\ln (1.6 \times 10^{12})}{R (298)}$

(b) $0.5[2 \times 86{,}600 - R(298) \ln(1.6 \times 10^{12})]$

(c) $R(298) \ln(1.6 \times 10^{12}) - 86600$

(d) $86600 + R(298) \ln(1.6 \times 10^{12})$

30. From the following statements regarding H_2O_2, choose the incorrect statement :

(a) It has to be stored in plastic or wax lined glass bottles in dark

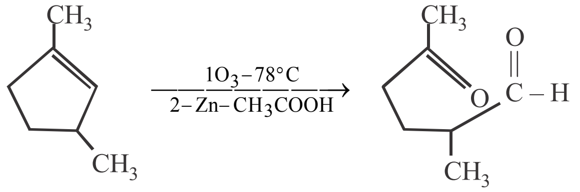
(b) It has to be kept away from dust

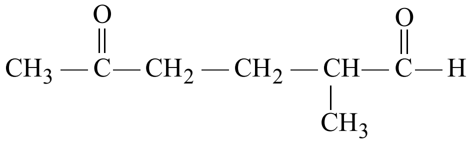
(c) It can act only as an oxidizing agent

(d) It decomposes on exposure to light

SOLUTIONS

1. **(d)** When 1, 3-dimethylcyclopentene is heated with ozone and then with zinc and acetic acid, oxidative cleavage leads to keto - aldehyde.





$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-H$$

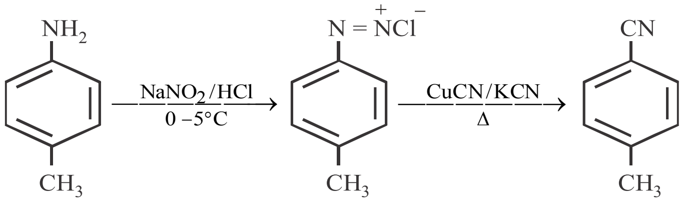
5- keto – 2 – methylhexanal

2. **(c)** Water-soluble vitamins dissolve in water and are not stored by the body. The water soluble vitamins include the vitamin B-complex group and vitamin C.

3. **(d)** In alkaline earth metals, ionic size increases down the group. The lattice energy remains constant because sulphate ion is so large, so that small change in cationic size does not make any difference. On moving down the group the degree of hydration of metal ions decreases very much leading to decrease in solubility.

$$\therefore\ BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$$

4. **(a)**



5. **(c)** In bcc the atoms touch along body diagonal

$$\therefore\quad 2r+2r=\sqrt{3}a$$

$$\therefore\quad r=\frac{\sqrt{3}a}{4}=\frac{\sqrt{3}\times 4.29}{4}=1.857\text{Å}$$

6. **(c)**

7. **(a)** Total energy $=\dfrac{-13.6Z^2}{n^2}$ eV

where $n = 2, 3, 4 ....$

Putting $n = 2$

$$E_T=\frac{-13.6}{4}=-3.4\text{eV}$$

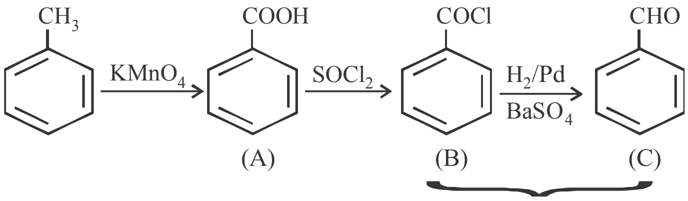
8. **(a)** Phenelzine is an antidepressant, while others are antacids.

9. **(a)** For isoelectronic species, size of anion increases as negative charge increases. Thus the correct order is

$$\begin{array}{ccccc} N^{3-} & > & O^{2-} & > & F^{-} \\ (1.71) & & (1.40) & & (1.36) \end{array}$$

10. **(b)** In the metallurgy of aluminium, purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 which lowers the melting point of the mix and brings conductivity.

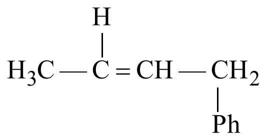
11. **(b)**



Rosenmund's reaction

12. **(c)** Reactions of higher order (>3) are very rare due to very less chances of many molecules to undergo effective collisions.

13. **(c)**



$$H_3C-\overset{\overset{H}{|}}{C}=CH-\underset{\underset{Ph}{|}}{CH_2}$$

1- Phenyl-2-butene the two groups around each of the doubly bonded carbon

Because, all are different. This compound can show *cis*-and *trans*-isomerism.

14. **(d)** (A) - (ii), (B) - (i), (C) - (iv), (D) - (iii)

15. **(b)** Hydrogen bond is a type of strong electrostatic dipole-dipole interaction and dependent on the inverse cube of distance between the molecular ion-dipole interaction $\propto \dfrac{1}{r^3}$.

16. **(b)** 2 mole of water softner require 1 mole of Ca^{2+} ion

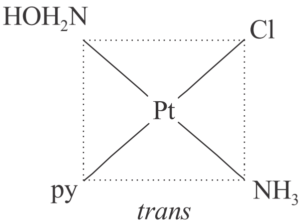
So, 1 mole of water softner require $\dfrac{1}{2}$ mole of Ca^{2+} ion

Thus, $\dfrac{1}{2\times 206}=\dfrac{1}{412}$ mol/g will be maximum uptake

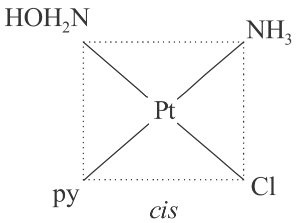
17. **(d)** $Cu^{2+}+2e^{-}\longrightarrow Cu$

2F i.e. 2 × 96500 C deposit Cu = 1 mol = 63.5 g

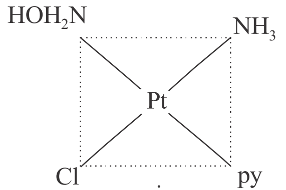
18. **(d)** Square planar complexes of type M[ABCD] form three isomers. Their position may be obtained by fixing the position of one ligand and placing at the *trans* position any one of the remaining three ligands one by one.



trans



cis



cis

19. **(c)** Mass of substance = 250 mg = 0.250 g
Mass of AgBr = 141 mg = 0.141 g
1 mole of AgBr = 1 g atom of Br
188 g of AgBr = 80 g of Br
∴ 188 g of AgBr contain bromine = 80 g

$$0.141 \text{ g of AgBr contain bromine} = \frac{80}{188} \times 0.141$$

This much amount of bromine present in 0.250 g of organic compound

$$\therefore \ \% \text{ of bromine} = \frac{80}{188} \times \frac{0.414}{0.250} \times 100 = 24\%$$

20. **(a)** L → M charge transfer spectra. $KMnO_4$ is colored because it absorbs light in the visible range of electromagnetic radiation. The permanganate ion is the source of color, as a ligand to metal, (L → M) charge transfer takes place between oxygen's *p* orbitals and the empty *d*-orbitals on the metal. This charge transfer takes place when a photon of light is absorbed, which leads to the purple color of the compound.

21. **(b)** Alkyl fluorides are more conveniently prepared by heating suitable chloro – or bromo-alkanes with organic fluorides such as AsF_3, SbF_3, CoF_2, AgF, Hg_2F_2 etc. This reaction is called **Swarts reaction**.

$$CH_3Br + AgF \longrightarrow CH_3F + AgBr$$

$$2CH_3CH_2Cl + Hg_2F_2 \longrightarrow 2CH_3CH_2F + Hg_2Cl_2$$

22. **(c)** Let the weight of acetic acid initially be w_1 in 50 ml of 0.060 N solution.

$$\text{Let the N} = \frac{w_1 \times 1000}{\text{M.wt.} \times 50} \qquad \text{(Normality} = 0.06\text{ N)}$$

$$0.06 = \frac{w_1 \times 1000}{60 \times 50}$$

$$\Rightarrow \quad w_1 = \frac{0.06 \times 60 \times 50}{1000} = 0.18 \text{ g} = 180 \text{ mg.}$$

After an hour, the strength of acetic acid = 0.042 N so, let the weight of acetic acid be w_2

$$N = \frac{w_2 \times 1000}{60 \times 50}$$

$$0.042 = \frac{w_2 \times 1000}{3000}$$

$\Rightarrow \ w_2 = 0.126 \text{ g} = 126 \text{ mg}$
So amount of acetic acid adsorbed per 3g
= 180 – 126 mg = 54 mg
Amount of acetic acid adsorbed per g

$$= \frac{54}{3} = 18 \text{ mg}$$

23. **(d)** Using relation,

$$\frac{p^\circ - p_s}{p_s} = \frac{w_2 M_1}{w_1 M_2}$$

where w_1, M_1 = mass in g and mol. mass of solvent
w_2, M_2 = mass in g and mol. mass of solute
Let $M_2 = x$
p° = 185 torr
p_s = 183 torr

$$\frac{185 - 183}{183} = \frac{1.2 \times 58}{100x} \quad \text{(Mol. mass of acetone} = 58)$$

$x = 64$
∴ Molar mass of substance = 64

24. **(b)** ICl
Order of reactivity of halogens
$Cl_2 > Br_2 > I_2$
But, the interhalogen compounds are generally more reactive than halogens (except F_2), since the bond between two dissimilar electronegative elements is weaker than the bond between two similar atoms i.e, X – X

25. **(d)** ΔG° = 2494.2J

$$2A \rightleftharpoons B + C.$$

R = 8.314 J/K/mol.
e = 2.718

$$[A] = \frac{1}{2}, [B] = 2, [C] = \frac{1}{2}$$

$$Q = \frac{[B][C]}{[A]^2} = \frac{2 \times 1/2}{\left(\frac{1}{2}\right)^2} = 4$$

$\Delta G^\circ = -2.303 \text{ RT} \log K_C.$
$2494.2 \text{ J} = -2.303 \times (8.314 \text{ J/K/mol}) \times (300\text{K}) \log K_C$

$$\Rightarrow \quad \log K_C = -\frac{2494.2 \text{ J}}{2.303 \times 8.314 \text{ J/K/mol} \times 300 \text{ K}}$$

$\Rightarrow \quad \log K_C = -0.4341$
$K_C = 0.37$
$Q > K_C.$

26. **(c)** Nitrogen and oxgen in air do not react to form oxides of nitrogen in atmosphere because the reaction between nitrogen and oxygen requires high temperature.

27. **(b)** Xe. As we move down the group, the melting and boiling points show a regular increase due to corresponding increase in the magnitude of their van der waal forces of attraction as the size of the atom increases.

28. **(d)** Glyptal is used in the manufacture of paints and lacquers.

29. **(b)** $\Delta G^\circ_{NO(g)} = 86.6\text{k J/mol} = 86600 \text{ J/mol}$
$G^\circ_{NO_2(g)} = x \text{ J/mol}$
$T = 298, K_p = 1.6 \times 10^{12}$
$\Delta G^\circ = -RT \ln K_P$
Given equation,

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

$\therefore \ 2\Delta G^\circ_{NO_2} - 2\Delta G^\circ_{NO} = -R(298) \ln (1.6 \times 10^{12})$
$2\Delta G^\circ_{NO_2} - 2 \times 86600 = -R(298) \ln (1.6 \times 10^{12})$
$2\Delta G^\circ_{NO_2} = 2 \times 86600 - R(298) \ln (1.6 \times 10^{12})$

$$\Delta G^\circ_{NO_2} = \frac{1}{2}\, [2 \times 86600 - R(298) \ln (1.6 \times 10^{12}]$$

$= 0.5\, [2 \times 86600 - R(298) \ln (1.6 \times 10^{12})]$

30. **(c)** H_2O_2 has oxidizing and reducing properties both.

JEE MAIN 2014 CHEMISTRY

(Held on 6th April-2014)

1. The correct set of four quantum numbers for the valence electrons of rubidium atom ($Z = 37$) is:

(a) $5, 0, 0, +\frac{1}{2}$ (b) $5, 1, 0, +\frac{1}{2}$

(c) $5, 1, 1, +\frac{1}{2}$ (d) $5, 0, 1, +\frac{1}{2}$

2. If Z is a compressibility factor, van der Waals equation at low pressure can be written as:

(a) $Z = 1 + \frac{RT}{Pb}$ (b) $Z = 1 - \frac{a}{VRT}$

(c) $Z = 1 - \frac{Pb}{RT}$ (d) $Z = 1 + \frac{Pb}{RT}$

3. CsCl crystallises in body centred cubic lattice. If 'a' is its edge length then which of the following expressions is correct?

(a) $r_{Cs^+} + r_{Cl^-} = 3a$ (b) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$

(c) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$ (d) $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$

4. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl method and the evolved ammonia was absorbed in 60 mL of $\frac{M}{10}$ sulphuric acid. The unreacted acid required 20 mL of $\frac{M}{10}$ sodium hydroxide for complete neutralization. The percentage of nitrogen in the compound is:

(a) 6% (b) 10%

(c) 3% (d) 5%

5. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.4 S m^{-1}. The resistance of 0.5 M solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5 M solution of the electrolyte in S m^2 mol^{-1} is:

(a) 5×10^{-4} (b) 5×10^{-3}

(c) 5×10^{3} (d) 5×10^{2}

6. For complete combustion of ethanol,

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l),$$

the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25°C. Assuming ideality the enthalpy of combustion, $\Delta_c H$, for the reaction will be:
($R = 8.314$ kJ mol^{-1})

(a) -1366.95 kJ mol^{-1} (b) -1361.95 kJ mol^{-1}

(c) -1460.95 kJ mol^{-1} (d) -1350.50 kJ mol^{-1}

7. The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_C and λ_∞, respectively. The correct relationship between λ_C and λ_∞ is given as:
(Where the constant B is positive)

(a) $\lambda_C = \lambda_\infty + (B)C$ (b) $\lambda_C = \lambda_\infty - (B)C$

(c) $\lambda_C = \lambda_\infty - (B)\sqrt{C}$ (d) $\lambda_C = \lambda_\infty + (B)\sqrt{C}$

8. Consider separate solutions of 0.500 M $C_2H_5OH(aq)$, 0.100 M $Mg_3(PO_4)_2(aq)$, 0.250 M $KBr(aq)$ and 0.125 M $Na_3PO_4(aq)$ at 25°C. Which statement is **true** about these solutions, assuming all salts to be strong electrolytes?

(a) They all have the same osmotic pressure.

(b) 0.100 M $Mg_3(PO_4)_2(aq)$ has the highest osmotic pressure.

(c) 0.125 M $Na_3PO_4(aq)$ has the highest osmotic pressure.

(d) 0.500 M $C_2H_5OH(aq)$ has the highest osmotic pressure.

9. For the reaction $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$, if $K_P = K_C(RT)^x$ where the symbols have usual meaning then the value of x is (assuming ideality):

(a) -1 (b) $-\frac{1}{2}$

(c) $\frac{1}{2}$ (d) 1

10. For the non - stoichimetre reaction $2A + B \rightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

Initial Concentration (A)	**Initial Concentration (B)**	**Initial rate of formation of C ($mol\ L^{-1}\ s^{-1}$)**
0.1 M	0.1 M	1.2×10^{-3}
0.1 M	0.2 M	1.2×10^{-3}
0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is:

(a) $\frac{dc}{dt} = k[A][B]$ (b) $\frac{dc}{dt} = k[A]^2[B]$

(c) $\frac{dc}{dt} = k[A][B]^2$ (d) $\frac{dc}{dt} = k[A]$

11. Among the following oxoacids, the correct decreasing order of acid strength is:

(a) $HOCl > HClO_2 > HClO_3 > HClO_4$

(b) $HClO_4 > HOCl > HClO_2 > HClO_3$

(c) $HClO_4 > HClO_3 > HClO_2 > HOCl$

(d) $HClO_2 > HClO_4 > HClO_3 > HOCl$

12. The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is:

(a) Ag (b) Ca

(c) Cu (d) Cr

13. The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1, L_2, L_3 and L_4 absorb wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is:

(a) $L_4 < L_3 < L_2 < L_1$ (b) $L_1 < L_3 < L_2 < L_4$

(c) $L_3 < L_2 < L_4 < L_1$ (d) $L_1 < L_2 < L_4 < L_3$

14. Which one of the following properties is **not** shown by NO?

(a) It is diamagnetic in gaseous state

(b) It is neutral oxide

(c) It combines with oxygen to form nitrogen dioxide

(d) It's bond order is 2.5

15. In which of the following reactions H_2O_2 acts as a reducing agent?

(a) $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

(b) $H_2O_2 + 2e^- \rightarrow O_2 + 2H^+$

(c) $H_2O_2 + 2e^- \rightarrow 2OH^-$

(d) $H_2O_2 + 2OH^- - 2e^- \rightarrow O_2 + 2H_2O$

16. The correct statement for the molecule, CsI_3 is:

(a) It is a covalent molecule.

(b) It contains Cs^+ and I_3^- ions.

(c) It contains Cs^{3+} and I^- ions.

(d) It contains Cs^+, I^- and lattice I_2 molecule.

17. The ratio of masses of oxygen and nitrogen in a particular gaseous mixture is 1 : 4. The ratio of number of their molecule is:

(a) 1 : 4 (b) 7 : 32

(c) 1 : 8 (d) 3 : 16

18. Given below are the half-cell reactions:

$$Mn^{2+} + 2e^- \rightarrow Mn; \; E^0 = -1.18\,V$$

$$2\left(Mn^{3+} + e^- \rightarrow Mn^{2+}\right); \; E^0 = +1.51\,V$$

The E^0 for $3Mn^{2+} \rightarrow Mn + 2Mn^{3+}$ will be:

(a) –2.69 V; the reaction will not occur

(b) –2.69 V; the reaction will occur

(c) –0.33 V; the reaction will not occur

(d) –0.33 V; the reaction will occur

19. Which series of reactions correctly represents chemical reactions related to iron and its compound?

(a) $Fe \xrightarrow{\text{dil. } H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4,\, O_2} Fe_2(SO_4)_3 \xrightarrow{\text{heat}} Fe$

(b) $Fe \xrightarrow{O_2,\, \text{heat}} FeO \xrightarrow{\text{dil. } H_2SO_4} FeSO_4 \xrightarrow{\text{heat}} Fe$

(c) $Fe \xrightarrow{Cl_2,\, \text{heat}} FeCl_3 \xrightarrow{\text{heat, air}} FeCl_2 \xrightarrow{Zn} Fe$

(d) $Fe \xrightarrow{O_2,\, \text{heat}} Fe_3O_4 \xrightarrow{CO,\, 600°C} FeO \xrightarrow{CO,\, 700°C} Fe$

20. The equation which is balanced and represents the correct product(s) is:

(a) $Li_2O + 2KCl \rightarrow 2LiCl + K_2O$

(b) $\left[CoCl(NH_3)_5\right]^+ + 5H^+ \rightarrow Co^{2+} + 5NH_4^+ + Cl^-$

(c) $\left[Mg(H_2O)_6\right]^{2+} + (EDTA)^{4-} \xrightarrow{\text{excess NaOH}} \left[Mg(EDTA)\right]^{2+} + 6H_2O$

(d) $CuSO_4 + 4KCN \rightarrow K_2\left[Cu(CN)_4\right] + K_2SO_4$

21. In S_N2 reactions, the correct order of reactivity for the following compounds:

$CH_3Cl, CH_3CH_2Cl, (CH_3)_2CHCl$ and $(CH_3)_3CCl$ is:

(a) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$

(b) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(c) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(d) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

22. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is:

(a) an alkanol (b) an alkanediol

(c) an alkyl cyanide (d) an alkyl isocyanide

23. The most suitable reagent for the conversion of

$R - CH_2 - OH \rightarrow R - CHO$ is:

(a) $KMnO_4$

(b) $K_2Cr_2O_7$

(c) CrO_3

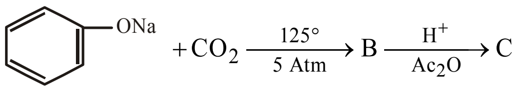
(d) PCC (Pyridinium Chlorochromate)

24. The major organic compound formed by the raction of 1, 1, 1-trichloroethane with silver powder is:

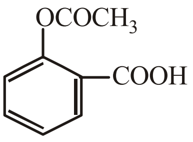
(a) Acetylene (b) Ethene

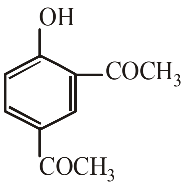
(c) 2 - Butyne (d) 2 - Butene

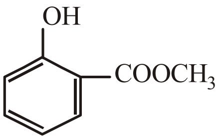
25. Sodium phenoxide when heated with CO_2 under pressure at 125ºC yields a product which on acetylation produces C.

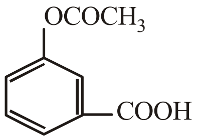


The major product C would be

(a)


(b)


(c)


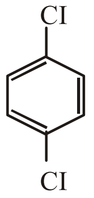
(d)


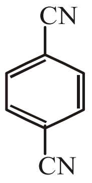
26. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value?

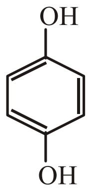
(a) $(CH_3)_2NH$ (b) CH_3NH_2

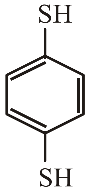
(c) $(CH_3)_3N$ (d) $C_6H_5NH_2$

27. For which of the following molecule significant $\mu \neq 0$?

(i)


(ii)


(iii)


(iv)


(a) Only (i) (b) (i) and (ii)

(c) Only (iii) (d) (iii) and (iv)

28. Which one is classified as a condensation polymer?

(a) Dacron (b) Neoprene

(c) Teflon (d) Acrylonitrile

29. Which one of the following bases is **not** present in DNA?

(a) Quinoline (b) Adenine

(c) Cytosine (d) Thymine

30. In the reaction,

$$CH_3COOH \xrightarrow{LiAH_4} A \xrightarrow{PCl_5} B \xrightarrow{Alc.KOH} C,$$

the product C is:

(a) Acetaldehyde (b) Acetylene

(c) Ethylene (d) Acetyl chloride

SOLUTIONS

1. **(a)** The electronic configuration of Rubidium (Rb = 37) is

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$

Since last electron enters in 5*s* orbital

Hence $n = 5, l = 0, m = 0, s = \pm\frac{1}{2}$

2. **(b)** Compressibility factor $(Z) = \frac{PV}{RT}$

(For one mole of real gas)

van der Waals equation

$$(P + \frac{a}{V^2})(V - b) = RT$$

At low pressure, volume is very large and hence correction term *b* can be neglected in comparison to very large volume of *V*.

i.e. $V - b \approx V$

$$\left(P + \frac{a}{V^2}\right) V = RT$$

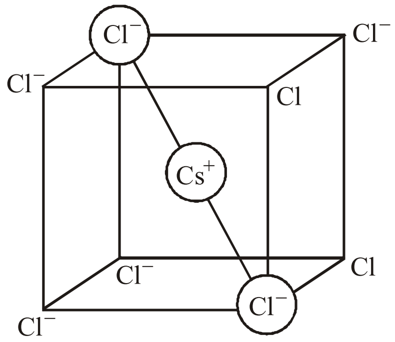
$$PV + \frac{a}{V} = RT$$

$$PV = RT - \frac{a}{V}$$

$$\frac{PV}{RT} = 1 - \frac{a}{VRT}$$

Hence, $\boxed{Z = 1 - \frac{a}{VRT}}$

3. **(c)**



Relation between radius of cation, anion and edge length of the cube

$$2r_{Cs^+} + 2r_{Cl^-} = \sqrt{3}a$$

$$r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}a}{2}$$

4. **(b)** $\% \text{ of N} = \frac{1.4 \times \text{meq. of acid}}{\text{mass of organic compound}}$

$$\text{meq. of } H_2SO_4 = 60 \times \frac{M}{10} \times 2 = 12$$

$$\text{meq. of NaOH} = 20 \times \frac{M}{10} = 2$$

$\therefore$ meq. of acid consumed = 12 – 2 = 10

$$\therefore \% \text{ of N} = \frac{1.4 \times 10}{1.4} = 10\%$$

5. **(a)** Given for 0.2 *M* solution

$R = 50\,\Omega$

$\kappa = 1.4 \text{ S } m^{-1} = 1.4 \times 10^{-2} \text{ S cm}^{-1}$

Now, $R = \rho\frac{\ell}{a} = \frac{1}{\kappa} \times \frac{\ell}{a}$

$$\Rightarrow \frac{\ell}{a} = R \times \kappa = 50 \times 1.4 \times 10^{-2}$$

For 0.5 *M* solution

$R = 280\,\Omega$

$\kappa = ?$

$$\frac{\ell}{a} = 50 \times 1.4 \times 10^{-2}$$

$$\Rightarrow R = \rho\frac{\ell}{a} = \frac{1}{\kappa} \times \frac{\ell}{a}$$

$$\Rightarrow \kappa = \frac{1}{280} \times 50 \times 1.4 \times 10^{-2}$$

$$= \frac{1}{280} \times 70 \times 10^{-2} = 2.5 \times 10^{-3} \text{ S cm}^{-1}$$

Now, $\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{2.5 \times 10^{-3} \times 1000}{0.5}$

$= 5 \text{ S cm}^2 \text{ mol}^{-1} = 5 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$

6. **(a)** $C_2H_5OH(\ell) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$

Bomb calorimeter gives ΔU of the reaction

Given, $\Delta U = -1364.47 \text{ kJ mol}^{-1}$

$\Delta n_g = -1$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$= -1364.47 - \frac{1 \times 8.314 \times 298}{1000} = -1366.93 \text{ kJ mol}^{-1}$$

7. **(c)** According to Debye Huckle onsager equation,

$$\lambda_C = \lambda_\infty - B\sqrt{C}$$

8. **(a)** $\pi = i\,CRT$

$$\pi_{C_2H_5OH} = 1 \times 0.500 \times R \times T = 0.5RT$$

$$\pi_{Mg_3(PO_4)_2} = 5 \times 0.100 \times R \times T = 0.5RT$$

$$\pi_{KBr} = 2 \times 0.250 \times R \times T = 0.5RT$$

$$\pi_{Na_3PO_4} = 4 \times 0.125 \times RT = 0.5RT$$

Since the osmotic pressure of all the given solutions is equal. Hence all are isotonic solution.

9. **(b)** $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

$$K_P = K_C(RT)^x$$

where $x = \Delta n_g =$ number of gaseous moles in product – number of gaseous moles in reactant

$$= 1 - \left(1 + \frac{1}{2}\right) = 1 - \frac{3}{2} = -\frac{1}{2}$$

10. **(d)** Let rate of reaction $= \frac{d[C]}{t} = k[A]^x[B]^y$

Now from the given data

$1.2 \times 10^{-3} = k[0.1]^x[0.1]^y$ .....(i)

$1.2 \times 10^{-3} = k[0.1]^x[0.2]^y$ .....(ii)

$2.4 \times 10^{-3} = k[0.2]^x[0.1]^y$ .....(iii)

Dividing equation (i) by (ii)

$$\Rightarrow \frac{1.2 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k[0.1]^x[0.1]^y}{k[0.1]^x[0.2]^y}$$

We find, $y = 0$

Now dividing equation (i) by (iii)

$$\Rightarrow \frac{1.2 \times 10^{-3}}{2.4 \times 10^{-3}} = \frac{k[0.1]^x[0.1]^y}{k[0.2]^x[0.1]^y}$$

We find, $x = 1$

Hence $\frac{d[C]}{dt} = k[A]^1[B]^0$

11. **(c)** Acidic strength increases as the oxidation number of central atom increases.

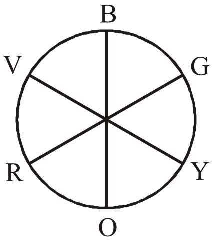
Hence acidic strength order is

$$\overset{(+7)}{HClO_4} > \overset{(+5)}{HClO_3} > \overset{(+3)}{HClO_2} > \overset{(+1)}{HClO}$$

12. **(b)** On electrolysis of aqueous solution of *s*-block elements H_2 gas discharge at cathode.

At cathode: $H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^-$

13. **(b)**



For a given metal ion, weak field ligands create a complex with smaller Δ, which will absorbs light of longer λ and thus lower frequency. Conservely, stronger field ligands create a larger Δ, absorb light of shorter λ and thus higher v i.e. higher energy.

$$\underset{\lambda = 650\text{ nm}}{\text{Red}} < \underset{570\text{ nm}}{\text{Yellow}} < \underset{490\text{ nm}}{\text{Green}} < \underset{450\text{ nm}}{\text{Blue}}$$

So order of ligand strength is

$$L_1 < L_3 < L_2 < L_4$$

14. **(a)** Nitric oxide is paramagnetic in the gaseous state because of the presence of one unpaired electron in its outermost shell.

The electronic configuration of NO is

$$\sigma_{1s}^2\,\sigma_{1s}^{*2}\,\sigma_{2s}^2\sigma_{2s}^{*2}\sigma_{2p_z}^2\,\pi_{2p_x}^2 = \pi_{2p_y}^2\,\pi_{2\ p_x}^{*1}$$

15. **(d)** The reducing agent loses electron during redox reaction i.e. oxidises itself.

(a) $H_2\overset{-1}{O_2} + 2H^+ + 2e^- \longrightarrow 2H_2\overset{-2}{O}$ (Red.)

(b) $H_2\overset{-1}{O_2} \longrightarrow \overset{0}{O_2} + 2H^+ + 2e^-$ (Ox.)

(c) $H_2\overset{-1}{O_2} + 2e^- \longrightarrow 2\overset{-2}{O}H^-$ (Red.)

(d) $H_2O_2^{-1} + 2OH^- \longrightarrow \overset{0}{O_2} + H_2O + 2e^-$ (Ox.)

16. **(b)** CsI_3 dissociates as

$CsI_3 \to Cs^+ + I_3^-$

17. **(b)** Number of moles of $O_2 = \frac{w}{32}$

Number of moles of $N_2 = \frac{4w}{28} = \frac{w}{7}$

$\therefore$ Ratio $= \frac{w}{32} : \frac{w}{7} = 7 : 32$

18. **(a)** (a) $Mn^{2+} + 2e^- \to Mn; E^0 = -1.18V;$ ... (i)

(b) $Mn^{3+} + e \to Mn^{2+}; E^0 = -1.51V;$ ... (ii)

Now multiplying equation (ii) by two and subtracting from equation (i)

$3Mn^{2+} \to Mn^+ + 2Mn^{3+};$

$E^0 = E_{Ox.} + E_{Red.} = -1.18 + (-1.51) = -2.69\,V$

(–ve value of EMF (i.e. ΔG = +ve) shows that the reaction is non-spontaneous)

19. **(c)** In equation (i) $Fe_2(SO_4)_3$ and in equation (ii) $Fe_2(SO_4)_3$ on decomposing will form oxide instead of Fe.

The correct sequence of reactions is

$$Fe \xrightarrow{O_2,\text{heat}} Fe_3O_4 \xrightarrow{Co,600°C} Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe$$

20. **(b)** The complex $[CoCl(NH_3)_5]^+$ decomposes under acidic medium, so

$$[CoCl(NH_3)_5]^+ + 5H^+ \longrightarrow Co^{2+} + 5NH_4^+ + Cl^-$$

21. **(b)** Steric congestion around the carbon atom undergoing the inversion process will slow down the S_N2 reaction, hence less congestion faster will the reaction. So, the order is

$CH_3Cl > (CH_3)CH_2-Cl > (CH_3)_2CH-Cl > (CH_3)_3CCl$

22. **(d)** $R-CH_2-NH_2 + CHCl_3 + 3KOH\,(alc) \longrightarrow$

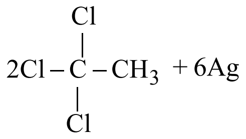
Carbyl amine reaction

$R-CH_2-NC + 3KCl + 3H_2O$

Alkyl isocynide

23. **(d)** An excellent reagent for oxidation of 1° alcohols to aldehydes is PCC.

$$R-CH_2-OH \xrightarrow{PCC} R-CHO$$

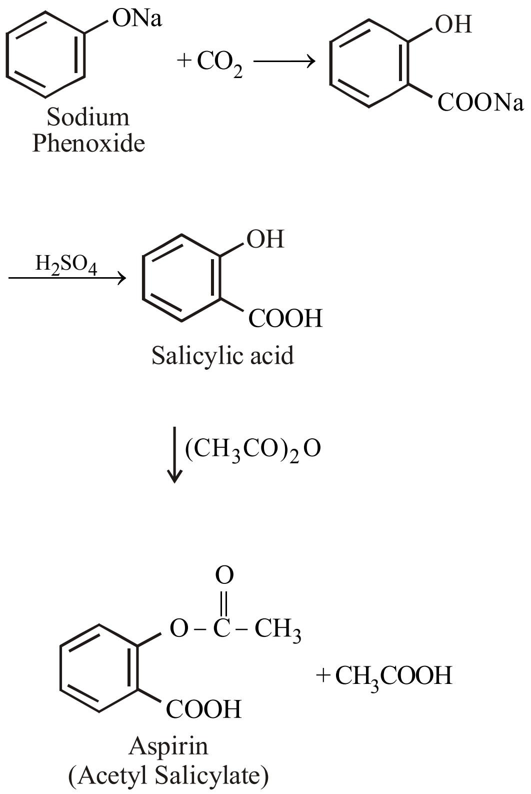
24. **(c)** 

$2Cl-\underset{Cl}{\overset{Cl}{C}}-CH_3 + 6Ag$

1, 1, 1-trichloroethane

$\longrightarrow CH_3C \equiv CCH_3 + 6AgCl$

2-butyne

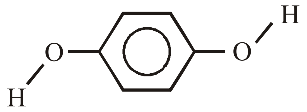
25. **(a)** 

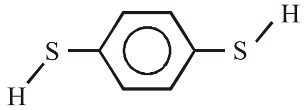
26. **(a)** Arylamines are less basic than alkyl amines and even ammonia. This is due to resonance. In aryl amines the lone pair of electrons on N is partly shared with the ring and is thus less available for sharing with a proton.

In alkylamines, the electron releasing alkyl group increases the electron density on nitrogen atom and thus also increases the ability of amine for protonation. Hence more the no. of alkyl groups higher should be the basicity of amine. But a slight discrepancy occurs in case of trimethyl amines due to steric effect. Hence the correct order is

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$

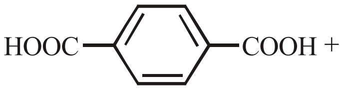
27. **(d)**





In both the molecules the bond moments are not canceling with each other and hence the molecules has a resultant dipole and hence the molecule is polar.

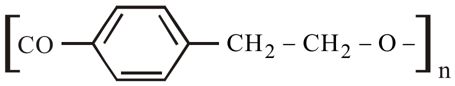
28. **(a)** Except Dacron all are additive polymers. Terephthalic acid condenses with ethylene glycol to give Dacron.



Terephthalic acid

$\mathrm{HO-CH_2-CH_2-OH} \longrightarrow$

Ethylene glycol



Dacron (Polyester)

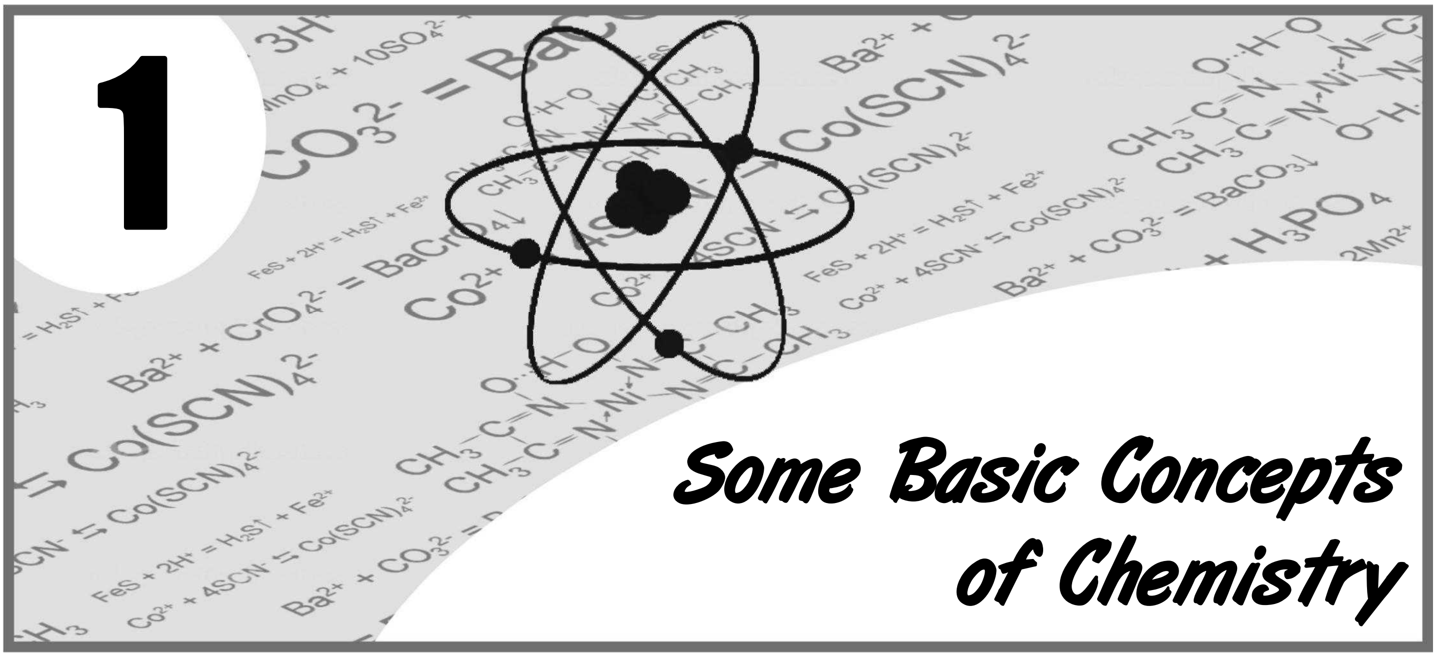
29. **(a)** DNA contains ATGC bases

So quinoline is not present in DNA.

30. **(c)**

$$\mathrm{CH_3COOH} \xrightarrow{\mathrm{LiAlH_4}} \underset{(A)}{\mathrm{CH_3CH_2OH}} \xrightarrow{\mathrm{PCl_5}} \underset{(B)}{\mathrm{CH_3CH_2Cl}} \xrightarrow{\text{Alc. KOH}} \underset{(C)}{\mathrm{CH_2=CH_2}}$$

Hence the product (C) is ethylene.



1

Some Basic Concepts of Chemistry

PHYSICAL QUANTITIES AND SI UNITS :

The 11th general conference of weights and measures in 1960 recommended the use of international system of units.

Abbreviated as SI Units (after the French expression La System International de units). The SI system has seven basic units of physical quantities as follows :

Physical quantity	*Abbreviation*	*Name of unit*	*Symbol*
time	t	second	s
mass	m	kilogram	kg
length	l	metre	m
temperature	T	kelvin	K
electric current	I	ampere	A
light intensity	Iv	candela	Cd
amount of substance	n	mole	mol

DERIVED UNITS :

The units obtained by combination of basic units are known as derived units e.g. velocity is expressed as distance/ time. Hence unit is m/s or ms^{-1}. Some common derived units are

Physical Quantity	*Definition*	*SI Unit*
volume	length cube	m^3
area	length square	m^2
speed	distance travelled	ms^{-1} per unit time
acceleration	speed changed per unit time	ms^{-2}
density	mass per unit volume	$kg\ m^{-3}$
pressure	force per unit area	$kgm^{-1}s^{-2}$ or Nm^{-2} (pressure = Pa)
force	mass times acceleration of object	$kgms^{-2}$ (Newton N)
energy	force times distance travelled	kgm^2s^{-2} (Joule J)
frequency	cycles per second	s^{-1} (hertz = Hz)
power	energy per second	kgm^2s^{-3} or Js^{-1} (Watt = W)
electric charge	ampere times second	As (coloumb = C)
electric potential difference	energy per unit charge	$JA^{-1}s^{-1}$ or $kgm^2s^{-3}A^{-1}$ (volt = V)

SOME NON SI UNITS IN COMMON USE :

Quantity	*Unit*	*Symbol*	*SI definition*	*SI Name*
Length	angstrom	Å	10^{-10} m	0.1 nanometers (nm)
Volume	litre	L	10^{-3} m^3	1 decimeter (dm^3)
Energy	calorie	cal	$kg\ m^2s^{-2}$	4.184 Joule (J)

Mass	atomic mass unit	amu	1.66057×10^{-27} kg
	pound	lb	0.453502 kg
Force	dyne	dyn	10^{-5} N
	pound force	lbf	4.44822 N
Pressure	bar	bar	10^5 Nm^{-2} (or Pa)
	atmosphere	atm	101325 Nm^{-2} (or Pa)
	Torr	torr	101325 / 760 Nm^{-2} (or Pa)
	mm of Hg	mmHg	$13.5951 \times 980.665 \times 10^{-2}$ Nm^{-2}

STANDARD PREFIXES FOR EXPRESSING THE DECIMAL FRACTIONS OR MULTIPLES OF FUNDAMENTAL UNITS :

Fraction	*Prefix*	*Symbol*	*Multiple*	*Prefix*	*Symbol*
10^{-1}	deci	d	10^1	Deka	da
10^{-2}	centi	c	10^2	Hecta	h
10^{-3}	milli	m	10^3	kilo	k
10^{-6}	micro	μ	10^6	Mega	M
10^{-9}	nano	n	10^9	Giga	G
10^{-12}	pico	p	10^{12}	Tera	T
10^{-15}	femto	f	10^{15}	Peta	P
10^{-18}	atto	a	10^{18}	Exa	E

SOME CONVERSION FACTORS :

1. Mass : 1 kg = 10^3g = 2.2046 lb; 1 mg (milligram) = 10^{-3}g; 1 μg (micro gram) = 10^{-6}g

   $$1 \text{ amu} = \frac{1}{12} \text{ mass of isotope of } C^{12}$$

   1 amu = 1.6605×10^{-24} g = 1.6605×10^{-27} kg
2. Length : 1Å = 10^{-8} cm = 10^{-10} m;
   1 pm = 10^{-10} cm = 10^{-12} m = 10^{-2}Å
   1 nm = 10^{-7} cm = 10^{-9} m = 10 Å
   1 nm = 10^3 pm
3. Volume : 1 litre = 1000 cm^3 = 1000 ml = 1 dm^3 = 10^{-3} m^3 = 0.22 gal
   1 m^3 = 10^6 cm^3 = 35.3146 ft^3
4. Pressure : 1 atm = 760 torr = 760 mm Hg = 76 cm Hg = 1.013×10^5 Pa
   = 1.01325 bars = 101325 Nm^{-2} = 14.7 lb m^{-2} (psi)
   = $76.0 \times 13.595 \times 980.66 = 1.01325 \times 10^6$ dyne cm^{-2}
5. Work & Energy :
   1J = 10^7 erg = 0.7373 ft lbf
   1 cal = 4.184 J = 4.184×10^7 erg
   1 eV = 1.602×10^{-12} erg = 1.602×10^{-19} J
   1 eV/molecule or atom = 96.4853 kJmol^{-1} = 23.06 kcal mol^{-1}
   1 J = 1 kg m^2 sec^{-2} = 1 V × 1C = 1VA sec
6. Force : 1 N = 10^5 dyne = 0.22481 lbf
7. Power : 1 Watt = 10^7 ergs^{-1} = 1.341×10^{-3} hP
   1 W = 1 J sec^{-1} = 1 VA
   1 hP = 745.7 Watt
8. Temperature :

   $$K = °C + 273.15$$

   $$°C = \frac{5}{9} \times (°F - 32)$$

   $$°F = \frac{9}{5} \times °C + 32$$

Dimensional analysis factor label method or unit factor method. It is conversion of units from one system to other.

Example : Conversion of L (litre) into m^3 (metre). Find unit factor relating L and m^3

$$1L = 1000 \text{cm}^3$$

$$\frac{1L}{1000 \text{ cm}^3} = 1 \qquad \text{...(i)}$$

$$1\text{m} = 100 \text{ cm or } 1\text{m}^3 = (100 \text{ cm})^3$$

$$\frac{1 \text{ m}^3}{10^6 \text{ cm}^3} = 1 \qquad \text{...(ii)}$$

From (i) and (ii) which are unit factors

$$\frac{1L}{1000\ \text{cm}^3} = \frac{1\ \text{m}^3}{10^6\ \text{cm}^3}$$

$$\therefore \quad 1L = 10^{-3}\text{m}^3 \text{ and}$$

$$1\text{m}^3 = 10^3 L$$

PRECISION AND ACCURACY

Precision : It is the closeness of various measurements for the same quantity.

Accuracy : It is the agreement of a particular value to the true value.

Example : Let the true weight of a substance be 3.00g. The measurement reported by three students are as follows

Student	Measurements/g		Average/g
	1	2	
A	2.95	2.93	2.94
B	3.01	2.99	3
C	2.94	3.05	2.99

Case of student : It is precision but no accuracy since measurements one close but not accurate.

Case of student : Measurements are close (precision) and accurate (Accuracy)

Case of C student : Measurement are not close (no precision) and not accurate (no accuracy)

Stoichiometry : It is calculation of masses or volumes of reactants and products involved in a chemically balanced reaction. Consider the formation of ammonia.

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3(g)$$

All are gases indicated by letter (g) and coefficients 3 for H_2 and 2 for NH_3 are called stoichiometric coefficients. The formation of ammonia can be interpreted in many ways.

- One mole of N_2(g) reacts with three moles of H_2(g) to give two moles of NH_3(g).
- 28g of N_2(g) reacts with 6g at H_2(g) to give 34g of NH_3(g).
- 22.4L of N_2(g) reacts with 67.2L of H_2(g) to give 44.8L of NH_3(g)

Scientific Notation : The representation of large numbers in the form of $N \times 10^n$ is known as scientific notation or exponential notation. N can have value 1 to 10 and n is exponent having positive or negative value.

Example (i) 0.000000028 can be written an 2.8×10^{-8}
(ii) 4200000000 can be written as 4.2×10^9

SIGNIFICANT FIGURES :

The weight 7.52 gm of a substance indicates that it is reliable to the nearest hundredth of a gram and may be expressed as 7.52 ± 0.01. It means slightest variation may occur at the second place of decimal or we can say that uncertainty is $\pm$ 0.01 g.

Now consider the weight 6.4234 g. It may correctly be expressed as 6.4234 ± 0.001 g.

In the first case the weight contains three significant figures and in the second case weight contains five significant figures.

(i) Significance of zero : If zero is used to locate the decimal point it is not considered as significant figure. Thus in 0.0072 there are only two significant figures whereas in 70.40, there are four significant figures since zero is after 4. Again in 0.0070 there are two significant figures, since zero after 7 is significant for it has a meaning when written in exponentials. If we compare 7.0×10^{-3} and 7×10^{-3}, the first term has uncertainty of one in seventy and second has uncertainty of one in seven. **The exponential term does not add to number of significant figures.**

(ii) Addition and substraction of quantities : In this case the uncertainty in the result is equal to the sum of the uncertainties of the individual quantities.

(iii) Multiplication and division : In this case the uncertainty in the result is equal to the sum of the percentage of individual uncertainties.

Examples :

(a) How many significant figures are there in following digits.
(i) 0.0426 (ii) 526
(iii) 4.50×10^3 (iv) 0.00269 (v) 2.725×10^4

Sol. (i) 0.0426 g has 3 significant figures.
(ii) 526 ml has 3 significant figures.
(iii) 4.50×10^3 kg has 3 significant figures.
(iv) 0.00269 has 3 significant figures.
(v) 2.725×10^4 has 4 significant figures.

(b) Write the following in exponential notation.
(i) 2365
(ii) 60000 g (three significant figures)
(iii) 72400 g (four significant figures)
(iv) 0.0030 g

Sol. (i) 2.365×10^3 or 23.65×10^2 or 0.2365×10^4
(ii) 6.00×10^4
(iii) 7.240×10^4
(iv) 3.0×10^{-3}

(iv) Rounding off : The following rules are observed.

(a) If the digit after the last digit to be retained is less than 5, the last digit is retained as such ***e.g.*** 1.752 = 1.75 (2 is less than 5).

(b) If the digit after the last digit to be retained is more than 5, the digit to be retained is increased by 1 ***e.g.*** 1.756 = 1.76 (6 is more than 5).

(c) If the digit after the last digit to be retained is equal to 5, the last digit is retained as such if it is even and increased by 1 if odd.

e.g. $1.7\overset{*}{5}5 = 1.76$ (* odd) & $1.7\overset{*}{6}5 = 1.76$ (* even)

(v) Calculations involving addition and substraction : In case of addition and substraction the final result should be reported to the same number of decimal places as the number with the minimum number of decimal places e.g.

(a) 34.72 (has two decimal places)
8.1 (has one decimal place)

42.82

Ans. = 42.82 but it should have only one decimal place so answer is 42.8.

(b) 59.273
– 24.92

34.353

Ans. = 34.35 (upto two decimal places)

(vi) Calculations involving multiplication and division : In this case the final result should be reported having same number of significant digits as that of the number having least significant digits.

Example : $9.24 \times 3.6 = 33.264$ Rounded off to 33.

3.6 is the number with least significant figures (two), hence final result is limited to two significant digits. Result is 33.

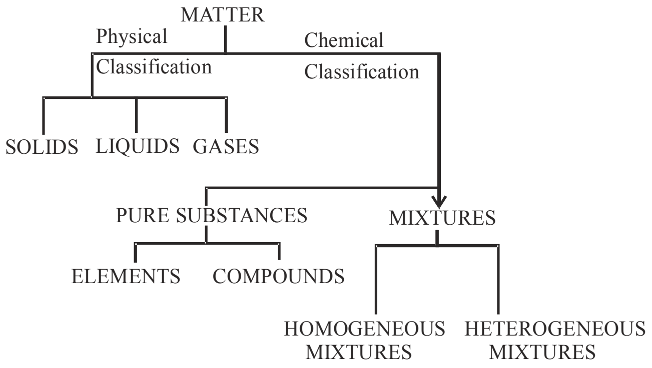
In case of division $\frac{5.235}{13.1} = 0.3996$. Rounded off to 0.400.

13.1 is the number with least (three) significant figures hence the result will be 0.400.

MATTER :

Anything which occupies space, possesses mass and can be felt is called matter.

CLASSIFICATION OF MATTER :



ELEMENT :

Pure substance consisting of one type of particles in the form of atoms eg. Cu, Na, Fe or molecules eg. H_2, O_2 etc.

COMPOUND :

Pure substance consisting of molecules formed by the combination of atoms of different elements eg. CO_2, H_2O etc.

MIXTURES :

Mixtures are substances made of two or more elements or compounds in any proportion. They may be homogeneous or heterogeneous.

SEPARATION OF MIXTURES :

Mixtures can be separated into constituents by following methods:

(i) ***Filtration*** can separate those mixtures whose one component is soluble in a particular solvent and other is not.

(ii) ***Distillation*** can be used to separate constituents of mixtures having different boiling points.

(iii) ***Extraction*** dissolves one out of several components of mixture.

(iv) ***Crystallisation*** is a process of separating solids having different solubilities in a particular solvent.

(v) ***Sublimation*** separates volatile solids which sublime on heating from non-volatile solids.

(vi) ***Chromatography*** is the technique of separating constituents of a mixture which utilises the property of difference of adsorption on a particular adsorbent.

(vii) ***Gravity separation*** separates constituents having different densities.

(viii) ***Magnetic separation*** can separate magnetic components from non magnetic ones.

PHYSICAL AND CHEMICAL CHANGES :

A change which does not affect chemical composition and molecular structure is a physical change and the one that involves alteration of chemical composition and molecular structure is a chemical change.

(i) Chemical Combination is reaction between two or more elements or compounds to form a single substance.

$$H_2 + I_2 \rightleftharpoons 2HI$$

(ii) Displacement means replacement of one element of compound by another.

(iii) Decomposition involves splitting of a compound to form two or more substances.

$$CaCO_3 \longrightarrow CaO + CO_2$$

(iv) Combustion is a complete and fast oxidation of a substance.

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

(v) Neutralisation is the reaction between acid and base to form a salt.

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

(vi) Polymerisation is the combination of molecules of same or different substances to form a single molecule called polymer.

$$nCH_2 = CH_2 \longrightarrow -(CH_2 - CH_2-)_n$$

(vii) Photochemical changes occur in presence of visible or ultraviolet light.

(viii) Double decomposition or metathesis is the exchange of oppositely charged ion on mixing two salt solutions.

(ix) Hydrolysis involves reaction of salts with water to form acidic or basic solutions.

LAWS OF CHEMICAL COMBINATIONS :

(i) **Law of conservation of mass :** This law was given by French chemist **A. Lavoisier (1774)** which states that "during any physical or chemical change, the total mass of products is equal to the total mass of reactants". It is also called law of indistinctibility. It does not hold good for nuclear reaction.

(ii) **Law of definite proportions :** This law was given by **Proust (1799)** and states that "a chemical compound always contains some elements combined together in same proportion by mass". For example different samples of pure CO_2 always have carbon and oxygen in 3 : 8 ratio by mass.

(iii) **Law of multiple proportions :** This law was given by **John Dalton (1803)** and states that "when two elements combine to form two or more compounds, the different mass of one of the elements and the fixed mass of the one with which it combines always form a whole number ratio". This law explains the concept of formation of more than one compound by two elements.

(iv) **Law of reciprocal proportions :** This was given by **Richter (1792)** and states that "when two elements combine separately with a fixed mass of third, the ratio of masses in which they do so is same or whole number multiple of the ratio in which they combine with each other." This law is also called law of equivalent proportions and is helpful in determining equivalent weights.

(v) **Gay Lussac's law of combining volumes :** This law states that when gases react with each other, their volumes bear a simple whole no. ratio to one another and to volume of products (if gases) and similar conditions of pressure and temperature.

(vi) **Dalton's atomic theory :**

Proposed by **John Dalton** in 1808. Main points are :

(a) Matter is made up, by indivisible particles called atoms
(b) Atoms of same elements are identical in physical and chemical properties.
(c) Atoms of different substances are different in every respect
(d) Atoms always combine in whole numbers to form compounds
(e) Atoms of resultant compounds possess similar properties

DRAWBACKS OF DALTON'S THEORY :

(i) Does not explain structure of atom.
(ii) Fails to explain binding forces between atoms in compounds.
(iii) Does not explain Gay Lussac's law.
(iv) Does not differentiate between atom and molecule.

AVOGADRO'S LAW :

It states that "equal volumes of all gases, under similar conditions of temperature and pressure contain equal number of molecules". Applications are

(i) Deducing atomicity of elementary gases
(ii) Deriving relationship between molecular mass and vapour density
(iii) Deriving formula of substances
(iv) Determining molecular wt. of a gas
(v) Deducing the gram molecular volume.

ATOM :

Atom is the smallest particle of element which might not be able to exist independently.

MOLECULE :

Molecule is the smallest particle of the substance which can exist independently. It can be subdivided as

(i) **Homoatomic** molecules are molecules of same element and can be further divided as monoatomic, diatomic and polyatomic molecules depending upon number of atoms. eg: He, O_2, P_4 etc.

(ii) **Heteroatomic** molecules are molecules of compound. They can be diatomic and polyatomic. eg: H_2O, PCl_5, H_2SO_4, NO etc.

ATOMIC MASS UNIT (A.M.U.) :

It is the unit of representing atomic masses. 1 a.m.u. = $\frac{1}{12}$ th the mass of C-12.

MOLE :

It is a unit which represents 6.023×10^{23} particles. The number 6.023×10^{23} is called Avogadro's number and is represented by N_0 or N_A. Avogadro's number of gas molecules occupy a volume of 22400 cm^3 at N.T.P. Number of molecules in 1 cm^3 of gas at NTP is **Loschmidt** N_0. With value 2.688×10^{19}.

ATOMIC MASS :

"It is the number of times the atom of the element is heavier than H atom" was the first proposed definition. Later on oxygen was preferred as standard. In 1961 C-12 was chosen as standard and thus "the number of times the atom of an element is heavier than 12th part of C-12 is called atomic mass of the element.

$$\text{Atomic mass} = \frac{\text{Mass of an atom of the element}}{\frac{1}{12} \times \text{mass of C-12 atom}}$$

AVERAGE ATOMIC MASS :

It is the mass of each isotope determined separately and then combined in ratio of their occurrence. Suppose a and b are two isotopes of an element with their occurence ratio p : q then

$$\text{Average atomic mass} = \frac{p \times a + q \times b}{p + q}$$

DETERMINATION OF ATOMIC MASS :

(i) **Dulong and petit's rule :** It is based on experimental facts. "At ordinary temperature, product of atomic mass and specific heat for solid elements is approximately 6.4 and this product is known as atomic heat of the element".

Atomic mass × specific heat = 6.4

The law is valid for solid elements except Be, B, Si and C.

Correct At. mass = Eq. mass × valency

(ii) **Specific heat method :** This method is for gases. $\gamma = \frac{C_p}{C_v}$,

where C_p = specific heat at constant pressure and C_v = specific heat at constant volume. the ratio γ is a constant = 1.66 for monoatomic, 1.40 for diatomic, 1.33 for triatomic gas

and atomic mass of gaseous element

$$= \frac{\text{Mol. mass}}{\text{atomicity}} = \frac{\text{Mol. mass}}{\gamma}.$$

(iii) **Chloride formation method** : This method converts the element (whose mass is to be determined) into volatile chloride whose vapour density is found by Victor Mayer method.

Molecular mass = 2 × V.D.

(iv) **Vapour density method** is suitable for elements having volatile chlorides.

Atomic mass = Eq. mass of metal × valency.

(v) **Mitscherlich's law of isomorphism :** It states that isomorphous substances have similar chemical constitution. Isomorphous substances form crystals of same shape and valencies of elements forming isomorphous salts are also same. eg: $ZnSO_4.7H_2O$, $MgSO_4.7H_2O$ and $FeSO_4.7H_2O$ are isomorphous.

GRAM ATOMIC MASS (GAM)

Is the mass of an atom expressed in gms.

$$\text{No. of Gm-atoms of element} = \frac{\text{Mass of element in grams}}{\text{GAM of element}}$$

MOLECULAR MASS :

It is the average relative mass of the molecule as compared with mass of C-12 atom.

$$\text{Molecular mass} = \frac{\text{Average relative mass of one molecule}}{\frac{1}{12} \times \text{Mass of C-12 atom}}$$

CALCULATION OF MOLECULAR MASS :

(i) **Graham's law of diffusion :** It states that rate of diffusion of two gases is inversely proportional to the square root of ratio of their molecular weights.

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

(ii) **Victor meyer method :** This method can determine the molecular mass as

$$\text{Molecular mass} = \frac{W}{V} \times 22400$$

where W is the mass of liquid in gm. occupying a volume V ml at STP.

(iii) **Vapour density method :** Vapour density is the ratio of volume of a gas to the mass of same volume of hydrogen under identical conditions.

$$\text{V.D.} = \frac{\text{Mass of V litre of gas}}{\text{Mass of V litre of hydrogen}}$$

$$\text{or V.D.} = \frac{1}{2}\frac{\text{Weight of volatile substance}}{\text{Volume at STP}} \times 22400$$

Thus molecular mass = 2 × V.D.

(iv) **Colligative properties method :** This method can be helpful in determining molecular mass as

$$\text{elevation in boiling point } (\Delta T_b) = \frac{K_b \times w \times 1000}{W \times \text{mol. mass}}$$

Where ΔT_b is elevation in b.p., K_b is molal elevation constant w is wt. of solute W is wt. of solvent

$$\text{Depression in freezing point } (\Delta T_f) = \frac{K_f \times w \times 1000}{W \times \text{mol. mass}}$$

GRAM MOLECULAR MASS OR MOLAR MASS :

That amount of substance whose mass in grams is equal to its molecular mass or the equivalently molecular mass of a substance expressed in grams is called gram molecular mass. Gram molecular mass is also called one gram molecule. thus

$$\text{No. of gm molecules} = \frac{\text{Wt. of substance (gms.)}}{\text{GMM of substance}}$$

EQUIVALENT MASS :

It is the number of parts by weight of the substance that combines or displaces, directly or indirectly, 1.008 parts by mass of hydrogen or 8 parts by mass of oxygen or 35.5 parts by mass of chlorine.

It can be calculated as

(i) $\text{Equivalent mass for elements} = \frac{\text{Atomic mass}}{\text{Valency}}$

(ii) $\text{Equivalent mass for acids} = \frac{\text{Molecular mass}}{\text{Basicity of acids}}$

(iii) $\text{Equivalent mass for bases} = \frac{\text{Molecular mass}}{\text{Acidity of base}}$

(iv) Equivalent mass for salts

$$= \frac{\text{Formula mass}}{\text{(Valency of cation) (No. of cations)}}$$

(v) Equivalent mass for oxidising agents

$$= \frac{\text{Formula mass}}{\text{No. of electrons gained per molecule}}$$

(vi) Equivalent mass for reducing agents

$$\frac{\text{Formula mass}}{\text{No. of electrons lost per molecule}}$$

(vii) Equivalent weight of radicals

$$= \frac{\text{Formula mass of radical}}{\text{No. of units of charge}}$$

FORMULA MASS :

It is obtained by adding atomic masses of various atoms present in the formula and this term replaces molecular mass in ionic compounds.

ACIDITY :

It is the number of OH^- ions that can be displaced from one molecule of a substance.

BASICITY :

It is the number of H^+ ions that can be displaced from one molecule of a substance.

GRAM EQUIVALENT MASS (GEM) :

It is the mass of a substance expressed in grams or equivalently the quantity of substance whose mass in grams is equal to its equivalent mass is called one gram equivalent or gram equivalent mass.

$$\text{No. of gm equivalents} = \frac{\text{Mass in gm}}{\text{GEM}}.$$

METHODS OF DETERMINING EQUIVALENT MASSES :

(i) Hydrogen displacement method : It is for metals which can displace H_2 from acids.

Equivalent mass of metal

$$= \frac{\text{Weight of metal}}{\text{Weight of displaced hydrogen}} \times 1.008$$

$$= \frac{\text{Weight of metal in gram}}{\text{Vol. of } H_2 \text{ in litre}} \times 11.2 \text{ litre}$$

(ii) Metal displacement method : It utilises the fact that one GEM of a more electropositive metal displaces one GEM of a less electropositive metal from its salt. $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

(iii) Conversion method : When one compound of a metal is converted to another compound of similar metal then

$$\frac{\text{Weight of first compound}}{\text{Weight of second compound}}$$

$$= \frac{\text{E + Eqv. mass of first radical}}{\text{E + Eqv. mass of second radical}}$$

where E is the eqv. mass of the metal.

(iv) Electrolytic method : It states that the quantity of substance that reacts at electrode when 1 Faraday of electricity is passed is equal to its GEM.

GEM = Electrochemical equivalent × 96500

and ratio of weights deposited by equal amount of electricity is in ratio of their equivalent masses.

(v) Oxide method :

$$\text{Equivalent mass of metal} = \frac{\text{Weight of metal}}{\text{Weight of oxygen}} \times 8.0$$

$$= \frac{\text{Weight of metal in gram}}{\text{Vol. of } O_2 \text{ in litre}} \times 5.6 \text{ litre}$$

(vi) Double decomposition :

$$AB + CD \longrightarrow AD\downarrow + CB$$

$$\frac{\text{Weight of compound AB}}{\text{Weight of AD}}$$

$$= \frac{\text{Eqv. mass of A + Eqv. mass of B}}{\text{Eqv. mass of A + Eqv. mass of D}}$$

$$\Rightarrow \frac{\text{Wt. of salt}}{\text{Wt. of ppt.}} = \frac{\text{Eqv. mass of salt}}{\text{Eqv. mass of salt in ppt.}}$$

(vii) Neutralisation method for acids and bases :

Equivalent mass of acid (base)

$$= \frac{\text{Wt. of acid (base)}}{\text{Vol. of acid (base) in one litre required for neutralization} \times \text{Normality of acid (base)}}$$

(viii) Silver salt is method commonly used for organic acids.

$$\text{Eqv. mass of acid} = \frac{108 \times \text{Mass of silver salt}}{\text{Mass of Ag metal}} - 107$$

Mol. mass of acid = Eqv. mass of acid × Basicity

(ix) Platinichloride method for bases :

Eqv. mass of base

$$= \frac{195 \times \text{Mass of platinum salt}}{\text{Mass of pt. metal} \times 2} - 205$$

Mol. mass of base = Eqv. mass of base × Acidity

(x) Chloride method :

$$\text{Eqv. mass of metal} = \frac{\text{Weight of metal}}{\text{Weight of chlorine}} \times 35.5$$

$$= \frac{\text{Weight of metal in gram}}{\text{Vol. of } Cl_2 \text{ in litre}} \times 11.2 \text{ litre}$$

(xi) Volatile chloride method

Valency of metal

$$= \frac{2 \times \text{VD of chloride}}{\text{Eq. mass of metal chloride}} = \frac{2 \times \text{VD}}{\text{E} + 35.5}$$

$$\Rightarrow \text{E} = \frac{2 \times \text{VD of chloride}}{\text{Valency}} - 35.5$$

CHEMICAL EQUATION :

It is the equation representing chemical change in terms of formula of reactants and products

(i) An equation which has not been equalised in terms of number of atoms of reactants and products is called a **skeleton equation.**

(ii) An equation having equal number of atoms of various kinds on both sides is **a balanced equation.**

EMPIRICAL FORMULA :

It is the simplest formula of a compound giving simplest whole number ratio of atoms present in one molecule. e.g. CH is empirical formula of benzene.

MOLECULAR FORMULA :

It is the actual formula of a compound showing the total number of atoms of constituent elements e.g. C_6H_6 is molecular formula of benzene.

Molecular formula = n × empirical formula, where n is simple whole number.

SOLUTION :

It is a homogenous mixture of two or more substances. The component of solution having larger proportion is solvent and others are solute.

MOLE FRACTION :

It is the ratio of moles of a constituent to the total number of moles in a solution.

Let A be solute & B is solvent then mole fraction of solute (x_A)

$= \frac{n_A}{n_A + n_B}$, where n is the number of moles.

Mole fraction of solution $x_A + x_B = 1$

MASS PERCENTAGE :

It is the number of parts by mass of solute per hundred parts by mass of solution. If W_A is mass of solute and W_B the mass of solvent, then

Mass percentage of A = $\frac{W_A}{W_A + W_B} \times 100$.

VOLUME PERCENTAGE :

It is the number of parts by volume of solute per hundred parts by volume of solution. If V_A is volume of solute and V_B is the volume of solvent then

Volume percentage of A = $\frac{V_A}{V_A + V_B} \times 100$

PARTS PER MILLION (ppm) :

It is the mass of solute present in one million parts by mass of solution.

$$\text{ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

NORMALITY :

It is the number of gram equivalents of a solute present in one litre of solution.

$$\text{Normality} = \frac{\text{Gram equivalents of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{\text{Mass of solute in gms.}}{\text{GEM of solute} \times \text{volume of solution in litre}}$$

Normality depends on temperature. Also if strength is given in normalities, N_1 of A & N_2 of B

Then $N_1V_1 = N_2V_2$.

MOLARITY :

It is the number of moles of solute present in one litre of solution.

$$\text{M} = \frac{\text{Moles of solute}}{\text{Volume of solution (L)}}$$

$$= \frac{\text{Weight of solute}}{\text{GMM of solute} \times \text{Volume of solution (L)}}$$

$\Rightarrow$ Moles = M × $V_{(\text{in litre})}$ and millimoles = M × $V_{(\text{in ml})}$.

Molarity and mass percentage have the relation M

$= \frac{\text{mass percentage} \times 10 \times d}{\text{GMM of solute}}$, where d = density

If a solution of molarity M_1 and volume V_1 adds up with a solvent to a final volume V_2, then molarity M_2 is given by

$$M_2 = \frac{M_1V_1}{V_2}$$

If two different solutions (M_1, V_1) and (M_2, V_2) are mixed then molarity of resulting solution is

$$M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$

Also, Molarity × GMM of solute = Normality × GEM of solute

MOLALITY :

It is the number of moles of solute in 1 kg of solvent.

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Weight of solvent (Kg)}}$$

$$= \frac{\text{Weight of solute} \times 1000}{\text{Mol. wt. of solute} \times \text{Wt. of solvent}}$$

Molality is independent of temperature.

FORMALITY (F) :

It is the number of gram formula mass of ionic solute dissolved in 1 litre of solution.

$$\text{Formality} = \frac{\text{Mass of solute (gm)}}{\text{Volume of solution (litre)} \times \text{GFM of solute}}$$

LIMITING REAGENT :

It is the reactant which is completely consumed during the reaction.

Miscellaneous Solved Examples

1. Calculate the weight of Iron which will be converted into its oxide by the action of 18 g of steam.

Sol. The required equation is

$$\begin{array}{ccc} 3Fe & + \ 4H_2O \longrightarrow & Fe_3O_4 + 4H_2 \\ 3 \times 56 \text{ g} & 4 \times 18 \text{ g} & \\ \dfrac{3 \times 56}{4} \text{g} & 18 \text{ g} & \end{array}$$

$\therefore$ Weight of Fe converted into oxide = 42 g.

2. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 27°C. Calculate the moles of NO_2 in 100 g mixture.

Sol. Molecular weight of mixture = 2 × 38.3 = 76.6

Let weight of NO_2 present in mixture be x g

then $\dfrac{x}{46} + \dfrac{100 - x}{92} = \dfrac{100}{76.6}$ $\quad \therefore x = 20.10$ g

Hence moles of NO_2 in mixture $= \dfrac{20.10}{46} = 0.43$

3. A mixture of 20 ml of CO, CH_4 and N_2 was burnt in excess of O_2, resulting in reduction of 13 ml of volume. The residual gas was then treated with KOH solution to show a contraction of 14 ml in Volume. Calculate volume of CO, CH_4 and N_2 in mixture. All measurements are made at constant T and P.

Sol. Let a, b and c be the volume of CO, CH_4 and N_2 in mixture.

$$\text{(I)} \quad \begin{array}{ccc} CO + & \dfrac{1}{2}O_2 \longrightarrow & CO_2 \\ a & \dfrac{a}{2} & a \end{array}$$

$$\text{(II)} \quad \begin{array}{ccc} CH_4 + & 2O_2 \longrightarrow & CO_2 + 2H_2O \\ b & 2b & b \end{array}$$

$$\text{(III)} \quad N_2 + O_2 \longrightarrow \text{No Reaction}$$

Since reduction in volume is 13. This is volume of O_2 used then we have

$$\frac{a}{2} + 2b = 13 \qquad \text{(I)}$$

Volume of CO_2 formed is volume absorbed by KOH

$$a + b = 14 \qquad \text{(II)}$$

$\therefore c = 20 - 14 = 6$ ml

Solving I & II we get a = 10 ml, b = 4 ml.

$\therefore$ CO = 10 ml, CH_4 = 4 ml and N_2 = 6 ml

4. The weight of one litre sample of ozonised oxygen at NTP was found to be 1.5 g. When 100 ml of this mixture at NTP were treated with terpentine oil the volume was reduced to 90 ml. Hence calculate the molecular weight of Ozone.

Sol. Since terpentine oil absorbs O_3, the volume of O_3 absorbed by terpentine oil is 10 ml.

Volume of O_2 = 100 – 10 = 90 ml

From gas equation (m)

$$PV = \frac{WRT}{M}$$

Mol. wt of ozonised oxygen

$$= \frac{WRT}{PV} = \frac{1.5 \times 0.0821 \times 273}{1 \times 1} = 33.62$$

Mol. ratio of O_2 and O_3 90 : 10.

M. wt. of ozonised oxygen

$$= \frac{90 \times 32 + 10 \times a}{100} = 33.62 \Rightarrow a = 48.2 .$$

Mol. wt. of ozone = 48.2.

5. How many millilitre of 0.5M H_2SO_4 are needed to dissolve 0.5 g of copper (II) carbonate.

Sol. Millimoles of H_2SO_4 = Millimoles of $CuCO_3$

$$0.5 \times V = \frac{0.5 \times 1000}{123.5} \quad \text{or} \quad V = 8.097 \text{ ml.}$$

6. The formula weight of an acid is 82.0. 100 cm^3 of a solution of this acid containing 39.0 g of the acid per litre were completely neutralised by 95.0 cm^3 of aqueous NaOH containing 40.0 g of NaOH per litre. What is the basicity of the acid?

Sol. Normality of NaOH $= \dfrac{40 \times 1000}{40 \times 1000} = 1$

$$\text{Normality of acid} = \frac{39 \times 1000}{\frac{82}{n} \times 1000} = \frac{39n}{82}$$

n = Basicity of acid

$N_1V_1 = N_2V_2$

$$\frac{39n \times 100}{82} = 1 \times 95 \qquad n = 1.99 = 2 \text{ Basicity is } 2.$$

7. For the reaction $N_2O_5 \text{ (g)} \rightleftharpoons 2NO_2 \text{ (g)} + 0.5 \ O_2 \text{ (g)}$. Calculate the mole fraction of N_2O_5 (g) decomposed at a constant volume and temperature if the initial pressure is 600 mm Hg and the pressure at any time is 960 mm Hg. Assume ideal gas behaviour.

Sol.	$N_2O_5 \rightleftharpoons$	$2NO_2 +$	$\frac{1}{2}O_2$
Initial pressure	600	0	0
Final pressure	$600-p$	$2p$	$\frac{p}{2}$

$p \propto n$

At constant T and V.

$$= \text{Total moles} = 600 - p + 2p + \frac{p}{2} = 960 \;;\; \therefore p = 240$$

$$\therefore \text{ mole fraction of } N_2O_5 \text{ decomposed} = \frac{240}{600} = 0.4\,.$$

8. 1.20 g sample of Na_2CO_3 and K_2CO_3 was dissolved in water to form 100 ml of a solution. 20 ml of this solution required 40 ml of 0.1 N HCl for complete neutralisation. Calculate the weight of Na_2CO_3 in mixture. If another 20 ml of this solution is treated with excess of $BaCl_2$. What will be the weight of precipitate?

Sol. Let weight of Na_2CO_3 in the sample be a g then weight of K_2CO_3 in the sample $(1.20 - a)$g.

gev of Na_2CO_3 + gev of K_2CO_3 = gev of HCl

$$\therefore \frac{a}{53} + \frac{(1.20-a)}{69} = \frac{40 \times 0.1 \times 5}{1000}$$

On solving a = 0.59629

$\therefore$ weight of $Na_2CO_3 = 0.59629$ g

Addition of $BaCl_2$ will form precipitate of $BaCO_3$

Meq of $BaCO_3$ = (Meq of Na_2CO_3 + Meq. of K_2CO_3) in 20 ml = Meq of HCl in 20 ml $= 40 \times 0.1 = 4$

$$\therefore \frac{W}{98.5} \times 1000 = 4 \quad \therefore \text{ Wt. of } BaCO_3 = 0.394\,g$$

9. A mixture of ethane (C_2H_6) and ethene C_2H_4 occupies 40 litre at 1.00 atm and at 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O. Assuming ideal gas behaviour, calculate the mole fraction of C_2H_4 and C_2H_6 in the mixture.

Sol. Moles of C_2H_6 and C_2H_4 in the mixture

$PV = nRT$

$1 \times 40 = n \times 0.0821 \times 400$

$n = 1.2195$

Let a be the moles of ethane, then moles of ethene $(1.2195 - a)$

$$\text{Again} \quad C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$$

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

moles of O_2 required for complete combustion

$$\frac{7}{2}a + (1.2195 - a) \times 3 = \frac{130}{32}$$

On solving a = 0.08.

$$= \text{Mole fraction of ethane} = \frac{0.808}{1.2195} = 0.66$$

Mole fraction of $C_2H_4 = 0.34$.

10. A mixture in which the mole ratio of H_2 and O_2 is 2 : 1 is used to prepare water by the reaction ;

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O\ (g)$$

The total pressure in the container is 0.8 atm at 20°C before the reaction. Determine the final pressure at 120°C after reaction assuming 80% yield of water.

Sol.	$2H_2 +$	$O_2 \longrightarrow$	$2H_2O$	
Initial mole	2a	a	0	Total : = 3a

$$\text{Moles of water formed} = \frac{2a \times 80}{100} = 1.6a$$

Final moles=	0.4 a	2a	1.6a	Total = 2.2 a

Now PV = nRT

$$\frac{0.8 \times V}{P \times V} = \frac{3a \times 0.0821 \times 293}{2.2a \times 0.821 \times 393} \quad \text{or} \quad P = 0.787\ \text{atm.}$$

11. 1.00g of copper was dissolved in nitric acid and on ignition gave 1.25g of cupric oxide. 1.00g of cuprous oxide when ignited in a current of hydrogen gave 0.888g of copper. Show that these results illustrate the law of multiple proportion.

Sol. Weight of cupric oxide = 1.25g

Weight of copper = 1.00g

Weight of oxygen reacting with 1g of copper = (1.25 - 1.00) = 0.25g

Weight of Cuprous oxide = 1.00g

Weight of Copper = 0.888g

Weight of oxygen reacting with 0.888g of Copper = (1.00 – 0.888)

Weight of oxygen reacting with 1.00g of Copper = 0.112g

$$\frac{1.112}{0.888} = 0.127g$$

Ratio of oxygen reacting with fixed amount of copper in two oxides 0.25 : .0127 = 2:1

It shows the law of multiple proportion.

12. Show that the following figures illustrate the law of Reciprocal proportion :

Methane	Carbon dioxide	Water
C = 75%	C = 42.86%	H = 11.11%
H = 25%	O = 57.14%	O = 88.89%

Sol. In methane 75g carbon combines with 25g of H_2

In CO_2 75g of carbon combines with $\frac{57.14}{42.86} \times 75g = 100g$ of O_2.

Ratio of H_2 and O_2 reacting with fixed amount of carbon= 1:4

In water the ratio of hydrogen and oxygen

= 11.11:88.89

= 1:8 = 1:2×4

It show the law of Reciprocal Proportion.

13. Three oxides of a metal contain respectively 92.85%, 90.63% and 86.51% of the metal. Examine if these figure are in agreement with the law of multiple proportion.

Sol.

	I	II	III
Metal	92.85	90.63	86.51
Oxygen	7.15	9.37	13.49

Ratio of oxygen reacting with 1 part of metal

$$\frac{7.15}{92.85} : \frac{9.37}{90.63} : \frac{13.49}{86.51}$$

$$0.077 : 0.103 : 0.156$$

$$2 : 3 : 4$$

It shows the law of multiple proportion.

14. A chloride of phosphorous contains 22.57% of phosphorous, Phosphine contains 8.82% hydrogen and hydrogen chloride gas contains 97.23% chlorine. Prove that these data illustrate the law of equivalent proportion

Sol. (i) In phosphorous chloride, phosphorous is $= 22.57\%$

So chlorine is $(100 - 22.57) = 77.43\%$

Ratio between masses of phosphrous and chlorine $22.57 : 77.43 = 1 : 3.43$

(ii) In phosphine, hydrogen is $= 8.82\%$

So phosphorous is $(100 - 8.82) = 91.18\%$

Ratio between masses of phosphorous and hydrogen $91.18 : 8.82 = 1 : 0.096$

In compounds (i) and (ii) the ratio between masses of hydrogen and chlorine $= 0.096 : 3.43 = 1.35.7$

(iii) In hydrogen chloride gas, chlorine is $= 97.23\%$

So hydrogen is $(100 - 97.23) = 2.77\%$

therefore $H : Cl = 2.77 : 97.23 = 1 : 35.5$

The ratio is the same, hence it illustrates the law of equivalent proportion.

15. Hydrogen sulphide contains 5.88% of hydrogen Water contains 11.11% of hydrogen and sulphur dioxide contains 50% of sulphur. Show that these figures illustrate the law of reciprocal proportion

Sol. Find the same amount of hydrogen which combines with sulphur in H_2S and oxygen in H_2O

5.88g hydrogen combines with 94.12g sulphur in H_2S

5.88g of hydrogen combines with $\frac{88.89}{11.11} \times 5.88\text{g}$ oxygen in H_2O.

The ratio of S and O combining with fixed amount of H is 2:1. In SO_2 the S:O is 1:1

It illustrates the law of Reciprocal proportion.

16. 0.50g of Ag in nitric acid gave on addition of hydrochloric acid, 0.665g of silver chloride. Find the equivalent weight of silver.

Sol. Equivalent Wt. of Silver

$$= \frac{\text{wt of silver}}{\text{wt of chlorine}} \times 35.46 = \frac{0.50}{0.165} \times 35.46 = 107.99$$

(wt of chlorine $= 0.665 - 0.50 = 0.165$)

17. 1g of KCl solution gives 1.925g of AgCl when heated with excess of $AgNO_3$ solution. Taking equivalent wt of Ag as 108 and that of Cl as 35.5 calculate the equivalent wt of potassium

Sol.

$$\frac{\text{wt of KCl}}{\text{wt of AgCl}} = \frac{\text{eq. wt. of K} + \text{eq. wt. of Cl}}{\text{eq. wt. of Ag} + \text{eq. wt. of Cl}}$$

$$\frac{1}{1.925} = \frac{\text{Eq. wt of K} + 35.5}{108 + 35.5}$$

$\therefore$ Eq. wt. of K $= 39.05$

18. 0.622g of a nitrate of heavy metal on heating to constant weight gave 0.466g of its oxide. Calculate the equivalent weight of the metal from the above data

Sol.

$$\frac{\text{wt of metal nitrate}}{\text{wt of metal oxide}} = \frac{\text{Eq. wt. of metal nitrate}}{\text{Eq. wt. of metal oxide}}$$

$$\frac{0.662}{0.466} = \frac{E + 62}{E + 8}$$

$$\therefore \quad E = 120.4$$

19. 0.4426g of a metallic chloride was dissolved in water and solution made up to 100 ml., 50 ml of this solution required 1.02g of $AgNO_3$ to precipitate the chloride completely. The specific heat of the metal was 0.057. Calculate the equivalent weight, atomic weight and valency of metal.

Sol. Let the equivalent wt of metal be E, then

$$\frac{\text{weight of metal chloride}}{\text{weight of silver nitrate}} = \frac{\text{Eq. wt. of metal chloride}}{\text{Eq. wt. of silver nitrate}}$$

$$\frac{0.4426}{1.02} = \frac{E + 35.5}{170}$$

$\therefore$ $E = 38.26$

According to Dulong Petit's rule : Atomic wt × Sp. heat = 6.4

$$\therefore \quad \text{Atomic wt} = \frac{6.4}{0.057} = 112.3$$

$$\text{valency} = \frac{\text{Atomic wt.}}{\text{Eq. wt.}} = \frac{112.3}{38.26} = 3$$

Hence exact atomic wt. $= 38.26 \times 3 = 114.78$

20. One g of the chloride of an element was found to contain 0.835 g of chlorine. It's vapour density is 85. Find the molecular formula of chloride.

Sol. Weight of element = (1 – 0.835) = 0.165g

$$\text{Eq. wt. of element} = \frac{0.165}{0.835} \times 35.5 = 7.014$$

Let x be the valency of element

Atomic wt. of element = 7.014 x

The Molecular formula of chloride MCl_x

$\therefore$ Molecular weight of chloride

$= 7.014.x + x.35.3 = V.D \times 2$

or, $(42.541)x = 2 \times 85$

$\therefore \quad x = 4$

Hence Molecular formula of chloride = MCl_4

21. Copper sulphide and Metal sulphide are isomorphous. In the first compound sulphur is 20.14% and in the second compound 12.94%. If the atomic weight of Copper is 63.57. Find the atomic weight of Metal

Sol. Find the fixed (same) amount of sulphur reacting with copper and Metal separately.

In the first-compound 1g sulphur combines with

$$\frac{(100-20.14)}{20.14} = 3.96 \text{ g Copper}$$

In the second compound 1g sulphur combines with

$$\frac{(100-12.94)}{12.94} = 6.72 \text{ g Metal}$$

$$\frac{\text{Atomic wt. of Metal}}{\text{Atomic wt. of Cu}} = \frac{\text{wt of Metal}}{\text{wt of Copper}}$$

$$\text{Atomic wt. of Metal} = \frac{6.72}{3.96} \times 63.57 = 107.87$$

22. 0.2988g of the silver salt of a dibasic acid on ignition gave 0.1944g of Silver. Find the equivalent weight of acid.

Sol. Equivalent weight of the acid

$$= \left(\frac{\text{wt. of silver salt} \times 108}{\text{wt. of silver}} - 107\right)$$

$$= \left(\frac{0.2988 \times 108}{0.1944} - 107\right) = 59$$

23. 0.298g platinichloride salt of the mono acid base yielded 0.0975g of platinum. Find the equivalent weight of mono acid base

Sol. Equivalent weight of the base

$$= \frac{1}{2}\left(\frac{\text{wt of Pt.salt} \times 195}{\text{wt of Pt.}} - 410\right)$$

$$= \frac{1}{2}\left(\frac{0.298 \times 195}{0.0975} - 410\right) = 93$$

24. 1.0g of metal on treatment with dilute mineral acid gave 1242 ml of hydrogen at NTP. Calculate the equivalent weight, atomic weight and valency of the metal, if its specific heat is 0.238

Sol. $\text{Equivalent weight of metal} = \frac{\text{wt. of metal}}{\text{wt. of hydrogen}} \times 1.008$

1 ml of hydrogen at NTP = 0.00009g

$$\therefore \quad \text{Eq. wt of metal} = \frac{1}{0.00009 \times 1242} \times 1.008 = 9 \text{ g}$$

By Dulong Petit's law

Atomic mass×sp. heat = 6.4

$$\text{Atomic mass} = \frac{6.4}{0.238} = 26.86$$

$$\text{valency} = \frac{26.86}{9} = 3$$

$\therefore$ Exact atomic mass = 9×3 = 27

Exercise-1 | NCERT BASED QUESTIONS

Very Short/ Short Answer Questions

1. A colourless liquid used in rocket engines, whose empirical formula is NO_2, has a molar mass of 92. What is its molecular formula?

2. Reaction, $2Br^-(aq) + Cl_2(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq)$, is used for commercial preparation of bromine from its salts. Suppose we have 50.0 ml of a 0.060M solution of NaBr. What volume of a 0.050 M solution of Cl_2 is needed to react completely with Br^-?

3. 45.4L of dinitrogen reacted with 22.7 L of dioxygen and 45.4 L of nitrous oxide was formed. The reaction is given below:

$2N_2(g) + O_2(g) \dashrightarrow 2N_2O(g)$

Which law is being obeyed in this experiment? Write the statement of the law.

4. Describe the difference between the mass of a mole of oxygen atoms (O) and the mass of a mole of oxygen molecules (O_2).

5. Alkaline solution of $KMnO_4$ reacts as follows:

$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$

Calculate the equivalent weight of $KMnO_4$ in basic medium.

6. Dinitrogen combines with dihydrogen to form ammonia according to the following reaction.

$$N_2(g) \quad 3H_2(g) \rightleftharpoons 2NH_3(g)$$

What is the ratio of their volumes under similar conditions of temperature and pressure?

7. Zinc and hydrochloric acid react according to the equation

$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$

If 0.30 mole of Zn are added to hydrochloric acid containing 0.52 mole of HCl. Which of the two reactant is limiting reagent and how many moles of H_2 are produced?

8. A glass of juice contains 9 gm of glucose ($C_6H_{12}O_6$). How many atoms of each element (C, H and O) are there in the juice.

9. Two bulbs B_1 and B_2 of equal capacity contain 10g oxygen (O_2) and ozone (O_3) respectively. Which bulb will have greater number of O-atoms and which will have greater number of molecules?

10. 4 g of copper chloride on analysis was founded to contain 1.890 g of copper (Cu) and 2.110 g of chlorine (Cl). What is the empirical formula of copper chloride? [Atomic mass of Cu = 63.5 u, Cl = 35.5 u]

11. Calculate the moles of NaOH required to neutralize the solution produced by dissolving 1.1 g P_4O_6 in water. Use the following reactions:

$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$

$2NaOH + H_3PO_3 \rightarrow Na_2HPO_3 + 2H_2O$

(Atomic mass/g mol^{-1}; P = 31, O = 16)

Long Answer Questions

12. (i) Concentrated aqueous sulphuric acid is 98% H_2SO_4 by mass and has a density of 1.84 g mL^{-1}. What volume of the concentrated acid is required to make 5.0L of 0.50 M H_2SO_4 solution? (Mol. weight of sulphuric acid = 98)

(ii) You are given a solution of 14.8M NH_3. How many milliliters of this solution do you require to give 100 ml of 1MNH_3? How much of water will you add?

13. (i) Copper oxide was prepared by the following methods:

(a) In one case, 1.75 g of the metal were dissolved in nitric acid and igniting the residual copper nitrate yielded 2.19 g of copper oxide.

(b) In the second case, 1.14 g of metal dissolved in nitric acid were precipitated as copper hydroxide by adding caustic alkali solution. The precipitated copper hydroxide after washing, drying and heating yielded 1.43g of copper oxide.

(c) In the third case, 1.45 g of copper when strongly heated in a current of air yielded 1.83 g of copper oxide.

Show that the given data illustrate the law of constant composition.

(ii) Elements A and B form two different compounds. In first case 0.52 grams of A combines with 0.72 grams of B and in second case 0.15 grams of A combines with 0.65 grams of B. Show that these data illustrate the Law of multiple proportion.

14. (i) Calculate the volume at STP occupied by (a) 14 g of nitrogen, (b) 1.5 moles of carbon dioxide and (c) 10^{21} molecules of oxygen.

(ii) Ammonia contains 82.35% of nitrogen and 17.65% of hydrogen. Water contains 88.90% of oxygen and 11.10% of hydrogen. Nitrogen trioxide contains 63.15% of oxygen and 36.85% of nitrogen. Show that these data illustrate the law of reciprocal proportions.

Multiple Choice Questions

15. Two students performed the same experiment separately and each one of them recorded two readings of mass which are given below. Correct reading of mass is 3.0 g. On the basis of given data, mark the correct option out of the following statements.

Students	**Readings**	
	(i)	(ii)
A	3.01	2.99
B	3.05	2.95

(a) Results of both the students are neither accurate nor precise.
(b) Results of student A are both precise and accurate.
(c) Results of student B are neither precise nor accurate.
(d) Results of student B are both precise and accurate.

16. A measured temperature on Fahrenheit scale is 200 °F. What will this reading be on Celsius scale ?
(a) 40° C (b) 94° C
(c) 93.3 °C (d) 30° C

17. Which of the following is an example of a heterogeneous substance?
(a) Bottled water (b) Table salt
(c) Pieces of copper (d) Candle

18. Which of the following statements about a compound is incorrect ?
(a) A molecule of a compound has atoms of different elements.
(b) A compound cannot be separated into its constituent elements by physical methods of separation.
(c) A compound retains the physical properties of its constituent elements.
(d) The ratio of atoms of different elements in a compound is fixed.

19. In compound A, 1.00g of nitrogen unites with 0.57g of oxygen. In compound B, 2.00g of nitrogen combines with 2.24g of oxygen. In compound C, 3.00g of nitrogen combines with 5.11g of oxygen. These results obey the following law
(a) law of constant proportion
(b) law of multiple proportion
(c) law of reciprocal proportion
(d) Dalton's law of partial pressure

20. One mole of a gas occupies a volume of 22.4 L. This is derived from
(a) Berzelius' hypothesis
(b) Gay-Lussac's law
(c) Avogadro's law
(d) Dalton's law

21. Two containers P and Q of equal volume (1 litre each) contain 6 g of O_2 and SO_2 respectively at 300 K and 1 atmosphere, then
(a) number of molecules in P is less than that in Q
(b) number of molecules in P and Q is same
(c) number of molecules in Q is less than that in P
(d) Either (a) or (b)

22. In a chemical reaction

$$K_2Cr_2O_7 + xH_2SO_4 + ySO_2 \longrightarrow K_2SO_4 + zCr_2(SO_4)_3 + H_2O$$

the values of x, y, z are
(a) 4, 1, 4 (b) 1, 3, 1
(c) 3, 2, 3 (d) 2, 1, 2

23. 25.4 g of I_2 and 14.2 g of Cl_2 are made to react completely to yield a mixture of ICl and ICl_3. Calculate moles of ICl and ICl_3 formed
(a) 0.1, 0.1 (b) 0.2, 0.2
(c) 0.1, 0.2 (d) 0.2, 0.1

24. The Statue of Liberty is made of 2.0×10^5 lbs of copper sheets bolted to a framework. (1lb = 454 g). How many atoms of copper are on the statue? (Atomic weight: Cu = 63.5).
(a) 2.1×10^{27} (b) 8.6×10^{29}
(c) 4.3×10^{26} (d) 8.6×10^{26}

Exercise-2 | CONCEPTUAL MCQs

1. In the final answer of the expression

$$\frac{(29.2 - 20.2)(1.79 \times 10^5)}{1.37}$$

the number of significant figures is
(a) 1 (b) 3 (c) 2 (d) 4

2. Given the numbers : 161 cm, 0.161 cm, 0.0161 cm. The number of significant figures for the three numbers are
(a) 3, 4 and 5 respectively (b) 3, 3 and 4 respectively
(c) 3, 3 and 3 respectively (d) 3, 4 and 4 respectively

3. One fermi is
(a) 10^{-15} cm (b) 10^{-13} cm
(c) 10^{-10} cm (d) 10^{-12} cm

4. A sample was weighted using two different balances. The results were
(i) 3.929 g (ii) 4.0 g

How would the weight of the sample be reported?
(a) 3.93 g (b) 3g
(c) 3.9 g (d) 3.929 g

5. Dimension of pressure are same as that of
(a) Energy (b) Force
(c) Force per unit volume (d) Energy per unit volume

6. The prefix 10^{18} is
(a) giga (b) kilo
(c) exa (d) nano

7. Which of the following halogen can be purified by sublimation?
(a) I_2 (b) Cl_2
(c) Br_2 (d) F_2

8. A mixture of sand and iodine can be separated by
(a) crystallisation (b) distillation
(c) sublimation (d) fractionation

9. Among the following pairs of compounds, the one that illustrates the law of multiple proportions is

(a) NH_3 and NCl_3 (b) H_2S and SO_2
(c) CS_2 and $FeSO_4$ (d) CuO and Cu_2O

10. Irrespective of the source, pure sample, of water always yields 88.89% mass of oxygen and 11.11% mass of hydrogen. This is explained by the law of

(a) conservation of mass (b) multiple proportions
(c) constant composition (d) constant volume

11. If N_A is Avogadro's number then number of valence electrons in 4.2 g of nitride ions (N^{3-}) is

(a) 4.2 N_A (b) 2.4 N_A
(c) 1.6 N_A (d) 3.2 N_A

12. Two containers P and Q of equal volume (1 litre each) contain 6 g of O_2 and SO_2 respectively at 300 K and 1 atmosphere. then

(a) Number of molecules in P is less than that in Q
(b) Number of molecules in P and Q is same
(c) Number of molecules in Q is less than that in P
(d) Either (a) or (b)

13. The number of moles of oxygen in one litre of air containing 21% oxygen by volume, under standard conditions are

(a) 0.0093 mole (b) 0.21 mole
(c) 2.10 mole (d) 0.186 mole

14. The vapour density of a gas is 11.2. The volume occupied by 11.2 g of the gas at NTP will be

(a) 22.4 L (b) 11.2 L
(c) 1 L (d) 44.8 L

15. The amount of zinc required to produce 224 ml of H_2 at STP on treatment with dil. H_2SO_4 will be

(a) 6.5 g (b) 0.65 g
(c) 65 g (d) 0.065 g

16. The volume occupied by 4.4 g of CO_2 at STP is

(a) 22.4 L (b) 0.224 L
(c) 2.24 L (d) 0.1 L

17. Assuming fully decomposed, the volume of CO_2 released at STP on heating 9.85 g of $BaCO_3$ (Atomic mass, Ba = 137) will be

(a) 1.12 L (b) 2.24 L
(c) 4.06 L (d) 0.84 L

18. 10 dm^3 of N_2 gas and 10 dm^3 of gas X at the same temperature contain the same number of molecules, the gas X is

(a) CO_2 (b) CO (c) H_2 (d) NO

19. 7.5 grams of a gas occupy 5.6 litres of volume at STP. The gas is

(a) N_2O (b) NO (c) CO (d) CO_2

20. 1 amu is equal to

(a) $\frac{1}{14}$ of O-16 (b) $\frac{1}{12}$ of C-12
(c) 1 g of H_2 (d) 1.66×10^{-23} kg

21. Which of the following contains maximum number of atoms?

(a) 6.023×10^{21} molecules of CO_2
(b) 0.44 g of CO_2
(c) 22.4 L of CO_2 at STP
(d) None of these

22. Number of g of oxygen in 32.2 g $Na_2SO_4.10\,H_2O$ is

(a) 20.8 (b) 2.24 (c) 22.4 (d) 2.08

23. The specific heat of a metal is 0.16, its approximate atomic weight would be

(a) 32 (b) 16 (c) 64 (d) 40

24. The weight of a molecule of the compound $C_{60}H_{122}$ is

(a) 1.09×10^{-21} g (b) 1.4×10^{-21} g
(c) 5.025×10^{23} g (d) 16.023×10^{23} g

25. The number of water molecules present in a drop of water (volume 0.0018 ml) density = 18 ml^{-1}at room temperature is

(a) 1.084×10^{18} (b) 6.023×10^{19}
(c) 4.84×10^{17} (d) 6.023×10^{23}

26. The percentage of Se in peroxidase anhydrous enzyme is 0.5% by weight (atomic weight = 78.4). Then minimum molecular weight of peroxidase anhydrous enzyme is

(a) 1.568×10^3 (b) 1.568×10^4
(c) 15.68 (d) 3.136×10^4

27. Equivalent weight of crystalline oxalic acid is

(a) 90 (b) 53 (c) 63 (d) 45

28. 3 g of an oxide of a metal is converted to chloride completely and it yielded 5 g of chloride. The equivalent weight of the metal is

(a) 3.325 (b) 33.25 (c) 12 (d) 20

29. The simplest formula of a compound containing 50% of element X (atomic mass 10) and 50% of element Y (atomic mass 20) is

(a) XY (b) XY_3 (c) X_2Y (d) X_2Y_3

30. The hydrogen phosphate of certain metal has formula $MHPO_4$. The formula of metal chloride would be

(a) MCl (b) M_2Cl_2 (c) MCl_2 (d) MCl_3

31. A compound contains atoms of three elements as A, B and C. If the oxidation number of A is +2, B is +5 and that of C is –2, the possible formula of the compound is

(a) $A_3(B_4C)_2$ (b) $A_3(BC_4)_2$
(d) ABC_2 (d) $A_2(BC_3)_2$

32. If 0.44 g of a colourless oxide of nitrogen occupies 224 ml at 1520 mm Hg and 273°C, then the compound is

(a) NO_2 (b) N_2O
(c) NO_4 (d) N_2O_2

33. The mass of a molecule of water is

(a) 3×10^{-25} kg (b) 3×10^{-26} kg
(c) 1.5×10^{-26} kg (d) 2.5×10^{-26} kg

34. Number of moles of $KMnO_4$ required to oxidize one mole of $Fe(C_2O_4)$ in acidic medium is

(a) 0.167 (b) 0.6 (c) 0.2 (d) 0.4

35. 100 cm^3 of 0.1 N HCl is mixed with 100 cm^3 of 0.2 N NaOH solution. The resulting solution is

(a) 0.1 N and the solution is basic
(b) 0.1 N and the solution is acidic
(c) 0.05 N and the solution is basic
(d) 0.05 N and the solution is acidic

36. For preparing 0.1 N solution of a compound from its impure sample of which the percentage purity is known, the weight of the substance required will be

(a) less than the theoretical weight

(b) more than the theoretical weight

(c) same as the theoretical weight

(d) none of these

37. 10 g $CaCO_3$ gives on strong heating CO_2. It gives quicklime (in grams)

(a) 5g (b) 4.4 g (c) 5.6 g (d) 4 g

38. Haemoglobin contains 0.33% of iron by weight. The molecular weight of haemoglobin is approximately 67200. The number of iron atoms (at. wt. of Fe = 56) present in one molecule of haemoglobin is

(a) 6 (b) 1 (c) 2 (d) 4

39. The number of molecules in 16 g of methane is

(a) 3.0×10^{23} (b) $\frac{16}{6.02} \times 10^{23}$

(c) 6.02×10^{23} (d) $\frac{16}{3.0} \times 10^{23}$

40. 50 ml 10 N H_2SO_4, 25 ml 12 N HCl and 40 ml 5 N HNO_3 were mixed together and the volume of the mixture was made 1000 ml by adding water. The normality of the resultant solution will be

(a) 2 N (b) 1 N (c) 3 N (d) 4 N

41. A molal solution is one that contains 1 mole of a solute in

(a) one litre of the solvent

(b) 1000 g of the solvent

(c) one litre of the solution

(d) 22.4 litres of the solution

42. A 100 ml solution of 0.1 N HCl was titrated with 0.2 N NaOH solution. The titration was discontinued after adding 30 ml of NaOH solution. The remaining titration was completed by adding 0.25 N KOH solution. The volume of KOH required for completing the titration is

(a) 16 ml (b) 32 ml

(c) 35 ml (d) 70 ml

43. An aqueous solution of 6.3 g of oxalic acid dihydrate is made up to 250 ml. The volume of 0.1 N NaOH required to completely neutralise 10 ml of this solution is

(a) 20 ml (b) 40 ml

(c) 10 ml (d) 4 ml

44. The percentage of nitrogen in urea is about

(a) 85 (b) 46 (c) 18 (d) 28

45. How much of NaOH is required to neutralise 1500 cm^3 of 0.1 N HCl? (Na = 23)

(a) 60 g (b) 4 g (c) 6 g (d) 40 g

46. The volume of water to be added to 100 cm^3 of 0.5 N H_2SO_4 to get deci normal concentration is

(a) 400 cm^3 (b) 450 cm^3

(c) 500 cm^3 (d) 100 cm^3

47. 250 ml of a sodium carbonate solution contains 2.65 grams of Na_2CO_3. If 10 ml of this solution is diluted to one litre, what is the concentration of the resultant solution?

(mol. wt. of Na_2CO_3 = 106)

(a) 0.1 M (b) 0.01 M

(c) 0.001 M (d) 10^{-4} M

48. 3.92 g of ferrous ammonium sulphate crystals are dissolved in 100 ml of water. 20 ml of this solution requires 18 ml of potassium permaganate during titration for complete oxidation. The weight of $KMnO_4$ present in one litre of the solution of

(a) 3.476 g (b) 12.38 g

(c) 1.238 g (d) 34.76 g

49. 30 g of Magnesium and 30 g of oxygen are reacted, then the residual mixture contains

(a) 50 g of Magnesium oxide and 10 g of oxygen

(b) 40 g of Magnesium oxide and 20 g of oxygen

(c) 45 g of Magnesium oxide and 15 g of oxygen

(d) 60 g of Magnesium oxide only

50. In order to prepare one litre normal solution of $KMnO_4$, how many grams of $KMnO_4$ are required if the solution is to be used in acid medium for oxidation?

(a) 158 g (b) 62.0 g

(c) 31.6 g (d) 790 g

51. In a chemical reaction

$$K_2Cr_2O_7 + xH_2SO_4 + ySO_2 \longrightarrow K_2SO_4 + zCr_2(SO_4)_3 + H_2O$$

the values of x, y, z are

(a) 4, 1, 4 (b) 1, 3, 1

(c) 3, 2, 3 (d) 2, 1, 2

52. The maximum amount of $BaSO_4$ precipitated on mixing equal volumes of $BaCl_2$ (0.5 M) with H_2SO_4 (1 M) will correspond to

(a) 1.0 M (b) 0.5 M

(c) 1.5 M (d) 2.0 M

53. In the reaction

$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l)$, when 1 mole of ammonia and 1 mole of O_2 are made to react to completion

(a) 1.0 mole of H_2O is produced

(b) 1.0 mole of NO will be produced

(c) all the ammonia will be consumed

(d) all the oxygen will be consumed

54. The set of numerical coefficients that balances the equation

$K_2CrO_4 + HCl \longrightarrow K_2Cr_2O_7 + KCl + H_2O$ is

(a) 2, 2, 1, 2, 1 (b) 2, 2, 1, 1, 1

(c) 2, 1, 1, 2, 1 (d) 1, 1, 2, 2, 1

Exercise-3 | PAST COMPETITION MCQs

1. The mass of carbon anode consumed (giving only carbondioxide) in the production of 270 kg of aluminium metal from bauxite by the Hall process is (Atomic mass: Al = 27) **[CBSE-PMT 2005]**

(a) 270 kg (b) 540 kg (c) 90 kg (d) 180 kg

2. The number of moles of $KMnO_4$ reduced by one mole of KI in alkaline medium is: **[CBSE-PMT 2005]**

(a) one (b) two (c) five (d) one fifth

3. Volume occupied by one molecule of water (density = 1 g cm^{-3}) is : **[CBSE-PMT 2008]**

(a) 9.0×10^{-23} cm^3 (b) 6.023×10^{-23} cm^3
(c) 3.0×10^{-23} cm^3 (d) 5.5×10^{-23} cm^3

4. Number of moles of MnO_4^- required to oxidize one mole of ferrous oxalate completely in acidic medium will be : **[CBSE-PMT 2008]**

(a) 0.6 moles (b) 0.4 moles
(c) 7.5 moles (d) 0.2 moles

5. An organic compound contains carbon, hydrogen and oxygen. Its elemental analysis gave C, 38.71% and H, 9.67%. The empirical formula of the compound would be : **[CBSE-PMT 2008]**

(a) CH_3O (b) CH_2O (c) CHO (d) CH_4O

6. How many moles of lead (II) chloride will be formed from a reaction between 6.5 g of PbO and 3.2 g of HCl ? **[CBSE-PMT 2008]**

(a) 0.044 (b) 0.333 (c) 0.011 (d) 0.029

7. 10 g of hydrogen and 64 g of oxygen were filled in a steel vessel and exploded. Amount of water produced in this reaction will be: **[CBSE-PMT 2009]**

(a) 3 mol (b) 4 mol (c) 1 mol (d) 2 mol

8. The number of atoms in 0.1 mol of a triatomic gas is :(N_A = 6.02×10^{23} mol^{-1}) **[CBSE-PMT 2010]**

(a) 6.026×10^{22} (b) 1.806×10^{23}
(c) 3.600×10^{23} (d) 1.800×10^{22}

9. Which has the maximum number of molecules among the following ? **[CBSE-PMT 2011 M]**

(a) 44 g CO_2 (b) 48 g O_3
(c) 8 g H_2 (d) 64 g SO_2

10. How many grams of concentrated nitric acid solution should be used to prepare 250 mL of 2.0M HNO_3 ? The concentrated acid is 70% HNO_3 **[NEET 2013]**

(a) 90.0 g conc. HNO_3 (b) 70.0 g conc. HNO_3
(c) 54.0 g conc. HNO_3 (d) 45.0 g conc. HNO_3

11. 6.02×10^{20} molecules of urea are present in 100 mL of its solution. The concentration of solution is : **[NEET 2013]**

(a) 0.01 M (b) 0.001 M (c) 0.1 M (d) 0.02 M

12. With increase of temperature, which of these changes? **[AIEEE 2002]**

(a) molality
(b) weight fraction of solute
(c) fraction of solute present in water
(d) mole fraction.

13. Number of atoms in 558.5 gram Fe (at. wt. of Fe = 55.85 g mol^{-1}) is **[AIEEE 2002]**

(a) twice that in 60 g carbon (b) 6.023×10^{22}
(c) half that in 8 g He (d) $558.5 \times 6.023 \times 10^{23}$

14. One mole of magnesium nitride on the reaction with an excess of water gives : **[AIEEE 2004]**

(a) two moles of ammonia (b) one mole of nitric acid
(c) one mole of ammonia (d) two moles of nitric acid

15. If we consider that 1/6, in place of 1/12, mass of carbon atom is taken to be the relative atomic mass unit, the mass of one mole of the substance will **[AIEEE 2005]**

(a) be a function of the molecular mass of the substance
(b) remain unchanged
(c) increase two fold
(d) decrease twice

16. How many moles of magnesium phosphate, $Mg_3(PO_4)_2$ will contain 0.25 mole of oxygen atoms? **[AIEEE 2006]**

(a) 1.25×10^{-2} (b) 2.5×10^{-2}
(c) 0.02 (d) 3.125×10^{-2}

17. The density (in g mL^{-1}) of a 3.60 M sulphuric acid solution that is 29% H_2SO_4 (molar mass = 98 g mol^{-1}) by mass will be **[AIEEE 2007]**

(a) 1.45 (b) 1.64
(c) 1.88 (d) 1.22

18. In the reaction, **[AIEEE 2007]**

$$2Al(s) + 6HCl(aq) \rightarrow 2Al^{3+}(aq) \quad 6Cl^-(aq) \quad 3H_2(g)$$

(a) 11.2 L $H_2(g)$ at STP is produced for every mole HCl(*aq*) consumed
(b) 6 L HCl(*aq*) is consumed for every 3 L $H_2(g)$ produced
(c) 33.6 L $H_2(g)$ is produced regardless of temperature and pressure for every mole Al that reacts
(d) 67.2 $H_2(g)$ at STP is produced for every mole Al that reacts.

19. The molality of a urea solution in which 0.0100 g of urea, $[(NH_2)_2CO]$ is added to 0.3000 dm^3 of water at STP is : **[AIEEE 2011 RS]**

(a) 5.55×10^{-4}m (b) 33.3 m
(c) 3.33×10^{-2} m (d) 0.555 m

20. A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g. of CO_2. The empirical formula of the hydrocarbon is : **[JEE Main 2013]**

(a) C_2H_4 (b) C_3H_4 (c) C_6H_5 (d) C_7H_8

21. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M, present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be : **[JEE Main 2013]**

(a) 7.01% (b) 4.08% (c) 6.05% (d) 5.08%

22. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is **[IIT-JEE 2007]**

(a) 3 (b) 4 (c) 5 (d) 6

Exercise-4 | Applied MCQs

1. The correctly reported answer of addition of 29.4406, 3.2 and 2.25 will have significant figures

(a) 3 (b) 4 (c) 2 (d) 5

2. On dividing 0.25 by 22.1176 the actual answer is 0.011303. The correctly reported answer will be

(a) 0.011 (b) 0.01 (c) 0.0113 (d) 0.013

3. In which of the following number all zeros are significant?

(a) 0.0005 (b) 0.0500 (c) 50.000 (d) 0.0050

4. If law of conservation of mass was to hold true, then 20.8 gm of $BaCl_2$ on reaction with 9.8 gm of H_2SO_4 will produce 7.3 gm of HCl and $BaSO_4$ equal to :

(a) 11.65 gm (b) 23.3 gm
(c) 25.5 gm (d) 30.6 gm

5. One of the following combination which illustrates the law of reciprocal proportions ?

(a) N_2O_3, N_2O_4, N_2O_5 (b) NaCl, NaBr, NaI
(c) CS_2, CO_2, SO_2 (d) PH_3, P_2O_3, P_2O_5

6. If isotopic distribution of C-12 and C-14 is 98% and 2% respectively then the no. of C-14 atoms in 12gm of carbon is

(a) 1.032×10^{22} (b) 3.0×10^{22}
(c) 5.88×10^{23} (d) 6.02×10^{23}

7. Which of the following contains maximum number of atom

(a) 2.0 mole of S_8 (b) 6.0 mole of S
(c) 5.5 mole of SO_2 (d) 44.8 litre of CO_2 of S.T.P.

8. A sample of AlF_3 contains 3.0×10^{24} F^- ions. The number of formula unit of this sample are

(a) 9×10^{24} (b) 3×10^{24}
(c) 0.75×10^{24} (d) 1.0×10^{24}

9. What mass of calcium chloride in grams would be enough to produce 14.35 gm of AgCl ?

(a) 5.55 gm (b) 8.295 gm (c) 16.5 gm (d) 11.19 gm

10. If potassium chlorate is 80% pure, then 48 gm of oxygen would be produced from (atomic mass of K =39)

(a) 153.12 gm of $KClO_3$ (b) 122.5 gm of $KClO_3$
(c) 245 gm of $KClO_3$ (d) 98 gm of $KClO_3$

11. If 224 ml of a triatomic gas has a mass of 1 gm at 273K and 1 atmospheric pressure then the mass of one atom is

(a) 8.30×10^{-23} gm (b) 2.08×10^{-23} gm
(c) 5.53×10^{-23} gm (d) 6.24×10^{-23} gm

12. A compound made up of two elements A and B is found to contain 25% A (atomic mass = 12.5) and 75% B (atomic mass = 37.5). The simplest formula of the compound is

(a) AB (b) AB_2 (c) AB_3 (d) A_3B

13. On analysis a certain compound was found to contain iodine and oxygen in the ratio of 254 gm of iodine (atomic mass 127) and 80 gm oxygen (at mass = 16). What is the formula of the compound.

(a) IO (b) I_2O (c) I_5O_3 (d) I_2O_5

14. Two oxides of a metal contain 50% and 40% metal (M) respectively. If the formula of first oxide is MO_2 the formula of second oxide will be

(a) MO_2 (b) MO_3 (c) M_2O (d) M_2O_5

15. The ratio of the molar amounts of H_2S needed to precipitate the metal ions form 20 ml each of 1 M $Ca(NO_3)_2$ and 0.5M $CuSO_4$ is

(a) 1 : 1 (b) 2 : 1 (c) 1 : 2 (d) indefinite

16. 12 gm of Mg (atomic mass 24) will react completely with hydrochloric acid to give

(a) One mol of H_2
(b) 1/2 mol of H_2
(c) 2/3 mol of O_2
(d) both 1/2 mol of H_2 and 1/2 mol of O_2

17. The total number of protons in 10 gm of calcium carbonate is ($N_o = 6.023 \times 10^{23}$)

(a) 1.5057×10^{24} (b) 2.0478×10^{24}
(c) 3.0115×10^{24} (d) 14.0956×10^{24}

18. 2.76 gm of silver carbonate (at mass of Ag 108) on being heated strongly yield a residue weighing

(a) 2.16 gm (b) 2.48 gm
(c) 2.32 gm (d) 2.64 gm

19. If 0.5 mol of $BaCl_2$ is mixed with 0.2 mol of Na_3PO_4 then maximum number of moles of $Ba_3(PO_4)_2$ that can be formed is

(a) 0.7 (b) 0.5 (c) 0.3 (d) 0.1

20. 1.12 ml of a gas is produced at S.T.P. by the action of 4.12 mg of alcohol ROH with methyl magnesium Iodide. The molecular mass of alcohol is

(a) 16.0 (b) 41.2 (c) 82.4 (d) 156.0

21. An unsaturated hydrocarbon weighing 1.68 gm has volume of 488 ml at S.T.P. If it contains 14% of hydrogen, then the family to which the hydrocarbon belongs is

(a) alkane (b) alkene (c) alkyl (d) benzene

22. The number of molecules in 8.96 litre of a gas at 0ºC and 1 atm. pressure is approximately

(a) 6.023×10^{23} (b) 12.04×10^{23}
(c) 18.06×10^{23} (d) 24.08×10^{22}

23. If 3.01×10^{20} molecules are removed from 98 mg of H_2SO_4, then the number of moles of H_2SO_4 left are

(a) 0.1×10^{-3} (b) 0.5×10^{-3}
(c) 1.66×10^{-3} (d) 9.95×10^{-2}

24. 25.4 g of I_2 and 14.2 g of Cl_2 are made to react completely to yield a mixture of ICl and ICl_3. Calculate moles of ICl and ICl_3 formed

(a) 0.1, 0.1 (b) 0.2, 0.2 (c) 0.1, 0.2 (d) 0.2, 0.1

25. 2 g of a mixture of CO and CO_2 on reaction with excess I_2O_5 produced 2.54 g of I_2. What be the mass % of CO_2 in the original mixture ?

(a) 35 (b) 70 (c) 30 (d) 60

26. The hydrated salt $Na_2CO_3.xH_2O$ undergoes 63% loss in mass on heating and becomes anhydrous. The value of x is

(a) 10 (b) 7 (c) 5 (d) 3

27. Gastric juice contains 3.0 g of HCl per litre. If a person produces 2.5 litre of gastric juice per day. How many antacid tablets each containing 400 mg of $Al(OH)_3$ are needed to neutralize all the HCl produced in one day ?

(a) 18 (b) 14 (c) 20 (d) 17

28. Sulfuryl chloride (SO_2Cl_2) reacts with water to give a mixture of H_2SO_4 and HCl. How many moles of baryta would be required to neutralize the solution formed by adding 4 mol of SO_2Cl_2 to excess of water ?

(a) 1 (b) 2 (c) 3 (d) 4

29. A chloride of a metal (M) contain 65.5% of chlorine. 100 ml of vapour of the chloride of metal at STP weights 0.72 g. The molecular formula of the metal chloride is

(a) MCl_4 (b) MCl_3 (c) MCl_2 (d) MCl

30. 7.36 g of a mixture of KCl and KI was dissolved in H_2O to prepare 1 litre solution. 25 ml of this required 8.45 ml of 0.2 N $AgNO_3$, what are % of KI in mixture ?

(a) 57.28 (b) 47.28 (c) 5.72 (d) 49.12

31. When burnt in air, 14.0 g mixture of carbon and sulphur gives a mixture of CO_2 and SO_2 in the volume ratio of 2 : 1, volume being measured at the same conditions of temperature and pressure moles of carbon in the mixture is

(a) 0.75 (b) 0.5 (c) 0.40 (d) 0.25

32. A gas mixture of 3 litres of propane (C_3H_8) and butane (C_4H_{10}) on complete combustion at 25° C produced 10 litre CO_2. Find out the composition of gas mixture (Propane : Butane)

(a) 2 : 1 (b) 1 : 2 (c) 1.5 : 1.5 (d) 0.5 : 2.5

33. On subjecting 10 ml mixture of N_2 and CO to repeated electro spark, 7 ml of O_2 was required for combustion. What was the mole percent of CO in the mixture? (All volumes were measured under identical conditions)

(a) 60 (b) 40 (c) 6 (d) 4

34. How many of 0.1N HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of two ?

(a) 157.7 ml (b) 15.77 ml
(c) 147.7 ml (d) 14.77 ml

35. 1 mole of mixture of CO and CO_2 requires exactly 28 g KOH in solution for complete conversion of all the CO_2 into K_2CO_3. How much amount more of KOH will be required for conversion into K_2CO_3. If one mole of mixture is completely oxidized to CO_2

(a) 112 g (b) 84 g (c) 56 g (d) 28 g

36. 10 g $CaCO_3$ were dissolved in 250 ml of M HCl or the solution was boiled. What volume of 2M KOH would be required to equivalence point after boiling ? Assume no change in volume during boiling.

(a) 50 ml (b) 25 ml (c) 75 ml (d) 60 ml

37. 2.24 ml of a gas 'X' is produced at STP by the action of 4.6 mg of alcohol (ROH) with methyl magnesium iodide the molecular mass of alcohol and the gas 'X' are respectively.

(a) 0.46, CH_4 (b) 4.6, C_2H_6
(c) 46, CH_4 (d) 46, C_2H_4

38. 1.575 g of oxalic acid $(COOH)_2.xH_2O$ are dissolved in water and the volume made upto 250 ml. On titration 16.68 ml of this solution requires 25 ml of N/15 NaOH solution for complete neutralization calculate x.

(a) 3 (b) 2 (c) 4 (d) 5

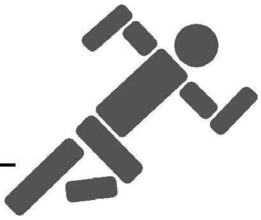
39. Suppose two elements X and Y combine to form two compounds XY_2 and X_3Y_2 when 0.1 mol of former weighs 10 g while 0.05 mol of the latter weights 9 g. The atomic masses of X and Y are respectively

(a) 60 & 40 (b) 30 & 40
(c) 40 & 30 (d) 40 & 60

40. The vapour density of a mixture containing NO_2 and N_2O_4 is 27.6. Mole fraction of NO_2 in the mixture is

(a) 0.8 (b) 0.6
(c) 0.4 (d) 0.2

Hints & Solutions



EXERCISE 1

1. The molecular formula is N_2O_4

2. V_1 (Volume of chlorine solution)
$= 3.00 \times 10^{-2}L$

5. Equivalent weight = 158 g

6. The ratio of their volumes is 1 : 3 : 2.

7. HCl is the limiting reagent. Moles of H_2 produced = 0.26 mol.

8. 36.12×10^{22} 'H' atoms and number of 'O' atoms will be similar to 'C' atoms as per the molecular formula of glucose.

9. Both contain the same number of atoms but bulb B_1 contains more number of molecules.

10. Empirical Formula = $CuCl_2$.

11. 0.04 moles of NaOH.

12. (i) $V_1 \quad \frac{0.50\times5}{18.4} \quad 0.136L$

(ii) $V_1 = 6.76$ ml,
Volume of water added = 93.24ml

14. (i) (a) 14 g of N_2 occupy = 11.2 litres at STP
(b) 1.5 moles of CO_2 occupy = 33.6 litres at STP
(c) 10^{21} molecules of O_2 occupy
$= 37.2\ cm^3$ at STP

15.	**(b)**	**16.**	**(c)**	**17.**	**(d)**	**18.**	**(c)**	**19.**	**(b)**
20.	**(c)**	**21.**	**(c)**	**22.**	**(b)**	**23.**	**(a)**	**24.**	**(b)**

EXERCISE 2

1. (c) Solution gives 1.1×10^6, hence significant figures are 2. The exponential term does not add to significant figures.

2. (c) Each has three significant figures. When zero is used to locate the decimal point it is not considered as singnificant figure.

3. (b) One fermi is 10^{-13} cm.

4. (a) Out of two 3.929 g is more accurate and will be reported as 3.93 after rounding off.

5. (d) $\frac{\text{Energy}}{\text{volume}}$ which can be shown

Pressure

$$= \frac{\text{Force}}{\text{area}} \quad \frac{\text{Work (energy/di stance)}}{\text{Area}} \quad \frac{\text{Energy}}{\text{Volume}}$$

6. (c) Exa = 10^{18} (see text.)

7. (a) Iodine undergoes sublimation (volatile solid). Others do not sublime.

8. (c) By sublimation since I_2 sublimes.

9. (d) In CuO and Cu_2O the O : Cu is 1 : 1 and 1 : 2. This is law of multiple proportion.

10. (c) The H : O ratio in water is fixed, irrespective of its source. Hence it is law of constant composition.

11. (b) Moles of nitride ion

$$= \frac{4.2}{14} \quad 0.3 \text{ mol} \quad 0.3 \times N_A \text{ nitride ions.}$$

Valence electrons $= 8 \times 0.3\ N_A = 2.4\ N_A$ (5 + 3 due to charge). One N^{3-} ion contains 8 valence electrons.

12. (c) Mol. of $O_2 = \frac{6}{32}$ & mol. of $SO_2 = \frac{6}{64}$. The number of molecules of SO_2 will be less than that of O_2.

13. (a) 21% of 1 litre is 0.21 litre.
22.4 litres = 1 mole at STP

$$\therefore 0.21 \text{ litre} = \frac{0.21}{22.4} \quad 0.0093 \text{ mol}$$

14. (b) V.D. = 11.2 $\quad\therefore$ M. Wt = 22.4 g
It corresponds to 22.4 litres at STP
$\therefore$ 11.2 g = 11.2 L

15. (b) $Zn \quad H_2SO_4 \longrightarrow ZnSO_4 \quad H_2$
65 g Zn gives 1 mole of H_2 = 22400 ml of H_2
224 ml of H_2 will be obtained from 0.65 g Zn.

16. (c) 1 Mol CO_2 = 44 g = 22.4 litre at N.T.P.
$\therefore$ 4.4 g CO_2 = 2.24 L at NTP.

17. (a) $BaCO_3 \longrightarrow BaO \quad CO_2$
192 g of $BaCO_3$ 1 gives mol of CO_2 = 22.4 L
9.85 g of $BaCO_3$ will give 0.05 mol of CO_2 which is equal to 1.12 litre.

18. (b) The number of molecules of N_2 and X are same. Hence they must have the same molecular weights.
$\therefore$ X is CO.

19. (b) $PV = nRT \quad \therefore 5.6 \times 1 = \frac{7.5}{M.Wt.} \times 0.0821 \times 273$

M. Wt = 30.12 $\quad$ Hence gas is NO.

20. (b) 1 amu = $\frac{1}{12}$ of the mass of C-12.

21. (c) 22.4 L of CO_2 at STP = 1 mole = 6.023 × 10^{23} molecules. Hence number of atoms 3 × 6.023 × 10^{23}.

22. (c) M. Wt of $Na_2SO_4.10\,H_2O$ is 322 g which contains 224 g oxygen. ∴ 32.2 g will contain 22.4 g oxygen.

23. (d) $\dfrac{6.4}{\text{Specific heat}} = \text{Apx. Atomic mass}$

$\therefore \text{Apx. At.wt} = \dfrac{6.4}{0.16} = 40$

24. (b) M. Wt of $C_{60}H_{122}$ = 842g

$\therefore \text{Wt of one molecule} = \dfrac{842}{6.023\times10^{23}} = 1.4\times10^{-21}\,\text{g}$

25. (b) 0.0018 ml = 0.0018 g = 0.0001 mole of water $= 10^{-4}$ mole

∴ Number of water molecules = $6.023\times10^{23}\times10^{-4}$ = 6.023 × 10^{19}

26. (b) 0.5% by weight means. If Mol. wt. is 100 then mass of Si is 0.5. If at least one atom of Se is present in the molecule then

$\text{M. Wt} = \dfrac{100}{0.5}\times78.4 = 1.568\times10^{4}$

27. (c) Eq. Wt of crystalline oxalic acid $(COOH)_2.\,2H_2O$

$= \dfrac{\text{M.Wt.}}{2} = \dfrac{126}{2} = 63$

28. (b) $\dfrac{\text{Wt. of metal oxide}}{\text{Wt. of metal chloride}}$

$= \dfrac{\text{Eq. wt of metal} + \text{Eq. wt of oxygen}}{\text{Eq. wt of metal} + \text{Eq. wt of chlorine}}$

$\dfrac{3}{5} = \dfrac{E+8}{E+35.5} \qquad \therefore E = 33.25$

29. (c) 50% x atomic mass 10, 50% y atomic mass 20. Relative

number of atoms of X = $\dfrac{50}{10} = 5$ and that Y = $\dfrac{50}{20} = 2.5$

Simple Ratio 2 : 1. Formula X_2Y

30. (c) Formula of metal phosphate is $M^{++}H^{+}PO_4^{---}$.
Valency of metal + 2. Hence metal chloride is MCl_2.

31. (b) Sum of oxidation states must be equal to zero which is given by $A_3(BC_4)_2 = A_3B_2C_8$ (+ 6 + 10 – 16 = 0)

32. (b) PV = nRT

$\dfrac{224\times1520}{1000\times760} = \dfrac{0.44}{M}\times0.0821\times546$

∴ M = 44 approx. Hence gas = N_2O

33. (b) Mass of one molecule of Water

$= \dfrac{18}{6.023\times10^{23}} = 3\times10^{-23}\,\text{g} = 3\times10^{-26}\,\text{Kg}$

34. (b) The required equation is

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 \quad 2MnSO_4 \quad 3H_2O \quad \underset{\text{nascent oxygen}}{5\ O}$$

$$2Fe(C_2O_4) + 3H_2SO_4 + 3[O] \longrightarrow Fe_2(SO_4)_3 + 2CO_2 + 3H_2O$$

O required for 1 mol. of $Fe(C_2O_4)$ is 1.5, 5O are obtained from 2 moles of $KMnO_4$

∴ 1.5 [O] will be obtained from = $\dfrac{2}{5}\times1.5 = 0.6$ moles of $KMnO_4$.

35. (b) $\text{Normality} = \dfrac{N_1V_1 - N_2V_2}{V_1+V_2} = \dfrac{0.2\times100 - 0.1\times100}{100+100}$

$= \dfrac{10}{200} = 0.05\text{N NaOH}$

36. (b) More than theoretical weight since impurity will not contribute.

37. (c) $CaCO_3 \rightleftharpoons CaO + CO_2$
100 g 56 g
10 g $CaCo_3$ will give 5.6 gCaO

38. (d) Weight of Iron in 67200 = $\dfrac{0.33}{100}\times67200 = 221.76$

Number of atoms of Iron = $\dfrac{221.76}{56} = 3.96 \equiv 4$

39. (c) 16 g CH_4 is 1 mol. Hence number of molecules = Avogadro number = 6.023 × 10^{23}.

40. (b) $N = \dfrac{N_1V_1 + N_2V_2 + N_3V_3}{\text{Total volume}}$

$= \dfrac{50\times10 + 25\times12 + 40\times5}{1000} = 1\text{N}$

41. (b) Molal solution contains 1 mole of solute in 1000 g solvent.

42. (a) $N_1V_1 = N_2V_2 + N_3V_3$
0.1 × 100 = 0.20 × 30 + 0.25 V_3 ∴ V_3 = 16 ml.

43. (b) Normality of oxalic acid = $\dfrac{6.3\times1000}{63\times250} = 0.4\,\text{N}$

$N_1V_1 = N_2V_2$ 10 × 0.4 = V × 0.1 = 40 ml.

44. (b) NH_2CONH_2 M. Wt of urea=60.

% N in urea = $\dfrac{28\times100}{60} = 46$

45. (c) For neutralisation gev of acid = gev of base

gev. of HCl = $\dfrac{0.1\times1500}{1000} = 0.15 \equiv$ gev. of NaOH

1 gev. of NaOH = 40 g
∴ 0.15 gev. of NaOH = 40 × 0.15 = 6 g.

46. (a) $N_1V_1 = N_2V_2$

$\therefore\ 100 \times 0.5 = 0.1 \times V_2$

$\therefore\ V_2 = 500$ water to be is added 400 ml. 100 ml is already present.

47. (c) $\text{Molarity} = \dfrac{\text{Wt} \times 1000}{\text{MW} \times \text{V}} = \dfrac{2.65 \times 1000}{106 \times 250} = 0.1\text{M}$

$M_1V_1 = M_2V_2$

$\therefore\ 10 \times 0.1 = 1000 \times M_2 = 0.001\text{ M}$

48. (a) Normality of ferrous Amm. sulphate

$= \dfrac{3.92 \times 1000}{392 \times 100} = 0.1$ (Eq. wt of FAS is 392)

$N_1V_1 = N_2V_2$

$20 \times 0.1 = 18 \times N_2$ $\qquad N_2 = 0.111$

1 gev. of $KMnO_4 = 31.6$g

0.111 gev. of $KMnO_4 = 31.6 \times 0.111 = 3.5$ g.

49. (a)

	$2Mg$	+ O_2 ⟶	$2MgO$
	2×24	2×16	2×40
	48 g	32 g	80 g
given	30 g		
Actually Reacting	30 g	20 g	50g (formed)

O_2 left $(30 - 20) = 10$ g MgO formed 50 g.

50. (c) Eq. wt of $KMnO_4$ in acid medium is 31.6 g. Hence this much amount must be dissolved in 1 litre to prepare normal solution.

51. (b) $\underset{1}{K_2Cr_2O_7} + \underset{1}{H_2SO_4} + \underset{3}{3SO_2} \longrightarrow$

$K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

52. (b) $BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$

$BaCl_2$	H_2SO_4	$BaSO_4$
1 Mole	1 Mole	1 Mole
0.5 Mole	0.5 Mole	0.5 Mole

53. (d) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l)$

	$4NH_3$	$5O_2$		$4NO$	$6H_2O$
	4 moles	5 moles		4 moles	6 moles
given	1 Mole	1 Mole			
Reacting	0.8	1	→	0.8	1.2 (formed)

All, O_2 consumed being limiting.

54. (a) $\underset{2}{2K_2CrO_4} + \underset{2}{2HCl} \longrightarrow \underset{1}{K_2Cr_2O_7} + \underset{2}{2KCl} + \underset{1}{H_2O}$

EXERCISE 3

1. (c) $2Al_2O_3 + 3C \longrightarrow Al + 3CO_2$

Gram equivalent of $Al_2O_3 \equiv$ gm equivalent of C

Now equivalent weight of $Al = \dfrac{27}{3} = 9$

Equivalent weight of $C = \dfrac{12}{4} = 3\ \ (\overset{0}{C} \to \overset{+4}{C}O_2)$

No. of gram equivalent of $Al = \dfrac{270 \times 10^3}{9} = 30 \times 10^3$

Hence,

No. of gram equivalent of $C = 30 \times 10^3$

Again,

No. of gram equivalent of C

$= \dfrac{\text{mass in gram}}{\text{gram equivalent weight}} \Rightarrow 30 \times 10^3 = \dfrac{\text{mass}}{3}$

$\Rightarrow \text{mass} = 90 \times 10^3\text{ g} = 90\text{ kg}$

2. (a) $K\overset{+7}{Mn}O_4 \xrightarrow{OH^-} K_2\overset{+6}{Mn}O_4$

Change in oxidation number of Mn in basic medium is 1. Hence mole of KI is equal to mole of $KMnO_4$.

3. (c) $\text{Density} = \dfrac{\text{Mass}}{\text{Volume}}$

$1\text{ gram cm}^{-3} = \dfrac{1\text{ gram}}{\text{cm}^3}$

$\text{Volume} = \dfrac{\text{Mass}}{\text{Density}} = \dfrac{1\text{ gram}}{1\text{ gram cm}^{-3}} = 1\text{cm}^3$

$\therefore$ Volume occupied by 1 gram water = 1 cm^3

or Volume occupied by

$\dfrac{6.023 \times 10^{23}}{18}$ molecules of water = 1 cm^3

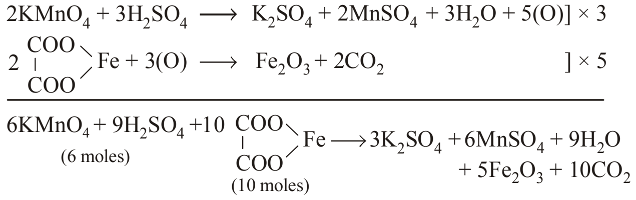
$[\therefore\ 1\text{g water} = \dfrac{1}{18}$ moles of water]

Thus volume occupied by 1 molecule of water

$= \dfrac{1 \times 18}{6.023 \times 10^{23}}\text{cm}^3 = 3.0 \times 10^{-23}\text{ cm}^3.$

i.e. the correct answer is option (c).

4. (a)



$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(O)] \times 3$$

$$2\begin{matrix}COO\\|\\COO\end{matrix}\!\!>Fe + 3(O) \longrightarrow Fe_2O_3 + 2CO_2 \qquad] \times 5$$

$$\underset{(6\text{ moles})}{6KMnO_4} + 9H_2SO_4 + \underset{(10\text{ moles})}{10\begin{matrix}COO\\|\\COO\end{matrix}\!\!>Fe} \longrightarrow 3K_2SO_4 + 6MnSO_4 + 9H_2O + 5Fe_2O_3 + 10CO_2$$

From above equation 6 moles MnO_4^- required to oxidise 10 moles of oxalate.

Thus number of moles of MnO_4^- required to oxidise one mole of oxalate $= \dfrac{6}{10} = 0.6$ moles

5. (a)

Element	Percentage	Atomic weight	Atomic ratio	Simple ratio
C	38.71	12	$\dfrac{38.71}{12} = 3.23$	$\dfrac{3.23}{3.23} = 1$
H	9.67	1	$\dfrac{9.67}{1} = 9.67$	$\dfrac{9.67}{3.23} = 3$
O	100 – (38.71+9.67) = 51.62	16	$\dfrac{51.62}{16} = 3.23$	$\dfrac{3.23}{3.23} = 1$

Thus empirical formula is CH_3O.

6. (d) Writing the equation for the reaction, we get

$$\underset{\substack{207+16\\=223\text{ g}}}{PbO} + \underset{\substack{2\times36.5\\=73\text{g}}}{2HCl} \longrightarrow \underset{\substack{207+71\\=278\text{g}}}{PbCl_2} + H_2O$$

$$\text{No. of moles of PbO} = \frac{6.5}{223} = 0.029$$

$$\text{No. of moles of HCl} = \frac{3.2}{36.5} = 0.0877$$

Thus PbO is the limiting reactant 1 mole of PbO produce 1 mole $PbCl_2$.

0.029 mole PbO produces 0.029 mole $PbCl_2$.

7. (b)

$$\underset{\substack{10\text{g}\\\left(\frac{10}{2}=5\text{ mol}\right)}}{H_2} + \underset{\substack{64\text{g}\\\left(\frac{64}{32}=2\text{ mol}\right)}}{\frac{1}{2}O_2} \longrightarrow H_2O$$

In this reaction oxygen is the limiting agent. Hence amount of H_2O produced depends on the amount of O_2 taken

$\because$ 0.5 mole of O_2 gives H_2O = 1 mol

$\therefore$ 2 mole of O_2 gives H_2O = 4 mol

8. (b) The number of atoms in 0.1 mole of a triatomic gas

$= 0.1 \times 3 \times 6.023 \times 10^{23}$

$= 1.806 \times 10^{23}$

9. (c)

		No. of molecules
Moles of $CO_2 = \frac{44}{44}$	1	N_A
Moles of $O_3 = \frac{48}{48}$	1	N_A
Moles of $H_2 = \frac{8}{2}$	4	$4N_A$
Moles of $SO_2 = \frac{64}{64}$	1	N_A

10. (d) $\text{Molarity (M)} = \dfrac{\text{wt} \times 1000}{\text{mol. wt.} \times \text{vol (ml)}}$

$$2 = \frac{\text{wt.}}{63} \times \frac{1000}{250}$$

$$\text{wt.} = \frac{63}{2}\text{ gm}$$

$$\text{wt. of 70\% acid} = \frac{100}{70} \times 31.5 = 45\text{ gm}$$

11. (a) $M = \dfrac{6.02\times10^{20}\times1000}{100\times6.02\times10^{23}} = \dfrac{6.02\times10^{21}}{6.02\times10^{23}}$

$= 0.01$ M

12. (c) Volume increases with rise in temperature. Thus, some water molecule may be evaporated at high temp.

13. (a) $\text{Fe (no. of moles)} = \dfrac{558.5}{55.85} = 10\text{ moles}$

C (no. of moles) = 60/12 = 5 moles.

14. (a) $Mg_3N_2 + 6H_2O \rightleftharpoons 3Mg(OH)_2 + 2NH_3$

15. (d) Relative atomic mass

$$= \frac{\text{Mass of one atom of the element}}{1/12^{\text{th}}\text{ part of the mass of one atom of Carbon} - 12}$$

$$\text{or } \frac{\text{Mass of one atom of the element}}{\text{mass of one atom of the C} - 12} \times 12$$

Now if we use $^1/_6$ in place of $^1/_{12}$ the formula becomes

$$\frac{\text{Mass of one atom of the element}}{\text{Mass of one atom of C} - 12} \times 6$$

16. (d) 1 Mole of $Mg_3(PO_4)_2$ contains 8 mole of oxygen atoms

$\therefore$ 8 mole of oxygen atoms $\equiv$ 1 mole of $Mg_3(PO_4)_2$

$$0.25\text{ mole of oxygen atom} \equiv \frac{1}{8} \times 0.25 = 3.125 \times 10^{-2}$$

17. (d) Since molarity of solution is 3.60 M. It means 3.6 moles of H_2SO_4 is present in its 1 litre solution.

Mass of 3.6 moles of H_2SO_4

= Moles × Molecular mass = 3.6 × 98 g = 352.8 g

$\therefore$ 1000 ml solution has 352.8 g of H_2SO_4

29% H_2SO_4 by mass means 29 g of H_2SO_4 is present in 100 g of solution

$\therefore$ 352.8 g of H_2SO_4 is present in

$$= \frac{100}{29} \times 352.8\text{ g of solution} = 1216\text{ g of solution}$$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{1216}{1000} = 1.216\text{ g/ml} = 1.22\text{ g/ml}$$

18. (a) $2Al(s) + 6HCl(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(g)$

$\because$ 6 moles of HCl produces = 3 moles of H_2

= 3 × 22.4 L of H_2 at S.T.P

$$\therefore \text{ 1 mole of HCl produces} = \frac{3\times22.4}{6}\text{ L of } H_2 \text{ at S.T.P}$$

= 11.2 L of H_2 at STP

19. (a) Molality = Moles of solute / Mass of solvent in kg

$$\text{Molality } \frac{0.01/60}{0.3} \quad \frac{0.01}{60\times0.3};$$

$d = 1$ g/ml

$= 5.55\times10^{-4}$ m

20. (d) $\because$ 18 gm, H_2O contains = 2 gm H

$$\therefore 0.72\text{ gm } H_2O \text{ contains} = \frac{2}{18} \times 0.72\text{ gm} \quad 0.08\text{ gm H}$$

$\because$ 44 gm CO_2 contains = 12 gm C

$$\therefore 3.08\text{ gm } CO_2 \text{ contains} = \frac{12}{44} \times 3.08 \quad 0.84\text{ gm C}$$

$$\therefore C : H = \frac{0.84}{12} : \frac{0.08}{1}$$

$= 0.07 : 0.08 = 7 : 8$

$\therefore$ Empirical formula = C_7H_8

21. **(b)** For one mole of the oxide

Moles of M = 0.98

Moles of $O^{2-} = 1$

Let moles of $M^{3+} = x$

$\therefore$ Moles of $M^{2+} = 0.98 - x$

on balancing charge

$(0.98 - x) \times 2 + 3x - 2 = 0$

$x = 0.04$

$$\therefore \% \text{ of } M^{3+} = \frac{0.04}{0.98} \times 100 = 4.08\%$$

22. **(d)** The following reaction occurs:

$$6Fe^{2+} \quad Cr_2O_7^{2-} \quad 14H \longrightarrow 6Fe^{3} \quad 2Cr^{3} \; + 7H_2O$$

From the above equation, we find that Mohr's salt ($FeSO_4.(NH_4)_2SO_4.6H_2O$) and dichromate reacts in 6 : 1 molar ratio.

EXERCISE 4

1. **(a)** Sum of the figures 29.4406, 3.2 and 2.25 is 34.8906. The sum should be reported to the first place of decimal as 3.2 has only one decimal place. After rounding off the sum is 34.9. Hence number of significant figures is three.

2. **(a)** 0.25/22.1176 = 0.011303. The least precise term has two significnat figures, hence the result is 0.011.

3. **(c)** If zero is used to locate the decimal point it is considered a significant figure. In 50.000 all zero are significant.

4. **(b)** The desired equation is

$$\underset{\substack{208g \\ 20.8g}}{BaCl_2} + \underset{\substack{98g \\ 9.8g}}{H_2SO_4} \rightarrow \underset{\substack{233g \\ 23.3g}}{BaSO_4} + \underset{\substack{73g \\ 7.3g}}{2HCl}$$

5. **(c)** In law of reciprocal proportions, the two elements combining with the third element, must combine with each other in the same ratio or multiple of that Ratio of S and O when combine with C is 2 : 1. Ratio of S and O is SO_2 is 1 : 1

6. **(a)** 2% of 12 gm of carbon is = $\frac{2 \times 12}{100} = 0.24g$ which is C-14

$\therefore$ The number of atoms in it

$$= \frac{0.24 \times 6.02 \times 10^{23}}{14} = 1.03 \times 10^{22} \text{ atoms}$$

7. **(c)** Number of atoms in 2.0 mole of S_8

$= 2 \times N_A \times 8 = 16 \; N_A$

number of atoms in 6.0 mole of S = $6 \times N_A = 16.5 \; N_A$

Number of atoms in in 5.5 mole of SO_2

$= 5.5 \times N_A \times 3 = 16.5 \; N_A$

Number of atoms in 44.8 litre at STP of

$CO_2 = 2 \times N_A \times 3 = 6 \; N_A$

8. **(d)** An, AlF_3 the number of F is 3 for one AlF_3 molecule

$3F^- \equiv 1$ formula unit of AlF_3

$$3.0 \times 10^{24} \; F^- \equiv \frac{1}{3} \times 3.0 \times 10^{24} \; AlF_3 \text{ units}$$

9. **(a)** The desired equation is

$$\underset{111g}{CaCl_2} + 2AgNO_3 \rightarrow \underset{143.5 \times 2g}{2AgCl} + Ca(NO_3)_2$$

$\therefore$ 14.35 g of AgCl will be obtained from

$$\frac{111 \times 14.35}{143.5 \times 2} = 5.55gm$$

10. **(a)** $$\underset{\substack{2 \times 122.5g \\ 245}}{2KClO_3} \xrightarrow{heat} 2KCl + \underset{\substack{3 \times 32g \\ 96}}{3O_2}$$

48 gm of oxygen will be produced from 122.5 g of $KClO_3$

$\therefore$ Amount of 80% $KClO_3$ needed

$$= \frac{100}{80} \times 122.5 = 153.12gm$$

11. **(c)** The conditions given are standard conditions

224 ml has mass = 1g ;

22400 ml will have mass = 100g. This is mol. wt of gas

6.023×10^{23} molecules have $3 \times 6.023 \times 10^{23}$ atoms since gas is triatomic

$\therefore$ weight of one atom

$$= \frac{100}{3 \times 6.023 \times 10^{23}} = 5.5 \times 10^{-23} g$$

12. **(a)** Proceed as follows :

Element	**%**	**At. wt.**	**RNA**	**Simplest ratio**
A	25	12.5	$\frac{25}{12.5} = 2$	1
B	75	37.5	$\frac{75}{37.5} = 2$	1

$\therefore$ The simplest formula of compound is AB

13. **(d)** Moles of Iodine present = $\frac{254}{127} = 2$

Moles of oxygen = $\frac{80}{16} = 5$

$\therefore$ The molecular formula is = I_2O_5

14. **(b)** Let the atomic weight of metal be M then

M = 50%　　50/M = 1

O = 50%　　50/16 = 2

The formula is = MO_2

$\therefore \frac{16}{M} = \frac{1}{2}$. Thus atomic weight of metal = 32

For second oxide

M = 40%　40/32 = 1.25　　1

O = 60%　60/16 = 3.75　　3

$\therefore$ Formula is MO_3

15. **(b)** Moles of Ca^{++} to be precipitated $= \frac{20\times1}{1000} = 0.02$

Moles of Cu^{++} to be precipitated $= \frac{20\times0.5}{1000} = 0.01$

Hence molar amount of H_2S will be in the ratio 2 : 1

$$\left(\text{Remember Moles} = \frac{\text{Molarity}\times\text{volume in ml}}{1000}\right)$$

16. **(b)**

$$\begin{array}{lllll} Mg & +2HCl & \to MgCl_2 & +H_2\uparrow & \\ 1\text{ mole} & & & 1\text{ mole} & \\ \frac{1}{2}\text{ mole} & & & \frac{1}{2}\text{mole} & (12g\text{ of }Mg = \frac{1}{2}\text{mol}) \end{array}$$

17. **(c)** 10g of $CaCO_3$ is $\frac{10}{100} = 0.1$ mole

Number of protons in 1 mole of $CaCO_3$ = (At. No. of Ca + At. No. of C + 3 At. No. of O) = 20 + 6 + 24 = 50 moles.
Protons in 0.1 mole of $CaCO_3$ = 0.1 × 50 × 6.02 × 10^{23}
= 3.01 × 10^{24}

18. **(a)** Decomposition of Ag_2CO_3 gives silver

$$\begin{array}{llll} 2Ag_2CO_3 & \to 4Ag & +2CO_2 & +O_2 \\ 2\times276g & 4\times108g & & \\ 2.76g & 2.16g & & \end{array}$$

19. **(a)** The chemical equation is

$$\begin{array}{llll} 3BaCl_2 + & 2Na_3PO_4 & \to Ba_3(PO_4)_2 & + 6NaCl \\ 3\text{Mole} & 2\text{mol} & 1\text{mol} & \\ 0.3\text{mol} & 0.2\text{mol} & 0.1\text{mol} & \end{array}$$

Hence $Ba_3(PO_4)_2$ obtained is 0.1 mole

20. **(c)** Let the alcohol be ROH and x its molecular weight

$$\underset{x\,g}{ROH} + CH_3MgI \to \underset{16g}{CH_4} + ROMgI$$

$\frac{4.12}{1000}$g of alcohol will produce $\frac{16}{x}\times\frac{4.12}{1000}$g of methane

Methane actually obtained is $= \frac{16\times1.12}{22400}$g

equal $= \frac{16\times4.12}{x\times1000} = \frac{16\times1.12}{22400} \therefore x = 82.4$

21. **(b)**

Element	**%**	**At. wt.**	**RNA**	**Simplest Ratio**
C	86	12	86/12=7.16	1
H	14	1	14/1 = 142	

∴ Empirical formula ∝ CH_2 corresponds to general formula C_nH_{2n} of alkene

22. **(d)** At S.T.P. 22.4 litre of gas contains 6.023 × 10^{23} molecules
∴ molecules in 8.96 litre of gas

$$= \frac{6.023\times10^{23}\times8.96}{22.4} = 24.08\times10^{22}$$

23. **(b)** Moles of H_2SO_4 in 98 mg of H_2SO_4

$$= \frac{1}{98}\times0.098 = 0.001$$

Moles of H_2SO_4 removes

$$= \frac{3.01\times10^{20}}{6.02\times10^{23}} = 0.5\times10^{-3} = 0.0005$$

Moles of H_2SO_4 left = 0.001 – 0.0005 = 0.5 × 10^{-3}

24. **(a)**

$$\begin{array}{lllll} I_2 & +\ 2Cl_2 & \longrightarrow ICl & +\ ICl_3 & \\ \frac{25.4}{254} & \frac{14.2}{71} & 0 & 0 & \text{moles in the beginning} \\ 0.1 & 0.2 & 0 & 0 & \\ 0 & 0 & 0.1 & 0.1 & \text{moles after reaction} \end{array}$$

25. **(c)** $5CO + I_2O_5 \to 5CO_2 + I_2$

Moles of $I_2O_5 = \frac{25.4}{254}$
= 0.01 ≡ 0.05 moles of CO
Weight of CO = 0.05 × 28 = 1.4 g;
Weight of CO_2 = 2 – 1.4 = 0.6 g

Hence % of $CO_2 = \frac{0.6}{2}\times100 = 30\%$

26. **(a)** $Na_2CO_3.xH_2O$. Its weight = 106 + 18 x.

Weight of anhydrous Na_2CO_3 = 106

% loss in weight $= \frac{18x\times100}{106+18x} = 63$

∴ x = 10

27. **(b)** geq of HCl $= \frac{3}{36.5}\times2.5 = 0.20548$ = geq of $Al(OH)_3$

Weight of $Al(OH)_3 = \frac{0.20548\times78}{3} = 5.342$ g = 5342 mg

∴ No of tablets $= \frac{5342}{400} = 13.35 = 14$

28. **(b)** $SO_2Cl_2 + 2H_2O \to H_2SO_4 + 2HCl$

$H_2SO_4 + Ba(OH)_2 \to BaSO_4 + 2H_2O$

$2HCl + Ba(OH)_2 \to BaCl_2 + 2H_2O$

Total moles of $Ba(OH)_2$ required = 2

29. **(b)** Molecular weight of metal chloride

$$= \frac{0.72\times22400}{100} = 161.28\text{ g}$$

Weight of chlorine in metal chloride

$$= \frac{65.5\times161.28}{100} = 105.64\text{ g}$$

Mole atoms of chlorine $= \frac{105.64}{35.5} = 3$

Hence metal chloride is MCl_3

30. **(a)** $\underset{xg}{KI} + \underset{(7.36-x)\,g}{KCl}$; (geq of mixture = geq of $AgNO_3$)

$$\left(\frac{x}{166}+\frac{7.36-x}{74.5}\right)=\frac{8.45\times 0.2\times 40}{1000}$$

∴ on solving $x = 4.216x$

∴ % of KI = 57.28%

31. **(b)** Let weight of C be xg, then S will be (14 – x) g

$$\frac{x/12}{(14-x)/32}=\frac{2}{1}$$

∴ $x = 6$ g ; Moles of C $=\frac{6}{12}=0.5$

32. **(a)** $\underset{a}{C_3H_8} + 5O_2 \rightarrow \underset{3a}{3CO_2} + 4H_2O$

$\underset{(3-a)}{C_4H_{10}} + \frac{13}{2}O_2 \rightarrow \underset{4(3-a)}{4CO_2} + 5H_2O$

But $3a + 4(3 - a) = 10$

∴ a = 2 (Propane) and 3 – 2 = 1 (Butane)

33. **(a)** $\underset{a}{N_2} + \underset{a}{O_2} \rightarrow \underset{2a}{2NO}$

$\underset{(10-a)}{CO} + \underset{\frac{(10-a)}{2}}{\frac{1}{2}O_2} \rightarrow \underset{(10-a)}{CO_2}$

$$a+\frac{(10-a)}{2}=7$$

∴ a = 4

volume of CO = 6 ml

Mole % of CO $=\frac{6\times 100}{10}=60$

34. **(a)** $\underset{x}{Na_2CO_3}$ $\underset{(1-x)}{NaHCO_3}$

$\frac{x}{106}=\frac{1-x}{84}$ given (moles are equal)

x = 0.557

$$\frac{0.557}{53}+\frac{0.443}{84}=\frac{V\times 0.1}{1000}$$

V = 157.7 ml

35. **(b)** $CO+\frac{1}{2}O_2 \rightarrow CO_2$;

$CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O$

Moles of KOH $=\frac{28}{56}=0.50$

It corresponds to 0.25 mol of CO_2

Hence mol of CO = 1 – 0.25 = 0.75 ≡ mole of CO_2 formed

Mol of KOH requred = 2 × 0.75 = 1.5 = 1.5 × 56 = 84 g

36. **(b)** Meq. of $CaCO_3=\frac{10}{50}\times 1000=200$

Meq. of HCl = 250 × 1 = 250

Meq. of HCl left in the solution = 250 – 200 = 50

∴ Meq. of KOH requred V × 2 = 50

∴ V = 25 ml

37. **(c)** $ROH + CH_3MgI \rightarrow CH_4 + ROMgI$

1 mol of ROH ≡ 1 mol of CH_4 ≡ 22400 at STP

Hence molecular wt of ROH $=\frac{0.0046}{2.224}\times 22400$

= 46 g

38. **(b)** Meq of oxalic acid in 16.68 ml = Meq of NaOH $=25\times\frac{1}{15}$

Meq of oxalic acid in 250 ml $=25\times\frac{1}{15}\times\frac{250}{16.68}=24.98$

$$\frac{1.575}{(90+18x)/2}\times 1000=24.98$$

∴ x = 2

39. **(c)** Molecular weight of $XY_2=\frac{10}{0.1}=100$

molecular weight of $X_3Y_2=\frac{9}{0.05}=180$

Let a and b be the atomic masses of X and Y respectively.

Then a + 2b = 100

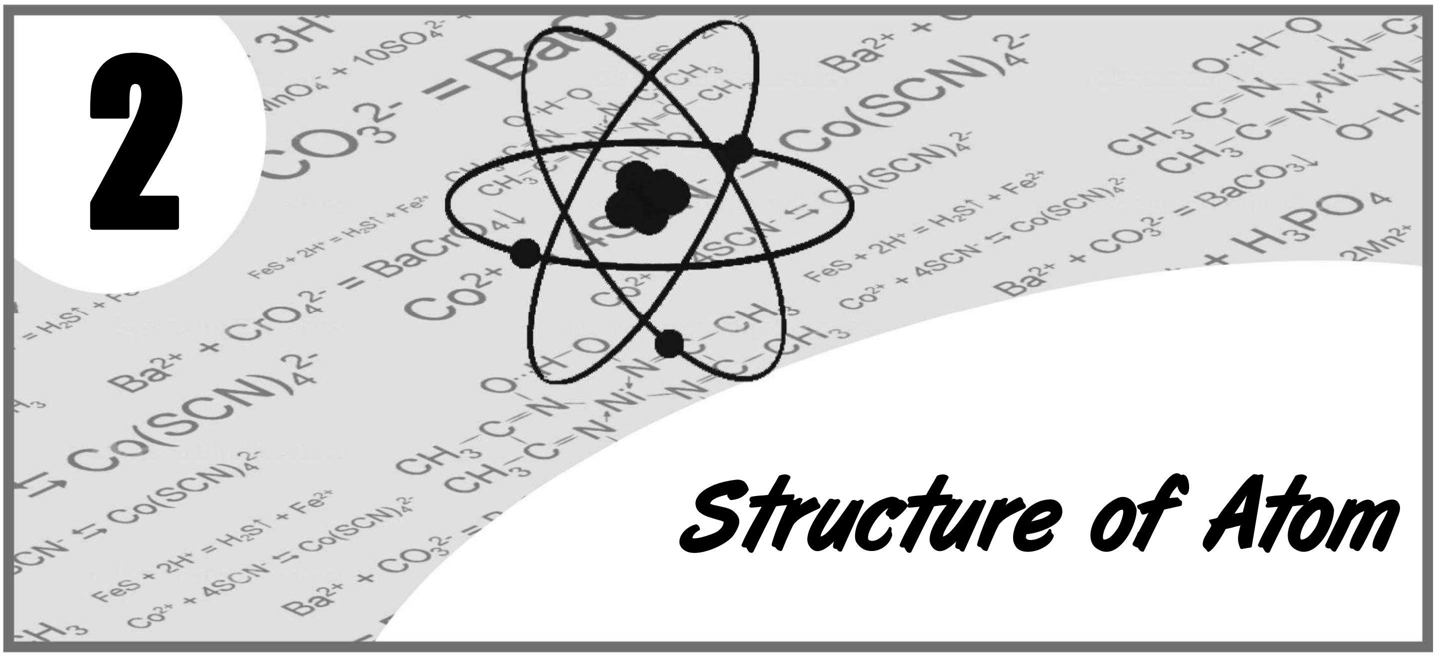
3a + 2b = 180

∴ a = 40 and b = 30

40. **(a)** $V.D_{max} = X_{NO_2}\,(V.D)_{NO_2} + X_{N_2O_4}\,(V.D)_{N_2O_4}$

$27.6 = X \times 23 + (1 - X) \times 46$

∴ $X_{NO_2} = 0.8$



2

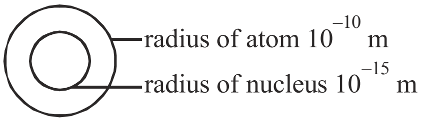
Structure of Atom

ATOM :

John Dalton proposed in 1808 that atom is the smallest indivisible particle of matter.

ATOMIC RADII :

Atomic radii are of the order of 10^{-8} cm (1Å) and radii of nuclei are nearly 10^{-13} cm. Radius of the nucleus is thus $\frac{1}{10^5}$ th of the radius of atom.



Radius of atom $= 10^5 \times$ Radius of nucleus

ELECTRON :

(I) It was discovered through the study of Cathode rays (discovered by Zulius Plucker) and the name was proposed by **Stoney.**

(II) **Charge :** It was determined by **Mullikan** by oil drop method as -1.602×10^{-19} coulombs or 4.803×10^{-10} e.s.u.

(III) **Mass :** It was found by **J. J. Thomson** as 9.11×10^{-28} g.

(IV) **Specific charge :** e/m ratio is called specific charge and was determined by **Thomson** as 1.76×10^8 coulombs/gm.

(V) **Radius :** It is of the order 10^{-15} cm.

(VI) **Density :** 2.17×10^{17} g/cc.

(VII) Mass of electron at speed v is $m = \frac{m_{rest}}{\sqrt{1-\left(\frac{v}{c}\right)^2}}$

(VIII) **Atomic mass unit :** It is 0.0005486 amu.

(IX) **Mass of one mole of electron :** It is 0.55 mg.

CATHODE RAYS :

Originate from cathode. Electrons were discovered by cathode ray experiment.

SOME PROPERTIES OF CATHODE RAYS :

(I) They cast shadow of the object in their path

(II) Rotate a mica wheel

(III) Deflected by electric and magnetic fields in a direction showing negative charge.

PROTON (H^+) :

Discovered by Goldstein (1886) through perforated cathode rays experiment which showed the presence of **anode or canal rays.**

(I) **Mass :** It was found to be 1.672×10^{-24} g or 1.672×10^{-27} kg or 1.00728 amu. It is about 1837 times heavier than an electron.

(II) **Charge :** It carries unit positive charge 1.602×10^{-19} coulombs or 4.803×10^{-10} esu.

(III) **Specific charge :** It is 9.58×10^4 coulomb/gm. It varies with nature of gas and is maximum if H_2 is used.

(IV) Charge on 1 mole of proton is 96500 coulomb or 1 Faraday.

(V) **Volume :** The volume $\left(\frac{4}{3}\pi r^3\right)$ for proton is approximately 1.5×10^{-38} cm^3.

NEUTRON ($_0n^1$) :

Discovered by Chadwick by bombarding Be or B atoms (sheet) with high speed α-particles

$${}_4Be^9 + {}_2He^4 \longrightarrow {}_6C^{12} + {}_0n^1$$

(I) **Mass :** Its mass is 1.675×10^{-24} gm or 1.675×10^{-27} kg or 1.00866 amu.

(II) It is heavier than proton by 0.18%.

(III) **Density :** Its density is 1.5×10^{14} g/cm^3.

(IV) **Specific Charge :** It is zero.

(V) **Stability :** It is least stable of all elementary particles present in an atom.

(VI) **Disintegration :** Isolated neutron is unstable and distintegrates into electron, proton and neutrino.

(VII) Among all elementary particles neutron is the heaviest and least stable.

OTHER SUBATOMIC PARTICLES :

(I) **Positron** (Positive electron $_{+1}e^0$). Discovered by Dirac (1930) and C. D. Anderson (1932). They are highly unstable and produce γ-rays on combining with electrons.

(II) **Neutrino** and **Antineutrino** are particles of small mass and no charge as stated by Fermi (1934). Anti-neutrino spin clockwise and neutrino spin anticlockwise.

(III) **Meson :** They are unstable particles and include **pions** (π^+, π^- or π^0) **Kaons** (K^+, K^-, K^0, K^{-0}) and eta meson (η^0).

Mass : They have mass intermediate of electron and proton.

Discovery : By **Yukawa** (1935) and **Kemmer.**

(IV) **Anti proton** ($_{-1}p^1$) **:** Negative proton produced by **Segre** and **Weigland** (1955) by proton-proton and proton-neutron collisions.

(V) **v-particles :** They may be positive, negative or neutral. Discovered by **G. D. Rochester** and **C C. Butler** v^- and v^0 are 2200 times heavier than electron. Heavier disintegrate into pions and lighter into mesons.

THOMSON'S ATOMIC MODEL :

Atom is a sphere of positive electricity with a number of electrons distributed within the sphere.

RUTHERFORD'S NUCLEAR MODEL :

It is based upon α particles scattering experiment. Only a few (one in 10,000) α-particles were returned back from the Au-foil (10^{-4} mm thick).

$$\text{Scattering of } \alpha\text{-particles} \propto \frac{1}{\sin^4\left(\frac{\theta}{2}\right)}$$

Conclusion : Atom consists of two parts - (a) Nucleus (b) Extra nuclear part.

Drawbacks - This model fails to explain the stability of the atoms and line spectrum of hydrogen.

THE NUCLEUS :

(I) **Nucleus** - It is small heavy and positively charged material located in the centre of atom and electrons are distributed in extra nuclear part of atom and revolve around the nucleus.

(II) **Radius of nucleus :** It is of the order 1.5×10^{-13} cm to 6.5×10^{-13} cm (1.5 – 6.5 Fermi). In general $r_n = r_0 \times A^{1/3}$ cm Where r_0 is a proportionality constant with value 1.4×10^{-13} cm. and A is mass number.

(III) **Volume of nucleus :** It is about 10^{-39} cm^3. and that of atom is 10^{-24} cm^3

(IV) **Density of nucleus :** It is about 10^{14} g/cm^3.

$$\text{Density} = \frac{\text{Mass of nucleus}}{\text{Volume of nucleus}} = \frac{\text{Mass number}}{6.023 \times 10^{23} \times \frac{4}{3}\pi r^3}$$

(V) **Diameter :** It is about 10^{-15} m or 1 fm (1 fm = 10^{-15} m)

(VI) Nucleus contains **neutrons** and **protons**, collectively known as **nucleons.**

ATOMIC NUMBER/MOSELEY'S POSTULATES :

The number of protons present in an atom is called the atomic number, denoted by Z. Moseley postulated that the frequency of X-rays produced when beam of strong electrons fall on metal target, called anti-cathode is related to the charge present on the nucleus of an atom of the element used as anti cathode. Mathematically

$\sqrt{\nu} = a(Z - b)$; where ν = frequency of X-rays, Z = nuclear charge, a and b = constants

MASS NUMBER :

It is sum of number of protons and neutrons present in the nucleus (**nucleons** as a whole) and denoted by A. It is always a whole number.

AVERAGE ATOMIC MASS :

It is the average mass of all existing isotopes and not necessarily a whole number.

ISOTOPES :

Isotopes are atoms of the same element having same atomic number but different mass number. e.g. $_8O^{16}$, $_8O^{17}$ and $_8O^{18}$. They were discovered by **Soddy** (1911).

ISOBARS :

Atoms of different elements having same mass number but different atomic numbers e.g. $_{19}K^{40}$, $_{20}Ca^{40}$.

ISOTONES :

Atoms of different elements with different atomic and mass numbers but same number of neutrons e.g. $_{14}Si^{30}$, $_{15}P^{31}$, $_{16}S^{32}$.

ISODIAPHERS :

Atoms having same Isotopic number.

ISOELECTRONIC SPECIES :

Species having same number of electrons e.g. CO and CN^- (both contain 14 electrons each) Na^+ and Ne (both contain 10 electrons each).

The ionic size decreases with increasing effective nuclear charge of iso-electronic species.

Ionic size of isoelectronic species depend on $\frac{P}{e}$ (effective nuclear charge).

$$\text{Ionic size} \propto \frac{1}{\text{Effective nuclear charge}}$$

Species	C^{4-}	N^{3-}	O^{2-}	$\bar{F}$
Nuclear Charge	6	7	8	9
Total electrons	10	10	10	10
$\frac{P}{e}$	.6	.7	.8	.9
Ionic Radius (Å)	2.60	1.70	1.40	1.36
Species	Na^{+}	Mg^{2+}	Al^{3+}	Si^{4+}
Nuclear Charge	11	12	13	14
Total electrons	10	10	10	10
$\frac{P}{e}$ (effective Nuclear charge)	1.1	1.2	1.3	1.4
Ionic radius (Å)	0.95	0.65	0.50	0.41

FAILURE OF RUTHERFORD'S MODEL :

According to classical theory of electromagnetism whenever a charge is subjected to an acceleration around an opposite charge, it emits radiations continuously. Therefore the electron while moving around nucleus in circular path must loose energy, go into spiral motion and ultimately fall into the nucleus. Practically it does not happen.

PLANCK QUANTUM THEORY :

According to Max Planck (1901) radiant energy is emitted or absorbed only in discrete units in form of bundle or packets of energy called **photon (quantum)**. Photon is not a material body. It is massless bundle of energy

Energy associated with each photon (quantum)

$E = h\nu = h\frac{c}{\lambda}$

h = Planck's constant = 6.626×10^{-34} Js in S.I. units (or 6.6726×10^{-27} ergs in c.g.s. units). ν = frequency of radiation (each photon).

c = velocity of light, λ = wavelength of radiation.

Thus a body can radiate energy in multiples of quantum $h\nu$, $2h\nu$, $3h\nu$ .... $nh\nu$ where n is an integer.

INTENSITY OF LIGHT :

It is defined as number of photons falling per unit area per sec. and depends upon wavelength of photons.

or it is defined as amount of energy falling per unit area per sec and depends upon wavelength of photons.

ELECTROMAGNETIC RADIATION :

Electromagnetic radiation by James maxwell (1870). An electrically changed particles moving under acceleration produces alternating electrical and magnetic fields mutually perpendicular to each other. These fields are transmitted in the form of waves having same wavelengths, frequency, speed and amplitude and are called **electromagnetic waves** or **electromagnetic radiations.** In vaccum all types of electromagnetic radiations travel at the same speed (3.0×10^{8} ms^{-1}) regardless of wavelengths.

WAVELENGTH :

It is the distance between two neighbouring crests or troughs of wave.

FREQUENCY :

It is the number of waves which pass through a particular point in one second. Unit is Hertz (Hz) or cycles per second. 1 Cps = 1 Hz.

VELOCITY :

It is the distance travelled by wave in one second. Unit is m sec^{-1} and denoted by c.

$c = \nu\lambda$.

WAVE NUMBER :

It is the number of wavelengths per cm. It is equal to the inverse of wavelength. Unit is cm^{-1} and is denoted by $\bar{\nu}$.

$$\bar{\nu} = \frac{1}{\lambda}$$

AMPLITUDE :

It is the height of crest or trough. Square of amplitude determines the amount of energy carried by the wave.

ELECTROMAGNETIC SPECTRUM :

Arrangement of all electro-magnetic radiations in the increasing order of their wavelengths or decreasing order of frequencies is called electromagnetic spectrum.

Rays	Wavelength (λ in Å)	Frequency ν in Hz
Cosmic Rays		3×10^{21} to ∞
γ Rays	0.01	3×10^{19} to 3×10^{20}
X Rays	1.0	2×10^{16} to 3×10^{19}
UV Rays	150	7.9×10^{14} to 2×10^{16}
Visible Light	3800	3.9×10^{14} to 7.9×10^{14}
Infra Red	7600	1×10^{11} to 3.95×10^{14}
Micro Waves	6×10^{6}	1×10^{9} to 5×10^{11}
Radio Waves	3×10^{9}	1×10^{5} to 1×10^{9}

ATOMIC SPECTRUM :

Atoms of different elements emit electromagnetic radiations of definite frequencies when excited by heating, passing current or electric discharge. Arrangement of these radiations in decreasing order of frequencies is called atomic spectrum.

DISPERSION :

Phenomenon of splitting of beam of light into radiations of different frequencies after passing through a prism is called dispersion.

CONTINUOUS SPECTRUM :

It is obtained by passing sunlight (white light) through a prism. The light is dispersed or resolved into continuous spectra of colours from **Violet to Red**. It contains radiations of all the frequencies.

LINE SPECTRUM :

It is an atomic spectrum of an element which consists of a number of bright lines separated by dark bands. Atomic Spectra of most elements is line spectrum.

ABSORPTION SPECTRUM :

It is obtained by passing white light through solutions or vapours of chemical substance and then is analysed by spectroscope. It has few dark lines in otherwise continuous spectrum.

EMISSION SPECTRUM :

It is obtained by passing radiations from the atoms through prism. It has few bright lines against a dark back ground.

HYDROGEN SPECTRUM :

It is obtained by passing light being emitted from discharge tube containing hydrogen at low pressure through spectrograph.

Hydrogen Spectrum has five Series

Spectral Line	Region	n_1	n_2
Lyman Series	U.V.	1	2, 3, 4.....
Balmer Series	Visible	2	3, 4, 5.....
Paschen Series	I.R.	3	4, 5, 6.....
Brackett Series	I.R.	4	5, 6, 7....
Pfund Series	I.R.	5	6, 7, 8....

> In Balmer Series of hydrogen spectrum
> the first line ($3 \rightarrow 2$) is known as L_α line
> the second line ($4 \rightarrow 2$) is L_β line.

Wavelength of line in spectrum is given by the expression

$$\bar{\nu} \quad \frac{1}{\lambda} \quad R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

R_H = Rydberg Constant, Z = charge on nucleus, n_1, n_2 = electronic levels involved in transition, $\bar{\nu}$ = **Wave number**

$$R_H = \frac{2\pi^2 me^4}{ch^3} = 109677.76 \text{ cm}^{-1} \text{ also for hydrogen}$$

$$\nu = 3.29 \times 10^{15} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{sec}^{-1}$$ where ν **is frequency.**

(I) For calculation of longest wavelength line use n_2 nearest and for shortest wavelength line use n_2 infinity e.g. value of longest wave length in Balmer Series of hydrogen spectrum use $n_1 = 2$ and $n_2 = 3$.

(II) Last line of spectrum is called Series limit. Last line is the line of shortest wavelength and high energy when $n_2 = \infty$ we get last wavelength

$$\frac{1}{\lambda} = \frac{R_H{}^2}{n_1^2} \quad \lambda \text{ (series limit)} = \frac{n_1^2}{R_H{}^2},$$

(III) **Number of Lines in a Transition :** Mathematical formula for number of lines is follows as

$$\text{No. of lines} = \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$

BLACK BODY RADIATION :

The radiation emitted by a body when heated is called black body radiation. The frequency of radiation increases with temperature. At a given temperature the intensity of radiation emitted increases with decrease of wavelength, reaches a maximum value and then starts decreasing with further decrease of wavelength. A black body can emit and absorb all frequencies.

PHOTOELECTRIC EFFECT :

Phenomenon of ejection of electrons from the surface of a metal when light of suitable frequency strikes on it is called photoelectric effect.

(I) **Threshold frequency (ν_0) :** The minimum frequency of incident radiation to cause the photoelectric effect is called threshold frequency.

(II) **Work function :** A part of the photons energy that is absorbed by the metal surface to release the electron is known as work function of the surface denoted by ϕ. The remaining part of the energy of photons goes into the Kinetic energy of the electron emitted.

If ν_0 is the threshold frequency and ν the frequency of incident light then $\phi = h\nu_0$ and $E = h\nu$.

$$\text{K.E.} = E - \phi = h\nu - h\nu_0 = h(\nu - \nu_0)$$

Note: • K.E. is independent of the intensity of light.

- Number of photoelectrons $\propto$ Intensity of light
- K.E. is directly proportional to frequency of incident light.
- $E = \text{K.E.} + \phi$ is known as Einstein's photoelectric equation.
- Energy required to stop the ejection of electrons is given by eV_0 where e is the electric charge and V_0 is stopping potential.

BOHR'S MODEL OF ATOM :

Proposed by Niel Bohr to overcome the drawbacks of Rutherford's model.

(i) Electrons revolve around nucleus only in certain selected circular orbits. These orbits are associated with definite energies and are **called energy shells or levels**.

(ii) Electrons can move only in those circular orbits where angular momentum is a whole number and multiple of $h/2\pi$.

i.e. $\mathbf{mvr} = \frac{\mathbf{nh}}{\mathbf{2\pi}}$. or simply an integral number of wavelengths should fit in given electron orbit of radius r i.e. $\mathbf{n\lambda = 2\pi r}$.

(iii) Electrons energy in a particular orbit is constant.

(iv) Lowest energy state is called **ground state** and when electron absorbs energy and jumps to higher state, it is called **excited state**

(v) **Electronic energy** is **negative** because at infinite distance there is no interaction between electron and nucleus thus energy is zero. While when close to nucleus, attraction takes place, energy is released and it becomes negative as it was already zero. The energy of electron increases with the value of n, but the difference of energy between two successive orbits decreases. Thus

$$E_2 - E_1 > E_3 - E_2 > E_4 - E_3 \text{ .... etc.}$$

(vi) **Energy of electron in nth orbit**

$$E_n = -\frac{k^2 2\pi^2 me^4 z^2}{n^2 h^2} = \frac{-13.6Z^2}{n^2} \text{eV atom}^{-1}$$

$$= \frac{-2.178\times10^{-18} Z^2}{n^2} \text{J atom}^{-1}$$

where m = Mass of the electron,

e = Charge on the electron,

h = Planck's constant

n = Principal quantum number,

k = A universal constant = 9.0×10^9 J.m/C^2

The constant k is inverse of permitivity factor $4\pi\varepsilon_0$ of the medium $k = \frac{1}{4\pi\varepsilon_0}$. The numerical value of permitivity factor is $4\pi\varepsilon_0 = 1.11264 \times 10^{-10}\, C^2N^{-1}m^{-2}$. In C.G.S. system k = 1.

(vii) **The radius of nth orbit**

$$r_n = \frac{n^2h^2}{4\pi^2 me^2 Zk} = \frac{a_0 n^2}{Z} = \frac{0.528\text{Å}n^2}{Z}\text{Å}$$

(viii) **The velocity of electron in nth orbit,**

$$v_n = \frac{nh}{2\pi mr} = \frac{2\pi Ze^2 k}{nh} = \frac{2.19\times10^8 Z}{n} \text{ cm/sec.}$$

The velocity of electron in first orbit of hydrogen is $\frac{1}{137}$ of the velocity of light.

(ix) **Kinetic energy of electron in nth orbit,**

$$E_k = \frac{2m\pi^2 e^4 Z^2 k^2}{n^2h^2} = \frac{13.6\times Z^2}{n^2}\text{eV}$$

(x) **Potential energy of electron in nth orbit,**

$$E_p = \frac{-e^2}{r} = \frac{-4m\pi^2 e^4 Z^2 k^2}{n^2h^2} = \frac{-27.2Z^2}{n^2}\text{eV}$$

(xi) **Total energy of electron in nth orbit,**

$$E_n \quad E_k \quad E_p \quad \frac{-k^2 2\pi^2 me^4 Z^2}{n^2h^2} \quad \frac{-13.6Z^2}{n^2}\text{eV}$$

(xii) **Number of revolutions per second in nth orbit,**

$$\frac{v_n}{2\pi r_n} = \frac{\text{velocity of electron in } n^{th} \text{ orbit}}{\text{circumference of the } n^{th} \text{ orbit}}$$

(xiii) **Angular velocity** $\omega = \frac{v}{r} = \frac{\text{Velocity}}{\text{radius}}$

(xiv) **Angular momentum** = mvr

(xv) Number of spectral lines when electron jumps from the nth to ground level = $= \frac{n(n-1)}{2}$

(xvi) The electrons energy is generally expressed in kcal or kJ mol^{-1} or in electron volts eV.

1 erg mol^{-1} = 1.44×10^{13} kcal mol^{-1} = 6.022×10^{13} kJ mol^{-1}

1eV = 1.602×10^{-19}J

(xvii) **Some important values :**

In c.g.s. system,

m = 9.109×10^{-28}g

e = 4.803×10^{-10} esu,

h = 6.626×10^{-27} ergs,

k = 1

$$R_H = \frac{2\pi^2 me^4}{ch^3}\text{cm}^{-1}$$

In S I system,

m = 9.109×10^{-31}kg

e = 1.602×10^{-19}C,

h = 6.626×10^{-34} J.s,

k = 9.0×10^9 Jm/C^2

$$R_H = = \frac{2\pi^2 me^4}{(4\pi\varepsilon_0)^2 ch^3}\text{m}^{-1}$$

In S I system the charge e is replaced by $\frac{e}{\sqrt{4\pi\varepsilon_0}}$

LIMITATIONS OF BOHR'S MODEL ARE :

(i) Explains the spectrum of elements having only one electron

(ii) Does not explain splitting of spectral lines under magnetic field **(Zeeman effect)** and electric field **(stark effect)**

(iii) Does not explain quantisation of angular momentum.

(iv) It goes against the Heisenberg's uncertainity principle.

SOMMERFIELD MODEL :

(i) Motion of electrons is in closed elliptical paths of definite energy levels having nucleus on either of the focii.

(ii) Angular momentum is quantized

(iii) $\frac{n}{k} = \frac{\text{major axis length}}{\text{minor axis length}}$ where k = 1, 2 ---------n.

(iv) It does not explain distribution of electrons in extranuclear part of atom and also does not explain for de Brogalie concept.

QUANTUM MECHANICS :

It was developed independently by Warner Heisenberg and Erwin Schrodinges and takes into account the dual behaviour (particle and wave nature) of matter proposed by de Broglie.

Planck's Quantum theory successfully explains.

(i) Photoelectric effect
(ii) Black-body radiation
(iii) Line spectra of H-atom
(iv) Variation of heat capacity of solids with temperature.

de- BROGLIE PRINCIPLE (1924) :

(i) Proposes that just as radiations have particle nature, the material particles are also associated with wave nature.

(ii) **de Broglie wavelength** is $\lambda = \frac{h}{mv} = \frac{h}{p}$ h = Planck's constant m = mass of object ; v= velocity and this equation is called the de Broglie equation.

DAVISSON AND GERMER'S EXPERIMENT :

Confirms the wave nature of electrons.

SCINTILLATION METHOD AND PHOTOELECTRIC EFFECT :

Confirm the particle nature.

HEISENBERG'S UNCERTAINITY PRINCIPLE :

"It is not possible to determine simultaneously the position and momentum of small moving sub-atomic e.g., ${}_1H$, He , ${}_{-1}B$, α, n particle, such as electron with entire certainty".

(i) Mathematically $\pm\ \Delta x \times \Delta p \geq \frac{h}{4\pi}$

where, Δx = uncertainity in position

Δp = uncertainity in momentum and h = Planck's constant

(ii) As the mass of particle increases, the uncertainity decreases

QUANTUM MECHANICAL MODEL OF ATOM :

(i) Based on de Broglie's and Heisenberg's principle.

(ii) Put forward by Schrodinger (1920). Behaviour of electron was described in terms of equation known as **Schrodinger wave equation**

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

where ψ is amplitude of electron wave and is also called wave function. x, y, z, are space coordinates, m is mass of electron, h is Planck's constant, E is total energy and V is potential energy of the electron.

(iii) Many solutions for this equation are possible for hydrogen but only certain solutions are permissible and are called **eigen values**

(iv) The solution must be single valued, should satisfy the relation $\int_0^\infty \psi dr \quad 0$ and must be finite and continuous.

(v) Ψ has no physical significance but Ψ^2 gives intensity of electrons and thus gives probability of electron in a particular region.

ORBITALS :

Orbitals are the regions in space around nucleus where probability of finding the electron is maximum.

(i) Probability does not become zero even at infinity and is given by Ψ^2.

(ii) Electron orbitals in atoms are called **atomic orbitals** while those in molecules are called **molecular orbitals**.

(iii) Orbitals have definite energy and momentum and are quantized. i.e, $E_n = -E_1/n^2$ thus Bohr's concept of well defined orbits is ruled out.

QUANTUM NUMBERS :

(i) Four quantum numbers (n, l, m, s) help in providing complete information about an electron in an atom.

(ii) **Principal quantum number** (n) determines the **energy** and **average distance** of electron. It has whole number values also denoted as K, L, M, N. etc. As n increases, distance of electron from nucleus increases and energy increases.

(iii) **Azimuthal quantum number** (*l*) determines **angular momentum of the electron.** It also determines the **shape of orbitals** and it may have all possible whole number values from 0 to n–1 for each principal energy level. The sublevels are:

Value of l	0	1	2	3
Sub-shell	s	p	d	f

Magnitude of angular momentum of an electron in **orbital**,

$$mvr = \frac{h}{2\pi}\sqrt{l(l+1)}$$

Angular momentum of an electron in any **orbit,**

$$mvr = \frac{nh}{2\pi}$$

(iv) **Magnetic quantum number** (m) defines the **orientation of electrons** cloud in a particular sub shell. Values of m are the number of orbitals associated with a particular sub shell in main shell. Values of m lie from 0 to $\pm l$. Total values of 'm' for a given n is n^2. Total values of 'm' for a given l is $2l+1$. The table shows a clear relation between quantum numbers.

Shell (n)	Sub -shells (l)	Orbitals (m)
$n=1 \Rightarrow$ K shell	$l=0 \Rightarrow$ 1s	m = 0
$n=2 \Rightarrow$ L shell	$l=0 \Rightarrow$ 2s	m = 0
	$l=1 \Rightarrow$ 2p	m = –1, 0, +1 $(2p_x, 2p_y, 2p_z)$
$n=3 \Rightarrow$ M shell	$l=0 \Rightarrow$ 3s	m = 0
	$l=1 \Rightarrow$ 3p	m = –1, 0, +1
	$l=2 \Rightarrow$ 3d	m = –2, –1, 0, +1, +2 $(3d_{xy}, 3d_{yz}, 3d_{zx}, 3d_{x^2-y^2}, 3d_{z^2})$

(v) **Spin quantum number** (s) tells the spin of the electron. It can have two value $\frac{+1}{2}$ (clockwise) and $\frac{-1}{2}$ (anticlockwise).

Mathematically $S=\frac{h}{2\pi}\sqrt{s(s+1)}$ where s is amplitude of spin quantum angular momentum.

SHAPE OF ORBITALS :

(i) *s* orbitals are spherically symmetrical.

(ii) *p* orbitals are dumbell shaped.

(iii) *d* orbitals have five different orientation. Three of them d_{xy}, d_{yz}, d_{xz} are identical in shape but have different orientation.

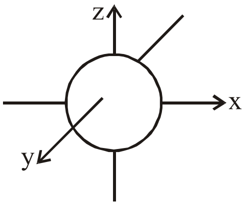
(iv) The plane passing through nucleus where probability of finding the electron is zero is called a **nodal plane.** Number of nodal planes in an orbital = *l*. Number of nodal planes increases with increasing value of n. e.g. 1s has no nodal plane. 2s has one nodal plane. **For e.g.** : s orbitals (*l*=0) have no nodal plane, p orbital (*l*=1) have one nodal plane, d orbitals (*l*=2) have two nodal planes.

Nodal plane $= n - l - 1$

(v) Orbitals of a sub shell having same energy are called **degenerated orbitals.**

(vi) Spherical surface within an orbital where probability of finding an electron is zero is called **spherical or radial node.** Number of spherical nodes = (n–*l*–1). **Angular or non spherical** nodes = (*l*). **Thus total nodes** = (n – 1).

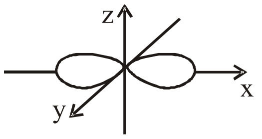
Shape of s-orbital :



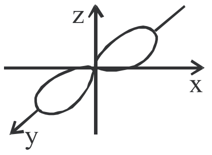
s orbital

Shape of p-orbital :

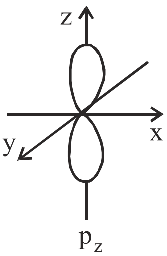
for $p_z m \quad 0$ and for p_x or p_y, $m = \pm 1$



p_x

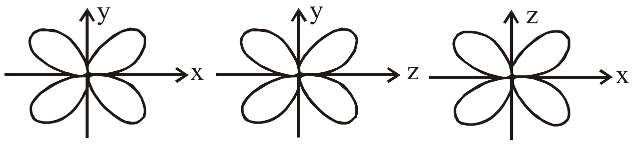


p_y



p_z

Shape of d-orbitals :

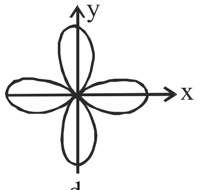


d_{xy} d_{yz} d_{xz}

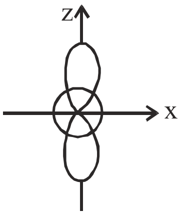
$m = 0$ for d_{z^2}

$m = \pm 1$ for $d_{x^2-y^2}$ and d_{xy}

$m = \pm 2$ for d_{x^2} and d_{y^2}



$d_{x^2-y^2}$



d_{z^2}

PAULI'S EXCLUSION PRINCIPLE :

No two electrons in an atom can have same values for all the four quantum numbers.

(i) It is not possible to accomodate more than two electrons in an orbital. In other words. s sub shell can have maximum of 2 electrons p sub shell can have maximum of 6 electrons. Thus max. no. of electrons in a shell can be **$2n^2$**.

(ii) Maximum number of electrons in a sub shell can be 2, 6, 10, 14 in s, p, d, f respectively and max. electrons in an atomic orbital can be 2.

Maximum number of electrons in a sub shell is equal to $4l + 2$

where $l = 0, 1, 2, 3$

$l = 0$ (s)	$l = 1$ (p)	$l = 2$ (d)	$l = 3$ (d)
Electrons	Electrons	Electrons	Electrons
$= 4 \times 0 + 2$	$= 4 \times 1 + 2$	$= 4 \times 2 + 2$	$= 4 \times 3 + 2$
$= 2$	$= 6$	$= 10$	$= 14$

Note : Maximum numbers of electrons in an orbital = 2

AUFBAU'S RULE :

Electrons are added to orbitals in increasing order of energies. The order of energies for orbitals is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s.

(i) The order of energies can be calculated by **(*n* + *l*) rule.** i.e. orbitals are filled in order of increasing **(*n*+*l*)** values the one with lower **n** value is filled first.

(ii) The energy of atomic orbitals for H-atom depends on the value of n only.

$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$

HUND'S RULE OF MAXIMUM MULTIPLICITY :

The pairing of electrons in orbitals of a subshell does not take place until all orbitals of sub shell are singly occupied.

(i) This arrangement leads to lower energy level.

(ii) Singly occupied orbitals should have same spins giving rise to lower energies.

RADIAL PROBABILITY DISTRIBUTION CURVES :

The electron density is directly proportional to ψ^2. The larger the value of ψ^2 more is the probability of finding the electrons. Schrodinger wave equation may be separated into a product of three functions dependent on r, θ, ϕ

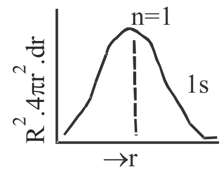
$$\psi(r,\theta,\phi) = \underbrace{R(r)}_{\substack{\downarrow \\ \text{Radial Part}}} \quad \underbrace{\theta(\theta)\,\varphi(\varphi)}_{\substack{\downarrow \\ \text{Angular part}}}$$

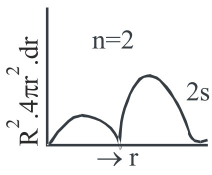
R (r) = Radial wave function, it may be 0, or ±

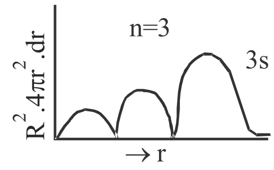
R^2 = Radial density in per unit volume of spherical shell. It is always positive.

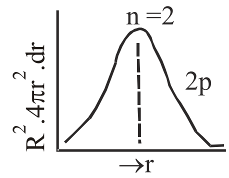
$4\pi r^2.dr.R^2 =$ Radial probability. It is defined as maximum density of electrons in the volume of spherical shell having small thickness dr.

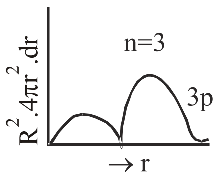
Note : → $4\pi r^2.dr$ is the volume of spherical shell having small thickness dr.

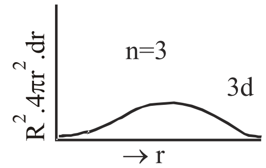












In case of s orbitals the number of peaks is equal to n,

In case of p orbitals the number of peaks is equal to (n–1),

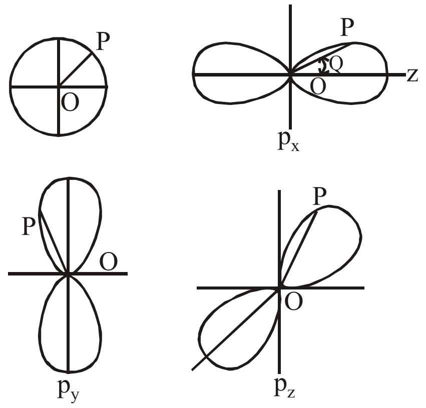
In case of d, orbitals the number of peaks is equal to (n–2)

The point at which the probability of finding the electrons is zero is called **nodal point.**

The distance of maximum probability increases with increase in the value of n. hence 2s, 2p electrons are greater distance than 1s. and have greater energy also.

ANGULAR PROBABILITY DISTRIBUTION CURVES :

The total angular θ (θ). φ (ϕ) depends only on the direction and remain independent of the distance electrons from the nucleus



Angular probability distribution curves for s and p orbitals. The length of the line OP is proportional to the probability of finding the electrons. The length of the line OP is the same in all directions for s orbital Hence there are equal chances for finding electrons in all directions from the nucleus.

The length of line decreases with increasing in the value of angle θ. Hence there are more chances for finding the electrons along the axes for p orbitals.

RITZ. COMBINATION PRINCIPLE :

It states that the wave number $\bar{v}$ (reciprocal of wavelength) of any line in hydrogen spectrum of a particular series can be represented as a difference of two terms, one of which is constant and other varies throughout the series. Mathematically,

$$\bar{v} = \frac{1}{\lambda} = \frac{v}{c} = R_H\left(\frac{1}{x^2} - \frac{1}{y^2}\right).$$

R_H = Rydberg constant

COMPTON EFFECT :

The decrease in energy (or increase in wavelength) of X-rays after the scattering from the surface of carbon or light element is known as Compton effect.

Miscellaneous Solved Examples

1. An electron beam can undergo diffraction by crystals. Through what potential a beam of electrons be accelerated so that its wavelength becomes equal to 1.54Å. **(IIT 1997)**

Sol. $\frac{1}{2}mv^2 = eV$ and $\lambda = \frac{h}{mv}$

$$\therefore V = \frac{1}{2} \cdot \frac{h^2}{m\lambda^2 e}$$

$$= \frac{(6.62\times10^{-34})^2}{2\times9.108\times10^{-31}(1.54\times10^{-10})^2\times1.6202\times10^{-19}}$$

$= 63.3$ volt.

2. Wavelength of photon having energy 2 eV.

Sol. $1\text{ eV} = 1.6\times10^{-19}\text{ J}$ or 1.6×10^{-12} ergs

$$\lambda = \frac{hc}{E} = \frac{6.62\times10^{-34}\times3\times10^{8}}{2\times1.6\times10^{-19}} = 6.20\times10^{3}\text{ Å}$$

3. The velocity of electron in a certain Bohr's orbit of H-atom bears the ratio 1: 275 to the velocity of light.

(i) What is quantum number n of orbit.

(ii) Wave number of radiations emitted when electron jumps from (n + 1) to ground state.

Sol. (i) Velocity of electron $= \frac{1}{275}\times$ Velocity of light

$$\text{Again } V_n = \frac{2.19\times10^{8}\times Z}{n}\text{ cm/sec}$$

$$\therefore \frac{2.19\times10^{8}\times1}{n} = \frac{1}{275}\times3\times10^{10}$$

$$\therefore n = \frac{2.19\times10^{8}\times275}{3\times10^{10}} = 2$$

(ii) Wave number $= \frac{1}{\lambda} = R_H Z^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$

$$= 109678\left(\frac{1}{1}-\frac{1}{3^2}\right) = 9.75\times10^{4}\text{ cm}^{-1}$$

4. A bulb emits light of λ 4500Å. The bulb is rated as 150 watt and 8% of the energy is emitted as light. How many photons are emitted by the bulb per second?

Sol. Energy of one photon

$$= E = h\upsilon = \frac{hc}{\lambda} = \frac{6.6\times10^{-34}\times3\times10^{8}}{4500\times10^{-10}} = 4.42\times10^{-19}\text{ J}$$

Energy emitted by bulb $= \frac{150\times8}{100}$ J

$$\therefore n\times.42\times10^{-19} \quad \frac{150\times8}{100}$$

$$\therefore n = 27.2\times10^{18}\text{ photons}$$

5. If the critical wavelength for producing photoelectric effect is 2000Å. Then what wavelength of light will be required to produce photoelectrons with double the K.E. of those produced by light of wavelength of 1500Å.

Sol. K.E. with 1500Å $= \left(\frac{hc}{1500}-\frac{hc}{2000}\right)$ (I)

KE with xÅ $= \left(\frac{hc}{x}-\frac{hc}{2000}\right)$ (II)

According to question 2I = II

$$2\left(\frac{hc}{1500}-\frac{hc}{2000}\right) = \left(\frac{hc}{x}-\frac{hc}{2000}\right)$$

$$\therefore x = 1200\text{Å}$$

6. Calculate the wavelength of radiations emitted producing a line in Lyman Series when an electron falls from fourth stationary state in hydrogen atom ($R_H = 1.1\times10^{7}\text{ m}^{-1}$)

Sol. $\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$

$$\frac{1}{\lambda} = 1.1\times10^{7}\left[\frac{1}{1^2}-\frac{1}{4^2}\right]$$

$$\therefore \lambda = 0.9696\times10^{-7}\text{ meter}$$

7. Calculate the momentum of a particle with de-Broglie wavelength 1Å.

Sol. $1Å = 10^{-10}$ m

$$p = \frac{h}{\lambda} = \frac{6.62\times10^{-34}}{10^{-10}} = 6.62\times10^{-24}\ \text{kgms}^{-1}$$

8. The uncertainity in the position of a bullet weighing 20 g is $\pm 10^{-4}$ m. Calculate the uncertainity in its velocity.

Sol. 20 g = 0.02 Kg

$$\pm\Delta x.\Delta p = \frac{h}{4\pi}$$

$$\text{or } \Delta x.m\Delta v = \frac{h}{4\pi}$$

$$\therefore \pm\Delta v = \frac{6.62\times10^{-34}}{4\times3.14\times0.02\times10^{-4}} = 2.63\times10^{-29}\ \text{ms}^{-1}$$

9. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition n = 4. (n = 2 of He^+ Spectrum).

Sol. For He^+ $\frac{1}{\lambda} = R_H Z^2\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$

For H $\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

Since λ is the same $Z^2\left[\frac{1}{2^2} - \frac{1}{4^2}\right] = \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

Since Z = 2 $\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$n_1 = 1$ and $n_2 = 2$

10. Find out the number of waves by a Bohr electron in one complete revolution in its 3rd orbit. **[IIT 1994]**

Sol. Number of waves in an orbit

$$= \frac{\text{Circumference of orbit}}{\text{Wavelength}} = \frac{2\pi r}{\lambda}$$

$$= \frac{2\pi r}{h/mv} = \frac{2\pi(mvr)}{h} = \frac{2\pi\left(\frac{nh}{2\pi}\right)}{h} = n$$

(Since angular momentum mvr = nh/ 2π) Ans. 3.

11. A compound of Vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the vanadium ion in the compound. **[IIT 1997]**

Sol. Magnetic moment = $\sqrt{n(n+2)}$

Where n is the number of unpaired electrons.

$1.73 = \sqrt{n(n+2)}$ $\qquad \therefore n = 1$

∴ Vanadium atom must have one unpaired electron hence its configuration is ${}_{23}V^{4+} = 1s^2, 2s^2p^6, 3s^2p^6\ 3d^1$

12. Find the ratio of the radius of the first Bohr orbit for the electron orbiting the hydrogen nucleus to that of the electron orbiting the deuterium nucleus (mass nearly twice that of the hydrogen nucleus).

Sol. $r_n = \frac{a_0 n^2}{Z}$;

$r_1 = \frac{a_0\times1}{1}$ for hydrogen; $r_2 = \frac{a_0\times1}{1}$ for deuterium;

$\frac{r_1}{r_2} = \frac{1}{1}$; 1 :1.

13. In an atom 2 electrons move round the nucleus in circular orbits of radii R and 4R. The ratio of the time taken by them to complete one revolution is.

Sol. $T^2 \quad R^3$

$T_1^2 = K(R)^3$; $T_2^2 = K(4R)^3$

$$\therefore \frac{T_1^2}{T_2^2} = \frac{R^3}{64R^3} \Rightarrow \frac{T_1}{T_2} = \frac{1}{8}$$

14. Calculate the speed of electron in third orbit of hydrogen atom. Also calculate the number of revolutions per second that this electron makes around the nucleus. Given $4\pi\varepsilon_0 = 1.112\times10^{-10}\ C^2N^{-1}m^{-2}$.

Sol. Speed $v = \frac{2\pi(Ze^2/4\pi\varepsilon_0)}{nh}$

$$= \frac{2\times3.14(1.6\times10^{-19}C)^2/1.112\times10^{-10}}{3\times6.626\times10^{-34}} = 7.27\times10^5\ \text{ms}^{-1}$$

Number of revolutions made by the electron = $\frac{v}{2\pi r}$

$$r \quad \frac{n^2h^2}{4\pi^2 m(Ze^2/4\pi\varepsilon_0)}$$

$$\frac{9\times(6.626\times10^{-34})}{4(3.14)^2(9.1\times10^{-31}\text{ kg})(1.6\times10^{-19})^2/1.112\times10^{-10}}$$

$$= 4.782\times10^{-10}\ \text{m}$$

$$v = \frac{7.27\times10^5}{2\times3.14\times4.782\times10^{-10}} = 2.42\times10^4\ \text{s}^{-1}$$

15. Calculate the frequency, energy and wavelength of the radiation corresponding to the spectral line of lowest frequency in Lyman series in the spectra of H atom. Also calculate the energy for the corresponding line in the spectra of Li^{2+}

$(R_H = 1.09678\times 10^7\ m^{-1},\ c = 3\times 10^8\ ms^{-1},$

$h = 6.625\times 10^{-34}\ Js)$

Sol. $$\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$= R_H\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{3}{4}R_H$$

$$\lambda = \frac{4}{3R_H} = \frac{4}{3} \times \frac{1}{1.09678\times 10^7\ m^{-1}} = 1.216\times 10^{-7}\ m$$

$$v = \frac{c}{\lambda} = \frac{3\times 10^8 ms^{-1}}{1.216\times 10^{-7} m}$$

$$= 2.47\times 10^{15} s^{-1}$$

$$E = h\upsilon = 6.625\times 10^{-34}\ Js \times 2.47\times 10^{15} s^{-1} = 16.36\times 10^{-19}\ J$$

$$E_{Li^{2+}} = Z^2 \times E_H = 3^2 \times 16.36\times 10^{-19}\ J$$

$$= 147.24\times 10^{-19}\ J$$

16. Calculate the wavelength and energy of radiation emitted for the electronic transition from infinity (∞) to stationary state of H-atom.

Sol. $$\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad = 1.09678\times 10^7 m^{-1}\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right]$$

$$= 1.09678\times 10^7\ m^{-1}$$

$$\lambda = 9.11\times 10^{-6}\ m$$

$$E = \frac{hc}{\lambda} = \frac{6.625\times 10^{-34} Js\times 3.0\times 10^8 ms^{-1}}{9.11\times 10^{-6} m}$$

$$= 2.18\times 10^{-20}\ J$$

17. Calculate the energy required to remove an electron completely from n = 2 orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition.

Sol. Electron energy in H - atom

$$E = \frac{2.17\times 10^{-11}}{n^2}\ ergs$$

$$E_2 = \frac{2.17\times 10^{-11}}{4}\ ergs = 0.5425\times 10^{-11}\ ergs$$

$$\Delta E = E_\infty - E_2 = 5.425\times 10^{-12}\ ergs$$

$$E = \frac{hc}{\lambda} = 5.425\times 10^{-12} = \frac{6.626\times 10^{-27}\times 3\times 10^{10}}{\lambda}$$

$$\lambda = \frac{6.626\times 10^{-27}\times 3\times 10^{10}}{5.425\times 10^{-12}}\ cm = 3.66\times 10^{-5}\ cm$$

18. Iodine molecule dissociates into atoms after absorbing light of 4500 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms (Bond energy of $I_2 = 240\ KJ\ mol^{-1}$)

Sol. Energy given to I_2 molecule $= \frac{hc}{\lambda}$

$$= \frac{6.626\times 10^{-34}\times 3\times 10^8}{4500\times 10^{-10}} = 4.417\times 10^{-19}\ J$$

Energy used for breaking up of I_2 molecules

$$= \frac{240\times 10^3}{6.023\times 10^{23}} = 3.984\times 10^{-19}\ J$$

$\therefore$ Energy used in imparting K.E. to two I atoms

$$= (4.417\times 10^{-19} - 3.984\times 10^{-19})\ J = 0.433\times 10^{-19}\ J$$

K.E. per atom $= 0.216\times 10^{-19}\ J$

19. The energy required to remove an electron from the surface of Na metal is 2.3 eV. What is the largest wavelength of radiation which can show the photoelectric effect

Sol. $$E = h\upsilon = \frac{hc}{\lambda}$$

$$2.3\times 1.6\times 10^{-19}\ J = \frac{6.62\times 10^{-34}\times 3\times 10^8}{\lambda}$$

$$\lambda = \frac{6.62\times 10^{-34}\times 3\times 10^8}{2.3\times 1.6\times 10^{-19}} = 5.38\times 10^{-7}\ m$$

20. A certain photochemical reaction is found to acquire 8.1×10^{-19} J energy per water molecule. Calculate the number of photons per water molecule of light with wavelength of 2.21×10^{-6} m that is required to initiate the reaction.

Sol. $$N = \frac{E\lambda}{hc} = \frac{8.1\times 10^{-19}\times 2.21\times 10^{-6}}{6.62\times 10^{-34}\times 3\times 10^8} = 9\ \text{photons}$$

21. An electron has a velocity of 300 ms^{-1}, that is accurate to 0.01%. With what accuracy we can locate the position of this electron.

Sol. Accurate velocity $= \dfrac{0.01 \times 300}{100} = 0.03 \text{ ms}^{-1}$

$$\Delta x = \frac{6.62 \times 10^{-34}}{4 \times 3.14 \times 0.03 \times 9.1 \times 10^{-31}} = 0.0019 \text{ m}$$

22. A photon of wavelength 4000 Å strikes a metal surface, the work function of the metal being 2.13 eV. Calculate

(i) the energy of photon in eV

(ii) the kinetic energy of the emitted photoelectron and

(iii) the velocity of the photoelectron

Sol. (i) Energy of the photon

$$E = h\upsilon = \frac{hc}{\lambda}$$

$$E = \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^{8} \text{ ms}^{-1}}{4000 \times 10^{-10} \text{ m}} = 4.97 \times 10^{-19} \text{ J}$$

$$\text{eV} = 1.602 \times 10^{-19} \text{ J}$$

$$E = \frac{4.97 \times 10^{-19} \text{ J}}{1.602 \times 10^{-19} \text{ J}} = 3.10 \text{ eV}$$

(ii) Kinetic energy of emitted photo electron

Work function $\phi = 2.13$ eV

Kinetic energy $= h\upsilon - \phi = 3.10 \text{ eV} - 2.13 \text{ V} = 0.97 \text{ eV}$

Velocity of photoelectron

$$\text{K.E.} = \frac{1}{2}mv^2 = 0.97 \text{ eV} = 0.97 \times 1.602 \times 10^{-19} \text{ J}$$

$$= 1.55 \times 10^{-19} \text{ J}$$

(iii) $v = \left[\dfrac{2 \times 0.97 \times 1.602 \times 10^{-19}}{9.109 \times 10^{-31}}\right]^{1/2} = 5.85 \times 10^{5} \text{ ms}^{-1}$

23. Find out the electronic state from which an electron drops to emit radiation with a wavelength of 926Å and lying in ultraviolet region (Lyman series) in the spectrum of hydrogen atom.

$R_H = 1.097 \times 10^{7} \text{ m}^{-1}$

Sol. $\lambda = 926 \text{ Å} = 926 \times 10^{-8} \text{ cm} = 926 \times 10^{-10} \text{ m}$

$$\bar{\upsilon} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Since the radiation is in the U.V region and belongs to Lyman series therefore $n_1 = 1$

$$\therefore \quad \bar{\upsilon} = \frac{1}{9.26 \times 10^{-10} \text{ m}} = 1.097 \times 10^{-7} \text{ m}^{-1} \left(\frac{1}{1^2} - \frac{1}{n_2^2}\right)$$

$$1 = \frac{1}{n_2^2} = \frac{1}{9.26 \times 10^{-10} \times 1.097 \times 10^{7}}$$

On solving, $n_2 = 8$

24. The normal human eye responds to visible light of wavelength raging from about 390 to 710 nm. Determine the frequency range of the human eye

Sol. Wavelength λ and frequency υ are related to the velocity by $\upsilon = \dfrac{c}{\lambda}$

$$\bar{\upsilon} = \frac{3.00 \times 10^{8} \text{ ms}^{-1}}{390 \times 10^{-9} \text{ m}} = 7.7 \times 10^{14} \text{ s}^{-1}$$

and $\upsilon = \dfrac{3.00 \times 10^{8} \text{ ms}^{-1}}{710 \times 10^{-9} \text{ m}} = 4.2 \times 10^{14} \text{ s}^{-1}$

The frequency range of the human eye is 4.2×10^{14} to 7.7×10^{14} Hz.

Exercise-1 | NCERT BASED QUESTIONS

Very Short/Short Answer Questions

1. From the following nuclei, select the isotopes and isobars:

$^{238}_{92}U$, $^{234}_{90}Th$, $^{234}_{92}U$, $^{234}_{91}Pa$

2. Which energy level do not have *p*-orbital?

3. Which orbital is non-directional in nature?

4. Name the experiments evidence to support the wave nature of light.

5. What is the probability of finding a 4*d* electron right at the nucleus?

6. When moving with the same velocity which one of the following particles has the largest de Broglie wavelength and why? (a) Electron (b) Proton (c) α-particle

7. What would you predict for the atomic number of the noble gas beyond Rn, if such an element had sufficient stability to be prepared or observed? Assume that 'g' orbitals are still not occupied in the ground states of the preceding elements.

8. Calculate the kinetic energy of the ejected electron when ultra–violet radiation of frequency 1.6×10^{15} s^{-1} strikes the surface of potassium metal. Threshold frequency of potassium is 5×10^{14} s^{-1}. ($h = 6.63 \times 10^{-34}$ Js)

9. Calculate the wavelength of an electron that has been accelerated in a particle accelerator through a potential difference of 100 million volts.

(1 eV = 1.6×10^{-19} J, $m_e = 9.1 \times 10^{-31}$ kg,
$h = 6.6 \times 10^{-34}$ Js, $c = 3.0 \times 10^{8}$ ms^{-1})

10. Energy in a Bohr orbit is given to be equal to $-\frac{B}{n^2}$, where $B = 2.179 \times 10^{-18}$ J. Calculate the wavelength of the emitted radiation when electron jumps from the third orbit to the second.

11. (i) An atomic orbital has n = 3. What are the possible values of l and m ?

(ii) List the quantum numbers (m and l) of electron for 3*d* orbital.

(iii) Which of the following orbitals are not possible ?
1*s*, 2*p*, 1*p*, 3*f*

12. Why does the charge to mass ratio of positive rays depends on the gas taken in the discharge tube whereas charge to mass ratio of cathode rays is same for all gases?

13. When light of frequency v is thrown on a metal surface with threshold frequency v_0, photo – electrons are emitted with maximum kinetic energy = 1.3×10^{-18}J.If the ratio, $v : v_0$ = 3 : 1, calculate the threshold frequency v_0.

Long Answer Questions

14. (i) Calculate the wavelength of photon which will be emitted when the electron of hydrogen atom jumps from the fourth shell to the first shell. The ionization energy of hydrogen atom is 1.312×10^{3} kJ mol^{-1}.

(ii) Which orbital in each of the following pairs is lower in energy in a multi–electron system?

(a) 2s,2p (b) 3p, 3d (c) 3s, 4s (d) 4d, 5f

15. (i) Calculate the shortest and the longest wavelengths of the Lyman series. Given, Rydberg constant = 10967700 m^{-1}.

(ii) Calculate the frequency, energy and wavelength of the radiation corresponding to the spectral line of lowest frequency in Lyman series in the spectrum of hydrogen atom.

16. What were the weaknesses or limitations of Bohr's model of atoms ? Briefly describe the quantum mechanical model of atom ?

17. (i) What is an emission spectrum ?

(ii) Explain the hydrogen spectrum.

18. (i) Write outer electronic configuration of Cr atom. Why are half filled orbitals more stable ?

(ii) State Heisenberg's uncertainty principle. An electron has a velocity of 50 ms^{-1} accurate upto 99.99%. Calculate the uncertainty in locating its position.

(Mass of electron = 9.1×10^{-31} kg,
$h = 6.6 \times 10^{-34}$ Js)

Multiple Choice Questions

19. Which of the following statements about the electron is incorrect?

(a) It is negatively charged particle

(b) The mass of electron is equal to the mass of neutron.

(c) It is a basic constituent of all atoms.

(d) It is a constituent of cathode rays.

20. Which of the following properties of atom could be explained correctly by Thomson Model of atom?

(a) Overall neutrality of atom.

(b) Spectra of hydrogen atom.

(c) Position of electrons, protons and neutrons in atom.

(d) Stability of atom.

21. Which of the following pairs have identical values of e/m?
(a) A proton and a neutron
(b) A proton and deuterium
(c) Deuterium and an α-particle
(d) An electron and γ-rays

22. Chlorine exists in two isotopic forms, Cℓ-37 and Cℓ-35 but its atomic mass is 35.5. This indicates the ratio of Cℓ-37 and Cℓ-35 is approximately
(a) 1 : 2
(b) 1 : 1
(c) 1 : 3
(d) 3 : 1

23. If E_1, E_2, and E_3 represent respectively the kinetic energies of an electron and an alpha particle and a proton each having same de-broglie wavelength then
(a) $E_1 > E_3 > E_2$
(b) $E_2 > E_3 > E_1$
(c) $E_1 > E_2 > E_3$
(d) $E_1 = E_2 = E_3$

24. If travelling at same speeds, which of the following matter waves have the shortest wavelength?
(a) Electron
(b) Alpha particle (He^{2+})
(c) Neutron
(d) Proton

25. The third line of the Balmer series, in the emission spectrum of the hydrogen atom, is due to the transition from the
(a) fourth Bohr orbit to the first Bohr orbit
(b) fifth Bohr orbit to the second Bohr orbit
(c) sixth Bohr orbit to the third Bohr orbit
(d) seventh Bohr orbit to the third Bohr orbit

26. In a Bohr model of an atom, when an electron jumps from $n = 3$ to $n = 1$, how much energy will be emitted?
(a) 2.15×10^{-11} ergs
(b) 2.389×10^{-12} ergs
(c) 0.239×10^{-10} ergs
(d) 0.1936×10^{-10} ergs

27. The uncertainty in the momentum of an electron is 1.0×10^{-5} kg ms^{-1}. The uncertainty in its position will be ($h = 6.62 \times 10^{-34}$ kg m^{2}s^{-1})
(a) 1.05×10^{-26} m
(b) 1.05×10^{-28} m
(c) 5.27×10^{-30} m
(d) 5.25×10^{-28} m

28. Which one of the following set of quantum numbers is not possible for 4p electron?
(a) $n = 4, l = 1, m = -1, m_s = +\frac{1}{2}$
(b) $n = 4, l = 1, m = 0, m_s = +\frac{1}{2}$
(c) $n = 4, l = 1, m = 2, m_s = +\frac{1}{2}$
(d) $n = 4, l = 1, m = -1, m_s = -\frac{1}{2}$

Exercise-2 | CONCEPTUAL MCQs

1. A neutral atom (Atomic No > 1) has
(a) electron and proton
(b) neutron and electron
(c) neutron, electron and proton
(d) neutron and proton.

2. Which of the following set of quantum numbers belong to highest energy?
(a) $n = 4, l = 0, m = 0, s = +\frac{1}{2}$
(b) $n = 3, l = 0, m = 0, s = +\frac{1}{2}$
(c) $n = 3, l = 1, m = 1, s = +\frac{1}{2}$
(d) $n = 3, l = 2, m = 1, s = +\frac{1}{2}$

3. The number of electrons in $\left[{}^{40}_{19}\mathrm{K}\right]^{1-}$ is
(a) 20
(b) 40
(c) 18
(d) 19

4. Which of the following statements is incorrect?
(a) Cathode rays carry negative charge
(b) Frequency of X-rays is higher than that of microwaves
(c) Unit for wave number is m^{-1}
(d) Threshold frequency is the same for all metals.

5. Which is not true with respect to cathode rays?
(a) A stream of electrons
(b) Charged particles
(c) Move with speed same as that of light
(d) Can be deflected by magnetic fields

6. Rutherford's α-particle dispersion experiment concludes
(a) all positive ions are deposited at small part
(b) all negative ions are deposited at small part
(c) proton moves around the electron
(d) neutrons are charged particles.

7. Ratio of mass of proton and electron is
(a) infinite
(b) 1.8×10^3
(c) 1.8
(d) None of these.

8. Which of the following is the main cause of late discovery of neutron?
(a) Neutron is chargeless particle
(b) Neutron is highly unstable particle
(c) Neutron in the nucleus moves very fast
(d) All of these.

9. Which of the following does not contain number of neutrons equal to that of $^{40}_{18}Ar$?

(a) $^{41}_{19}K$ (b) $^{43}_{21}Sc$

(c) $^{40}_{21}Sc$ (d) $^{42}_{20}Ca$

10. Rutherford's experiment which established the nuclear model of the atom used a beam of

(a) β-particles which impinged on a metal foil and got absorbed

(b) γ-rays which impinged on a metal foil and ejected electrons

(c) helium atoms, which impinged on a metal foil and got scattered

(d) helium nuclei, which impinged on a metal foil and got scattered

11. Number of protons, neutrons and electrons in the element $_{89}X^{231}$ is

(a) 89, 89, 242 (b) 89, 142, 89

(c) 89, 71, 89 (d) 89, 231, 89

12. An element has atomic number 11 and mass number 24. What does the nucleus contain?

(a) 11 protons, 13 neutrons

(b) 11 protons, 13 neutrons, 13 electrons

(c) 13 protons, 11 neutrons

(d) 13 protons, 11 electrons

13. The number of electrons and neutrons of an element is 18 and 20 respectively. Its mass number is

(a) 2 (b) 17

(c) 37 (d) 38

14. The hydride ion is isoelectronic with

(a) H^+ (b) He^+

(c) He (d) Be.

15. Which of the following isoelectronic species has the smallest atomic radius?

(a) N^{3-} (b) O^{2-}

(c) F^- (d) Ne.

16. Among the following groupings which represents the collection of isoelectronic species?

(a) $NO^+, C_2^{2-}, O_2^-, CO$ (b) N_2, C_2^{2-}, CO, NO

(c) CO, NO^+, CN^-, C_2^{2-} (d) NO, CN^-, N_2, O_2^-

17. Which of the following is not iso electronic

(a) $\overset{+}{Na}$ (b) Mg^{2+}

(c) $\overset{2-}{O}$ (d) Cl^-

18. Chloride ion and potassium ion are isoelectronic. Then

(a) their sizes are same

(b) chloride ion is bigger than potassium ion

(c) potassium ion is relatively bigger

(d) depends upon the other cation or anion

19. Ratio of energy of photon of wavelength 3000 Å and 6000Å is

(a) 3 : 1 (b) 2 : 1

(c) 1 : 2 (d) 1 : 3

20. The energy of a photon is given as ΔE/atom 3.03×10^{-19} J $atom^{-1}$. Then the wavelength (λ) of the photon is

(a) 65.6 nm (b) 656 nm

(c) 0.656 nm (d) 6.56 nm

21. If wavelength of photon is 2.2×10^{-11} m, h = 6.6×10^{-34} Js, then momentum of photon is

(a) 3×10^{-23} kg/s (b) 3.33×10^{22} kg/s

(c) 1.452×10^{-44} kg/s (d) 6.89×10^{43} kg/s

22. Which orbital of carbon can absorb photon but not emit it?

(a) 1 s (b) 2 s

(c) 3 p (d) 2 p.

23. Brackett series are produced when the electrons from the outer orbits jump to

(a) 2nd orbit (b) 3rd orbit

(c) 4th orbit (d) 5th orbit.

24. The first emission line in the atomic spectrum of hydrogen in the Balmer series appears at

(a) $\frac{9R}{400}cm^{-1}$ (b) $\frac{7R}{144}cm^{-1}$

(c) $\frac{3R}{4}cm^{-1}$ (d) $\frac{5R}{36}cm^{-1}$

25. In hydrogen spectrum which of the following lies in the wavelength range 350–700 nm?

(a) Balmer series (b) Lyman series

(c) Brackett series (d) paschen series.

26. In Balmer series of hydrogen atom spectrum which electronic transition causes third line?

(a) Fifth Bohr orbit to second one

(b) Fifth Bohr orbit to first one.

(c) Fourth Bohr orbit to second one

(d) Fourth Bohr orbit to first one.

27. The spectrum of He is expected to be similar to that of

(a) H (b) Na

(c) He^+ (d) Li^+

28. In hydrogen atom, energy of first excited state is –3.4eV. Then find out the KE of the same orbit of hydrogen atom

(a) + 3.4 eV (b) + 6.8 eV

(c) – 13.6 eV (d) + 13.6 eV

29. In the Bohr's orbit, what is the ratio of total kinetic energy and total energy of the electron?

(a) –1 (b) –2

(c) 1 (d) +2

30. The kinetic energy of an electron accelerated from rest through a potential difference of 5 V will be

(a) 5 J (b) 5 erg

(c) 5 eV (d) 8×10^{-19}eV

31. The angular momentum of an electron revolving around the nucleus is integral multiple of

(a) 2n (b) h

(c) h / 2π (d) 2πn

32. The orbital angular momentum of an electron in 2 s orbital is

(a) $+\frac{1}{2}\cdot\frac{h}{2\pi}$
(b) zero
(c) $\frac{h}{2\pi}$
(d) $\sqrt{2}\cdot\frac{h}{2\pi}$

33. The energy of an electron in the first Bohr orbit of H atom is – 13.6 eV. The possible energy value(s) of the excited state (s) for electrons in Bohr orbits of hydrogen is (are)

(a) -3.4eV
(b) -4.2eV
(c) -6.8 eV
(d) $+6.8$eV.

34. If the radius of first Bohr orbit be a_0, then the radius of the third orbit would be

(a) $3 \times a_0$
(b) $6 \times a_0$
(c) $9 \times a_0$
(d) $1/9 \times a_0$

35. According to Bohr's theory of hydrogen atom, which of the following is quantised for an electron?

(a) Angular momentum
(b) Angular acceleration
(c) Acceleration
(d) Velocity.

36. According to Bohr's theory the energy required for the transition of H-atom from n = 6 to n = 8 state is

(a) equal to the energy required for the transition from n = 5 to n = 6 state
(b) larger than in (a)
(c) less than in (a)
(d) equal to the energy required for the transition from n = 7 to n = 9 state.

37. The wave number of the light emitted by a certain source is 2×10^6 m . The wavelength of this light is

(a) 500 m
(b) 200 nm
(c) 500 nm
(d) 5×10^7 m

38. For which of the following species, Bohr's theory is not applicable?

(a) Be^{3+}
(b) Li^{2+}
(c) He^{2+}
(d) H.

39. As the nuclear charge increases from Neon to Calcium, the orbital energies

(a) increase
(b) increase very rapidly
(c) increase very slowly
(d) fall

40. The ratio of ionization energy of H and Be^{+3} is

(a) 1 : 1
(b) 1 : 3
(c) 1 : 9
(d) 1 : 16

41. In a Bohr model of on atom, when an electron jumps from n = 3 to n = 1, how much energy will be emitted?

(a) 2.15×10^{-11} ergs
(b) 2.389×10^{-12} ergs
(c) 0.239×10^{-10} ergs
(d) 0.1936×10^{-10} ergs

42. In H-atom electron jumps from 3rd to 2nd energy level, the energy released is

(a) 3.03×10^{-19} J/atom
(b) 1.03×10^{-19} J/atom
(c) 3.03×10^{-12} J/atom
(d) 6.06×10^{-19} J/atom

43. The value of the energy for the first excited state of hydrogen atom will be

(a) –13.6 eV
(b) –3.40 eV
(c) –1.51 eV
(d) –0.85eV

44. The radius of hydrogen atom in the ground state is 0.53Å. The radius of Li^{2+} ion (atomic number = 3) in a similar state is

(a) 0.17 Å
(b) 1.06 Å
(c) 0.53 Å
(d) 0.265 Å

45. The Bohr orbit radius for the H-atom (Z=1) is approximately 0.53 Å. The radius for the first excited state orbit is

(a) 0.13 Å
(b) 1.06Å
(c) 4.77 Å
(d) 2.12 Å

46. The ratio of the radius of the first Bohr orbit for the electron orbiting the hydrogen nucleus to that of the electron orbiting the deuterium nucleus (mass nearly twice that of the hydrogen nucleus) is approximately

(a) 2 : 1
(b) 1 : 1
(c) 1 : 2
(d) 4 : 1

47. The energy of the first electron in helium will be

(a) –13.6 eV
(b) –54.4 eV
(c) –5.44 eV
(d) zero

48. Who modified Bohr's theory by introducing eiliptical orbits for electron path?

(a) Hund
(b) Thomson
(c) Rutherford
(d) Sommerfeld.

49. Wavelength associated with electron motion

(a) increases with increase in speed of electron
(b) remains same irrespective of speed of electron
(c) decreases with increase of speed of e^- (electron)
(d) is zero.

50. If the Planck's constant h = 6.6×10^{-34} Js, the de Broglie wavelength of a particle having momentum of 3.3×10^{-24} kg ms $^{-1}$ will be

(a) 0.002 Å
(b) 0.5Å
(c) 2Å
(d) 500Å

51. What is the wavelength associated with an electron moving with a velocity of 10^6 m/s?
(given h = 6.63×10^{-34} Js and m = 9.11×10^{-31} kg)

(a) 72.7 nm
(b) 0.727 nm
(c) 7.27 nm
(c) None of these.

52. The wavelength associated with a golf balf weighing 200 g and moving at a speed of 5 m/h is of the order

(a) 10^{-10}m
(b) 10^{-20}m
(c) 10^{-30}m
(d) 10^{-40}m

53. The uncertainty in the position of an electron (mass = 9.1×10^{-28} g) moving with a velocity of 3.0×10^4 cm s^{-1} accurate upto 0.011% will be

(a) 1.92 cm
(b) 7.68 cm
(c) 0.175 cm
(d) 3.84 cm.

54. The uncertainty in the momentum of an electron is 1.0×10^{-5} kg ms $^{-1}$. The uncertainty in its position will be (h = 6.62×10^{-34} kg m^2 s^{-1})

(a) 1.05×10^{-26} m
(b) 1.05×10^{-28} m
(c) 5.27×10^{-30} m
(d) 5.25×10^{-28} m

55. Azimuthal quantum number determines the

(a) size
(b) spin
(c) orientation
(d) angular momentum of orbitals

56. When the value of azimuthal quantum number, l = 2, value of 'n' will be

(a) 3
(b) 4
(c) 5
(d) any one of these.

57. The values of quantum numbers n, l and m for the 5th electron of Boron will be

(a) $n = 1, l = 0, m = -1$
(b) $n = 2, l = 1, m = -1$
(c) $n = 2, l = 2, m = -1$
(d) $n = 1, l = 2, m = -1$

58. The total number of orbitals in a shell with principal quantum number 'n' is

(a) $2n$
(b) $2n^2$
(c) n^2
(d) n.

59. Which of the following combinations of quantum numbers is allowed?

	n	l	m	m_s
(a)	3	2	1	0
(b)	2	0	0	$-\frac{1}{2}$
(c)	3	–3	–2	$+\frac{1}{2}$
(d)	1	0	1	$+\frac{1}{2}$

60. Which one of the following set of quantum numbers is not possible for 4p electron?

(a) $n = 4, l = 1, m = -1, m_S = +\frac{1}{2}$
(b) $n = 4, l = 1, m = 0, m_S = +\frac{1}{2}$
(c) $n = 4, l = 1, m = 2, m_S = +\frac{1}{2}$
(d) $n = 4, l = 1, m = -1, m_S = -\frac{1}{2}$

61. The maximum number of electrons in subshell with l = 2 and n = 3 is

(a) 2
(b) 6
(c) 12
(d) 10

62. An electron has principal quantum number 3. The number of its (i) sub-shells and (ii) orbitals would be respectively

(a) 3 and 5
(b) 3 and 7
(c) 3 and 9
(d) 2 and 5

63. An e^- has magnetic quantum number as –3, what is its principal quantum number?

(a) 1
(b) 2
(c) 3
(d) 4

64. The four quantum numbers of the valence electron of potassium are

(a) 4, 1, 1, 1/2
(b) 4, 0, 0, 1/2
(c) 4, 5, 0, 1/2
(d) 4, 4, 0, 1/2

65. The electrons, identified by quantum numbers n and l (i) n = 4, l = 1 (ii) n = 4, l = 0 (iii) n = 3, l = 2 (iv) n = 3, l = 1 can be placed in order of increasing energy, from the lowest to highest, as

(a) (iv) < (ii) < (iii) < (i)
(b) (ii) < (iv) < (i) < (iii)
(c) (i) < (iii) < (ii) < (iv)
(d) (iii) < (i) < (iv) < (ii)

66. Bohr's model of atom is in conflict with

(a) Pauli's exclusion principle
(b) Heiseinberg's uncertainity principle
(c) Max Planck's quantum theory
(d) All the above three

67. What is the maximum number of electrons that can be accomodated in an atom in which the highest principal quantum number value is 4?

(a) 10
(b) 18
(c) 36
(d) 54.

68. The total number of orbitals possible for principal quantum number n is

(a) n
(b) n^2
(c) 2n
(d) $2n^2$

69. Which of the following is not possible ?

(a) $n = 3, l = 0, m = 0$
(b) $n = 3, l = 1, m = -1$
(c) $n = 2, l = 0, m = -1$
(d) $n = 2, l = 1, m = 0$.

70. For how many orbitals, the quantum numbers $n = 3, l = 2, m = +2$ are possible?

(a) 1
(b) 2
(c) 3
(d) 4

71. The correct set of quantum numbers for a 4d electron is

(a) $4, 3, 2, +\frac{1}{2}$
(b) 4, 2, 1, 0
(c) $4, 3, -2, +\frac{1}{2}$
(d) $4, 2, 1, -\frac{1}{2}$

72. For a, f-orbital, the values of m are

(a) –2, –1, 0, +1, +2
(b) –3, –2, –1, 0, +1, +2, 3
(c) –1, 0, +1
(d) 0, +1, +2, +3

73. The values of Planck's constant is 6.63×10^{-34} Js. The velocity of light is 3.0×10^8 m s^{-1}. Which value is closest to the wavelength in nanometres of a quantum of light with frequency of 8×10^{15} s^{-1}?

(a) 5×10^{-18}
(b) 4×10^1
(c) 3×10^7
(d) 2×10^{-25}

74. The number of nodal planes 'd' orbital has

(a) 1
(b) 2
(c) 3
(d) 0

75. What do you mean by degenerate orbitals?

(a) Orbitals having equal energy
(b) Oribitals having equal wave function
(c) Oribitals having equal energy but different wave function
(d) Orbitals having equal energy and equal wave function.

76. The number of nodal planes in a p_x orbital is
(a) one (b) two
(c) three (d) zero.

77. A 5f orbital has
(a) one node (b) two nodes
(c) three nodes (d) four nodes.

78. " No two electrons in an atom can have same set of all the four quantum numbers" is known as
(a) Hund's rule
(b) Aufbau principle
(c) Uncertainty principle
(d) Pauli's exclusion principle.

79. Which of the following has maximum number of unpaired electrons ?
(a) Mg^{2+} (b) Ti^{3+} (c) V^{3+} (d) Fe^{2+}

80. An element M has an atomic mass 19 and atomic number 9, its ion is represented by
(a) M^+ (b) M^{2+} (c) M^- (d) M^{2-}

81. The configuration $1s^2\ 2s^2\ 2p^5\ 3s^1$ shows
(a) ground state of fluorine
(b) excited state of fluorine
(c) excited state of neon atom
(d) excited state of O_2^- ion.

82. Heisenberg's Uncertainity principle is applicable to
(a) atoms only (b) electron only
(c) nucleus only (d) any moving object

83. Electronic configuration of four elements are given below. Which of the corresponding element would be most paramagetic?
(a) $1s^2\ 2s^2\ 2p^6$ (b) $1s^2\ 2s^2\ 2p^1$
(c) $1s^2\ 2s^2\ 2p^5$ (d) $1s^2\ 2s^2\ 2p^4$

84. Which of the following is the electronic configuration of Cu^{2+} (Z = 29)?
(a) $[Ar]\,4s^1\,3d^8$ (b) $[Ar]\,4s^2\,3d^{10}\,4p^1$
(c) $[Ar]\,4s^1\,3d^{10}$ (d) $[Ar]\,3d^9$

85. Which of the following explains the sequence of filling electrons in different shells ?
(a) Hund's rule (b) Octet rule
(c) Aufbau principle (d) All of these.

86. Which of the following has more unpaired d-electrons?
(a) Zn^+ (b) Fe^{2+} (c) Ni^{3+} (d) Cu^+

87. Which of the following configurations is correct for iron?
(a) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5$
(b) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^5$
(c) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^7$
(d) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^6$

88. The maximum number of electrons that can be accomodated in d-sub-shell is
(a) 10 (b) 8 (c) 6 (d) 4

89. The number of unpaired electrons in an atom of atomic number 24 (in ground state) is
(a) 3 (b) 4 (c) 5 (d) 6

90. The number of unpaired electrons in a Nickel atom (ground state) are (Atomic No. of Ni = 28)
(a) 2 (b) 5 (c) 3 (d) 7

91. The element with its electronic configuration of its atom $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$ is
(a) Fe (b) Co (c) Ni (d) Cu.

92. In Cu. (At. No. 29)
(a) 13 electrons have spin in one direction and 16 electrons in other direction
(b) 14 electrons have spin one direction and 15 electrons in other direction
(c) one electron can have spin only in the clockwise direction
(d) None of the above is correct.

93. Which of the following atom has no neutron in its nucleus?
(a) Helium (b) Lithium
(c) Protium (d) Tritium

94. In the ground state, an element has 13 electrons in its M-shell. The element is
(a) zinc (b) chromium
(c) nickel (d) iron

95. Which one of the following pairs of ions has the same electronic configuration?
(a) Cr^{3+}, Fe^{3+} (b) Fe^{3+}, Mn^{2+}
(c) Fe^{3+}, Co^{3+} (d) Sc^{3+}, Cr^{3+}

96. The correct order of increasing energy of atomic orbitals is
(a) $5p < 4f < 6s < 5d$ (b) $5p < 6s < 4f < 5d$
(c) $5p < 5d < 4f < 6s$ (d) none of these

97. The number of d-electrons retained in Fe^{2+} (At. no. of Fe = 26) ion is
(a) 3 (b) 4
(c) 5 (d) 6

98. The correct electronic configuration of Cu (29) is
(a) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$
(b) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6$
(c) $1s^2\,2s^2\,2p^6\,3s^1\,3p^3\,3d^{10}$
(d) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^4\,4s^2$

99. The paramagnetic character follows the order
(a) Mn > Cr > Zn (b) Fe > Zn > Co
(c) Cr > Fe > Zn (d) Hg > Mn > Fe.

100. If the nitrogen atom had electronic configuration $1s^7$ it would have energy lower than that of the normal ground state configuration $1s^2\ 2s^2\ 2p^3$ because the electrons would be closer to the nucleus. Yet $1s^7$ is not observed. It violates
(a) Heisenberg's uncertainty principle
(b) Hund's rule
(c) Pauli exclusion principle
(d) Bohr postulate of stationary orbits

101. Which of the following elements outermost orbit's last electron has magnetic quantum number m = 0?
(a) Na (b) O
(c) Cl (d) N

Exercise-3 | PAST COMPETITION MCQs

1. If uncertainty in position and momentum are equal, then uncertainty in velocity is : **[CBSE-PMT 2008]**

(a) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$ (b) $\sqrt{\frac{h}{2\pi}}$ (c) $\frac{1}{m}\sqrt{\frac{h}{\pi}}$ (d) $\sqrt{\frac{h}{\pi}}$

2. The measurement of the electron position is associated with an uncertainty in momentum, which is equal to 1×10^{-18} g cm s^{-1}. The uncertainty in electron velocity is, **[CBSE-PMT 2008]** (mass of an electron is 9×10^{-28} g)

(a) 1×10^{9} cm s^{-1} (b) 1×10^{6} cm s^{-1}

(c) 1×10^{5} cm s^{-1} (d) 1×10^{11} cm s^{-1}

3. The energy absorbed by each molecule (A_2) of a substance is 4.4×10^{-19} J and bond energy per molecule is 4.0×10^{-19} J. The kinetic energy of the molecule per atom will be: **[CBSE-PMT 2009]**

(a) 2.2×10^{-19} J (b) 2.0×10^{-19} J

(c) 4.0×10^{-20} J (d) 2.0×10^{-20} J

4. Maximum number of electrons in a subshell of an atom is determined by the following: **[CBSE-PMT 2009]**

(a) $2l+1$ (b) $4l-2$ (c) $2n^2$ (d) $4l+2$

5. Which of the following is **not** permissible arrangement of electrons in an atom? **[CBSE-PMT 2009]**

(a) $n = 5, l = 3, m = 0, s = +1/2$

(b) $n = 3, l = 2, m = -3, s = -1/2$

(c) $n = 3, l = 2, m = -2, s = -1/2$

(d) $n = 4, l = 0, m = 0, s = -1/2$

6. A 0.66 kg ball is moving with a speed of 100 m/s. The associated wavelength will be ($h = 6.6 \times 10^{-34}$ Js) : **[CBSE-PMT 2010]**

(a) 1.0×10^{-32}m (b) 6.6×10^{-32}m

(c) 6.6×10^{-34}m (d) 1.0×10^{-35}m

7. The total number of atomic orbitals in fourth energy level of an atom is : **[CBSE-PMT 2011]**

(a) 8 (b) 16 (c) 32 (d) 4

8. The energies E_1 and E_2 of two radiations are 25 eV and 50 eV, respectively. The relation between their wavelengths i.e., λ_1 and λ_2 will be : **[CBSE-PMT 2011]**

(a) $\lambda_1 = \lambda_2$ (b) $\lambda_1 = 2\lambda_2$

(c) $\lambda_1 = 4\lambda_2$ (d) $\lambda_1 = \frac{1}{2}\lambda_2$

9. If $n = 6$, the correct sequence for filling of electrons will be : **[CBSE-PMT 2011]**

(a) $ns \rightarrow (n-2)f \rightarrow (n-1)d \rightarrow np$

(b) $ns \rightarrow (n-1)d \rightarrow (n-2)f \rightarrow np$

(c) $ns \rightarrow (n-2)f \rightarrow np \rightarrow (n-1)d$

(d) $ns \rightarrow np \rightarrow (n-1)d \rightarrow (n-2)f$

10. According to the Bohr Theory, which of the following transitions in the hydrogen atom will give rise to the least energetic photon ? **[CBSE-PMT 2011 M]**

(a) $n = 6$ to $n = 1$ (b) $n = 5$ to $n = 4$

(c) $n = 6$ to $n = 5$ (d) $n = 5$ to $n = 3$

11. The value of Planck's constant is 6.63×10^{-34} Js. The speed of light is 3×10^{17} nm s^{-1}. Which value is closest to the wavelength in nanometer of a quantum of light with frequency of 6×10^{15} s^{-1}? **[NEET 2013]**

(a) 25 (b) 50 (c) 75 (d) 10

12. What is the maximum numbers of electrons that can be associated with the following set of quantum numbers? n = 3, l = 1 and m = –1 **[NEET 2013]**

(a) 6 (b) 4 (c) 2 (d) 10

13. Based on equation $E = -2.178 \times 10^{-18}\ \text{J}\left(\frac{Z^2}{n^2}\right)$, certain conclusions are written. Which of them is not correct ? **[NEET 2013]**

(a) Larger the value of n, the larger is the orbit radius.

(b) Equation can be used to calculate the change in energy when the electron changes orbit.

(c) For n = 1, the electron has a more negative energy than it does for n = 6 which mean that the electron is more loosely bound in the smallest allowed orbit.

(d) The negative sign in equation simply means that the energy or electron bound to the nucleus is lower than it would be if the electrons were at the infinite distance from the nucleus.

14. In a hydrogen atom, if energy of an electron in ground state is 13.6. eV, then that in the 2nd excited state is **[AIEEE 2002]**

(a) 1.51 eV (b) 3.4 eV (c) 6.04 eV (d) 13.6 eV.

15. Uncertainty in position of a minute particle of mass 25 g in space is 10^{-5} m. What is the uncertainty in its velocity (in ms^{-1})? ($h = 6.6 \times 10^{-34}$ Js) **[AIEEE 2002]**

(a) 2.1×10^{-34} (b) 0.5×10^{-34}

(c) 2.1×10^{-28} (d) 0.5×10^{-23}.

16. The number of d-electrons retained in Fe^{2+} **[AIEEE 2003]** (At. no. of Fe = 26) ion is

(a) 4 (b) 5 (c) 6 (d) 3

17. The orbital angular momentum for an electron revolving in an orbit is given by $\sqrt{l(l+1)}\cdot\frac{h}{2\pi}$. This momentum for an s-electron will be given by **[AIEEE 2003]**

(a) zero (b) $\frac{h}{2\pi}$ (c) $\sqrt{2}\cdot\frac{h}{2\pi}$ (d) $+\frac{1}{2}\cdot\frac{h}{2\pi}$

18. A reduction in atomic size with increase in atomic number is a characteristic of elements of **[AIEEE 2003]**

(a) d-block (b) f-block

(c) radioactive series (d) high atomic masses

19. Which one of the following groupings represents a collection of isoelectronic species ? **[AIEEE 2003]**
(At. nos. : Cs : 55, Br : 35)
(a) N^{3-}, F^-, Na^+
(b) Be, Al^{3+}, Cl^-
(c) Ca^{2+}, Cs^+, Br
(d) Na^+, Ca^{2+}, Mg^{2+}

20. In Bohr series of lines of hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electron for Bohr orbits in an atom of hydrogen **[AIEEE 2003]**
(a) $5 \to 2$ (b) $4 \to 1$ (c) $2 \to 5$ (d) $3 \to 2$

21. The de Broglie wavelength of a tennis ball of mass 60 g moving with a velocity of 10 metres per second is approximately Planck's constant, $h = 6.63 \times 10^{-34}$ Js **[AIEEE 2003]**
(a) 10^{-31} metres
(b) 10^{-16} metres
(c) 10^{-25} metres
(d) 10^{-33} metres

22. Which of the following sets of quantum numbers is correct for an electron in 4f orbital ? **[AIEEE 2004]**
(a) $n = 4, l = 3, m = +1, s = +½$
(b) $n = 4, l = 4, m = -4, s = -½$
(c) $n = 4, l = 3, m = +4, s = +½$
(c) $n = 3, l = 2, m = -2, s = +½$

23. Consider the ground state of Cr atom (X = 24). The number of electrons with the azimuthal quantum numbers, $\ell = 1$ and 2 are, respectively **[AIEEE 2004]**
(a) 16 and 4 (b) 12 and 5 (c) 12 and 4 (d) 16 and 5

24. The wavelength of the radiation emitted, when in a hydrogen atom electron falls from infinity to stationary state 1, would be (Rydberg constant $= 1.097 \times 10^7\ m^{-1}$) **[AIEEE 2004]**
(a) 406 nm
(b) 192 nm
(c) 91 nm
(d) 9.1×10^{-8} nm

25. Which one of the following sets of ions represents the collection of isoelectronic species? **[AIEEE 2004]**
(a) $K^+, Cl^-, Mg^{2+}, Sc^{3+}$
(b) $Na^+, Ca^{2+}, Sc^{3+}, F^-$
(c) $K^+, Ca^{2+}, Sc^{3+}, Cl^-$
(d) $Na^+, Mg^{2+}, Al^{3+}, Cl^-$
(Atomic nos. : F = 9, Cl = 17, Na = 11, Mg = 12, Al = 13, K = 19, Ca = 20, Sc = 21)

26. Of the following outer electronic configurations of atoms, the highest oxidation state is achieved by which one of them ? **[AIEEE 2004]**
(a) $(n-1)d^3\ ns^2$
(b) $(n-1)d^5\ ns^1$
(c) $(n-1)d^8\ ns^2$
(d) $(n-1)d^5\ ns^2$

27. In a multi-electron atom, which of the following orbitals described by the three quantum members will have the same energy in the absence of magnetic and electric fields ? **[AIEEE 2005]**
(A) $n = 1, l = 0, m = 0$
(B) $n = 2, l = 0, m = 0$
(C) $n = 2, l = 1, m = 1$
(D) $n = 3, l = 2, m = 1$
(E) $n = 3, l = 2, m = 0$
Options
(a) (D) and (E)
(b) (C) and (D)
(c) (B) and (C)
(d) (A) and (B)

28. Of the following sets which one does NOT contain isoelectronic species? **[AIEEE 2005]**
(a) $BO_3^{3-}, CO_3^{2-}, NO_3^-$
(b) $SO_3^{2-}, CO_3^{2-}, NO_3^-$
(c) CN^-, N_2, C_2^{2-}
(d) $PO_4^{3-}, SO_4^{2-}, ClO_4^-$

29. According to Bohr's theory, the angular momentum of an electron in 5th orbit is **[AIEEE 2006]**
(a) $10\ h/\pi$
(b) $2.5\ h/\pi$
(c) $25\ h/\pi$
(d) $1.0\ h/\pi$

30. Uncertainty in the position of an electron (mass $= 9.1 \times 10^{-31}$ kg) moving with a velocity 300 ms^{-1}, accurate upto 0.001% will be ($h = 6.63 \times 10^{-34}$ Js) **[AIEEE 2006]**
(a) 1.92×10^{-2} m
(b) 3.84×10^{-2} m
(c) 19.2×10^{-2} m
(d) 5.76×10^{-2} m

31. Which one of the following sets of ions represents a collection of isoelectronic species? **[AIEEE 2006]**
(a) $N^{3-}, O^{2-}, F^-, S^{2-}$
(b) $Li^+, Na^+, Mg^{2+}, Ca^{2+}$
(c) $K^+, Cl^-, Ca^{2+}, Sc^{3+}$
(d) $Ba^{2+}, Sr^{2+}, K^+, Ca^{2+}$

32. Which of the following sets of quantum numbers represents the highest energy of an atom? **[AIEEE 2007]**
(a) $n = 3, l = 0, m = 0, s = +1/2$
(b) $n = 3, l = 1, m = 1, s = +1/2$
(c) $n = 3, l = 2, m = 1, s = +1/2$
(d) $n = 4, l = 0, m = 0, s = +1/2$.

33. The ionization enthalpy of hydrogen atom is $1.312 \times 10^6\ J\ mol^{-1}$. The energy required to excite the electron in the atom from n = 1 to n = 2 is **[AIEEE 2008]**
(a) $9.84 \times 10^5\ J\ mol^{-1}$
(b) $6.56 \times 10^5\ J\ mol^{-1}$
(c) $7.56 \times 10^5\ J\ mol^{-1}$
(d) $8.51 \times 10^5\ J\ mol^{-1}$

34. Which one of the following constitutes a group of the isoelectronic species? **[AIEEE 2008]**
(a) C_2^{2-}, O_2^-, CO, NO
(b) $CN^-, N_2, O_2^{2-}, C_2^{2-}$
(c) $NO\ , C_2^{2-}, CN^-, N_2$
(d) $N_2, O_2^-, NO\ , CO$

35. Calculate the wavelength (in nanometer) associated with a proton moving at $1.0 \times 10^3\ ms^{-1}$. **[AIEEE 2009]**
(Mass of proton $= 1.67 \times 10^{-27}$ kg and $h = 6.63 \times 10^{-34}$ Js)
(a) 0.40 nm (b) 2.5 nm (c) 14.0 nm (d) 0.32 nm

36. In an atom, an electron is moving with a speed of 600 m/s with an accuracy of 0.005%. Certainity with which the position of the electron can be located is ($h = 6.6 \times 10^{-34}\ kg\ m^2s^{-1}$, mass of electron, $e_m = 9.1 \times 10^{-31}$ kg) **[AIEEE 2009]**
(a) 5.10×10^{-3} m
(b) 1.92×10^{-3} m
(c) 3.84×10^{-3} m
(d) 1.52×10^{-4} m

37. The energy required to break one mole of Cl – Cl bonds in Cl_2 is 242 kJ mol^{-1}. The longest wavelength of light capable of breaking a single Cl – Cl bond is **[AIEEE 2010]**
($c = 3 \times 10^8\ ms^{-1}$ and $N_A = 6.02 \times 10^{23}\ mol^{-1}$).
(a) 594 nm (b) 640 nm (c) 700 nm (d) 494 nm

38. Ionisation energy of He^+ is 19.6×10^{-18} J atom^{-1}. The energy of the first stationary state ($n = 1$) of Li^{2+} is **[AIEEE 2010]**

(a) 4.41×10^{-16} J atom^{-1} (b) -4.41×10^{-17} J atom^{-1}

(c) -2.2×10^{-15} J atom^{-1} (d) 8.82×10^{-17} J atom^{-1}

39. The frequency of light emitted for the transition $n = 4$ to $n = 2$ of the He^+ is equal to the transition in H atom corresponding to which of the following ? **[AIEEE 2011 RS]**

(a) $n = 2$ to $n = 1$ (b) $n = 3$ to $n = 2$

(c) $n = 4$ to $n = 3$ (d) $n = 3$ to $n = 1$

40. The electrons identified by quantum numbers n and ℓ :

(A) $n = 4, \ell = 1$ (B) $n = 4, \ell = 0$

(C) $n = 3, \ell = 2$ (D) $n = 3, \ell = 1$

can be placed in order of increasing energy as : **[AIEEE 2012]**

(a) (C) < (D) < (B) < (A) (b) (D) < (B) < (C) < (A)

(c) (B) < (D) < (A) < (C) (d) (A) < (C) < (B) < (D)

41. The increasing order of the ionic radii of the given isoelectronic species is : **[AIEEE 2012]**

(a) $Cl^-, Ca^{2+}, K^+, S^{2-}$ (b) $S^{2-}, Cl^-, Ca^{2+}, K^+$

(c) $Ca^{2+}, K^+, Cl^-, S^{2-}$ (d) $K^+, S^{2-}, Ca^{2+}, Cl^-$

42. Energy of an electron is given by $E = -2.178 \times 10^{-18} J\left(\frac{Z^2}{n^2}\right)$. Wavelength of light required to excite an electron in an hydrogen atom from level n = 1 to n = 2 will be :
($h = 6.62 \times 10^{-34}$ Js and $c = 3.0 \times 10^8$ ms^{-1}) **[JEE Main 2013]**

(a) 1.214×10^{-7} m (b) $2.816 \times 10.^{-7}$ m

(c) 6.500×10^{-7} m (d) 8.500×10^{-7} m

43. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is [a_0 is Bohr radius] : **[IIT-JEE 2009 S]**

(a) $\frac{h^2}{4\pi^2 m a_0^2}$ (b) $\frac{h^2}{16\pi^2 m a_0^2}$ (c) $\frac{h^2}{32\pi^2 m a_0^2}$ (d) $\frac{h^2}{64\pi^2 m a_0^2}$

44. Given that the abundances of isotopes ^{54}Fe, ^{56}Fe and ^{57} Fe are 5%, 90% and 5%, respectively, the atomic mass of Fe is **[IIT-JEE 2012]**

(a) 55.85 (b) 55.95 (c) 55.75 (d) 56.05

Exercise-4 | Applied MCQs

1. Which statement is not correct ?

(a) Volume of proton is approx. $\left(\frac{4}{3}\pi r^3\right) 1.5 \times 10^{-38}$ cm^3.

(b) Radius of e^- is 42.8×10^{-13} cm^3

(c) Density of nucleus is 10^{14} g/cm^3.

(d) All are correct

2. The potential energy of electron present in ground state of Li^{2+} ion is represented by :

(a) $\frac{+3e^2}{4\pi\varepsilon_0 r}$ (b) $\frac{-3e}{4\pi\varepsilon_0 r}$

(c) $\frac{-3e^2}{4\pi\varepsilon_0 r^2}$ (d) $\frac{-3e^2}{4\pi\varepsilon_0 r}$

3. Which principle/rule limits the maximum no. of electrons in an orbital to two ?

(a) Aufbau principle

(b) Pauli's exclusion principle

(c) Hund's rule of max. multiplicity

(d) Heisenberg's uncertainty principle

4. Photoelectric effect is the phenomenon in which

(a) photons come out of metal when hit by a beam of electrons

(b) photons come out of the nucleus of an atom under the action of an electric field

(c) electrons come out of metal with a constant velocity which depends on frequency and intesity of incident light.

(d) electrons come out of metal with different velocities not greater than a certain value which depends upon frequency of incident light and not on intensity.

5. If E_1, E_2 and E_3 represent respectively the kinetic energies of an electron and an alpha particle and a proton each having same de-broglie wavelength then

(a) $E_1 > E_3 > E_2$ (b) $E_2 > E_3 > E_1$

(c) $E_1 > E_2 > E_3$ (d) $E_1 = E_2 = E_3$

6. The angular speed of the electron in nth orbit of Bohr hydrogen atom is

(a) directly proportional to n

(b) inversely proportional of $\sqrt{n}$

(c) inversely proportional to n^2

(d) inversely proportional to n^3

7. The Bohr's energy equation for H atom reveals that the energy level of a shell is given by $E = -13.58/n^2$eV. The smallest amount that an H atom will absorb if in ground state is

(a) 1.0 eV (b) 3.39 eV

(c) 6.79 eV (d) 10.19 eV

8. If the Planck's constant $h = 6.6 \times 10^{-34}$ Js, the de-Broglie's wavelength of a particle having momentum of 3.3×10^{-24} m/s will be

(a) 0.02Å (b) 0.5Å

(c) 2Å (d) 500Å

9. Ionization potential of hydrogen atom is 13.6eV. Hydrogen atom in ground state are excited by monochromatic light of energy 12.1 eV. The spectral lines emitted by hydrogen according to Bohr's theory will be

(a) one (b) two
(c) three (d) four

10. The wavelength of radiations emitted when electrons falls from 4th Bohr's orbit to 2nd in H atom is : (R_H = $1.09678 \times 10^{-7}\ m^{-1}$).

(a) 972 nm (b) 486 nm
(c) 243 nm (d) 182 nm

11. The energy of e^- in first orbit of He^+ is -871.6×10^{-20} J. The energy of e^- in first orbit of H is:

(a) -871.6×10^{-20} (b) -435.8×10^{-20} J
(c) -217.9×10^{-20} J (d) -108.9×10^{-20}

12. The wave no. of radiation of wavelength 500 nm is :

(a) 5×10^{-7}/m (b) 2×10^{7}/m
(c) 2×10^{6}/m (d) 500×10^{-9}/m

13. In ground state of Cu^+. The no. of shells occupied, subshells, filled orbitals, and unpaired electrons respectively are :

(a) 4, 8, 15, 0 (b) 3, 6, 15, 1
(c) 3, 6, 14, 0 (d) 4, 7, 14, 2

14. The quantum numbers +1/2 and –1/2 for the electron spin represent

(a) rotation of the electron in clockwise and anticlockwise direction respectively
(b) rotation of the electron in anticlockwise and clockwise direction respectively
(c) magnetic moment of the electron pointing up and down respectively
(d) two quantum mechanical spin states which have no classical analogue

15. Let m_p be the mass of a proton, m_n that of a neutron, M_1 that of a $^{20}_{10}Ne$ nucleus and M_2 that of a $^{40}_{20}Ca$ nucleus. Then

(a) $M_2 = 2M_1$ (b) $M_1 < 10(m_p + m_n)$
(c) $M_2 > 2M_1$ (d) $M_1 = M_2$

16. Which of the following pairs have identical values of e/m?

(a) A proton and a neutron
(b) A proton and deuterium
(c) Deuterium and an α- particle
(d) An electron and γ-rays

17. The wavelength of the third line of the Balmer series for a hydrogen atom is

(a) $\dfrac{21}{100R_\infty}$ (b) $\dfrac{100}{21R_\infty}$

(c) $\dfrac{21R_\infty}{100}$ (d) $\dfrac{100R_\infty}{21}$

18. Which of the following electronic configurations have zero spin multiplicity ?

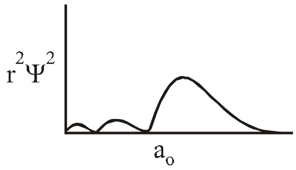
(a) $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ (b) $\boxed{\uparrow}\boxed{\uparrow}\boxed{\downarrow}$

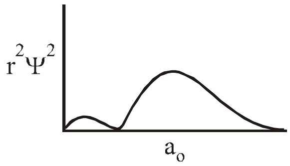
(c) $\boxed{\uparrow}\boxed{\downarrow}\boxed{\downarrow}$ (d) $\boxed{\downarrow}\boxed{\downarrow}\boxed{\uparrow}$

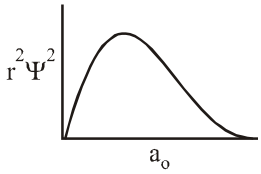
19. The angular distribution functions of all orbitals have

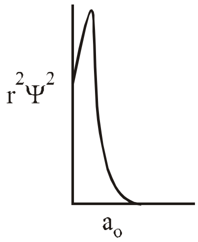
(a) l nodal surfaces (b) l – 1 nodal surfaces
(c) n + 1 nodal surfaces (d) n – l –1 nodal surfaces

20. Which of the following radial distribution graphs correspond to $\ell = 2$ for the H atom ?

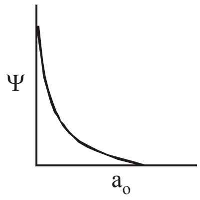
(a)


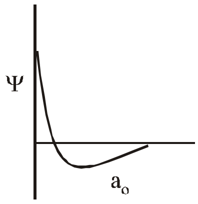
(b)


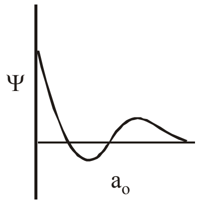
(c)


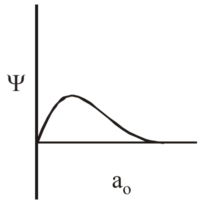
(d)


21. Which of the following graphs correspond to one node?

(a)


(b)


(c)


(d)


22. A body of mass 10 mg is moving with a velocity of 100 ms^{-1}. The wavelength of de-Broglie's wave associated with it would be

(a) 6.63×10^{-35} m (b) 6.63×10^{-31} m
(c) 6.63×10^{-37} m (d) 6.63×10^{-34} m

23. If N_0 represents the Avogadro number, then which of the following represent correct value of one atomic mass unit.

(a) $N_0 \times 10^{-3}$ kg (b) N_0 g

(c) N_0^{-1} g (d) $\frac{1}{16}$ Mass of 0-16 atom

24. If the shortest wavelength of the spectral line of H-atom in the Lyman series is X, then the longest wavelength of the line in Balmer series of Li^{2+} is

(a) 9x (b) $\frac{x}{9}$

(c) $\frac{5x}{4}$ (d) $\frac{4x}{5}$

25. If the subsidiary quantum number of a sub-energy level is 4, the maximum and minimum values of the spin multiplicities are

(a) 10, 2 (b) 4, – 4

(c) 10, 1 (d) 9, 1

26. Li^{3+} and a proton are accelerated by the same potential, then de-Broglie wavelengths λ_{Li} and λ_p have the ratio (assume $m_{Li} = 9\ m_p$)

(a) $1 : 3\sqrt{3}$ (b) 1 : 1

(c) 1 : 2 (d) 1 : 4

27. One Bohr magnet on is equal to

(a) $\frac{c}{4\pi h m_e}$ (b) $\frac{h}{4\pi e m_e}$

(c) $\frac{eh}{4\pi m_e}$ (d) $\frac{hc}{4\pi m_e}$

28. The dissociation energy of H_2 is 430.53 $KJmol^{-1}$. If hydrogen is dissociated by illumination with radiation of wavelength 253.7 nm the fraction of the radiant energy which will be converted into kinetic energy is given by

(a) 100% (b) 8.76%

(c) 2.22% (d) 1.22%

29. The magnetic moment of M^{x+} (atomic number M = 25) is $\sqrt{15}$ BM. The number of unpaired elections and the value of x respectively are

(a) 5, 2 (b) 3, 2

(c) 3, 4 (d) 4, 3

30. The threshold frequency of a metal is $1 \times 10^{15} s^{-1}$. The ratio of the maximum kinetic energies of the photoelectrons when the metal is irradiated with radiations of frequencies $1.5 \times 10^{15} s^{-1}$ and $2.0 \times 10^{15} s^{-1}$ respectively would be

(a) 4 : 3 (b) 1 : 2

(c) 2 : 1 (d) 3 : 4

31. The ratio of magnetic moments of Fe(III) and Co(II) is

(a) 7 : 3 (b) 3 : 7

(c) $\sqrt{7} : \sqrt{3}$ (d) $\sqrt{3} : \sqrt{7}$

32. The average life of an excited state of hydrogen atom is of the order 10^{-8} s. The number of revolutions made by an electron when it is in state n = 2 and before it suffers a transition to state n = 9 are

(a) 8.23×10^6 (b) 2.82×10^6

(c) 22.8×10^6 (d) 2.28×10^6

33. The number of concentric spherical surfaces for 3s orbital at which the probability of finding electrons is zero, are

(a) 3 (b) 2

(c) 1 (d) 0

34. If the second ionization potential of helium is 54.4 eV, then possible energy states of He^+ ion is/are

(a) 13.6 eV (b) – 13.6 eV

(c) + 3.4 eV (d) None of these

35. If the uncertainties in position and momentum are equal, the uncertainty in the velocity is

(a) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$ (b) $\sqrt{\frac{h}{2\pi}}$

(c) $\sqrt{\frac{h}{\pi}}$ (d) None of these

36. The de-Broglie wavelength of an electron accelerated by an electric field of V volts is given by

(a) $\lambda = \frac{1.23}{V}$ nm (b) $\lambda = \frac{1.23}{\sqrt{h}}$ nm

(c) $\lambda = \frac{1.23}{\sqrt{V}}$ nm (d) $\lambda = \frac{1.23}{\sqrt{m}}$ nm

37. The photoelectric current decreases if

(a) the intensity of the source of light is decreased

(b) the frequency of incident radiation decreases below threshold frequency

(c) the exposure time decreases

(d) None of these

38. If a proton and α -particle are accelerated through the same potential difference, the ratio of de-Broglie wavelengths λ_p and λ_α is

(a) 3 (b) $2\sqrt{2}$

(c) 1 (d) 2

39. Which of the following pairs of nucleides are isodiaphers ?

(a) ${}^{13}_{6}C$ and ${}^{16}_{8}O$ (b) ${}^{1}_{1}H$ and ${}^{2}_{1}H$

(c) ${}^{3}_{1}H$ and ${}^{4}_{2}He$ (d) ${}^{55}_{25}Mn$ and ${}^{65}_{30}Zn$

40. A system irradiated for 10 min. is found to absorb 3×10^{18} quanta per sec. If the amount of substance decomposed is 3×10^{-3} mol ($N_A = 6 \times 10^{23}$). The quantum efficiency of the reaction is

(a) 2.5 (b) 2

(c) 1.5 (d) 1

41. If the radius of first orbit of H-atom is a_0, then de-Broglie wavelength of electron in 4th orbit is

(a) $8\pi a_0$ (b) $\frac{a_0}{4}$

(c) $16a_0$ (d) $2\pi a_0$

42. The species ${}^{39}_{19}K$ and ${}^{19}_{9}F$ are called

(a) isosters (b) isobars

(c) isotones (d) isodiaphers

43. A particle of mass 1 micro gram is moving with a speed of 1 Kms^{-1}. The de-Broglie wavelength of the particle is

(a) 7.04×10^{-25} m (b) 6.626×10^{-28} m

(c) 6.626×10^{-15} m (d) 6.626×10^{-31} m

Hints & Solutions

EXERCISE 1

1. Isotopes = ${}^{238}_{92}\text{U}, {}^{234}_{92}\text{U}$

   Isobars = ${}^{234}_{90}\text{Th}, {}^{234}_{91}\text{Pa}, {}^{234}_{92}\text{U}$

2. First energy level.
3. *s*-orbital
4. Interference and diffraction
5. There is no probability of finding a *d* electron right at the nucleus.
6. Electron, because of its least mass.
8. K.E. = 7.29×10^{-19}J
9. $\lambda = 1.24 \times 10^{-14}$ m
10. $\lambda = 6572$ Å
13. $v_0 = 9.81 \times 10^{14}$ Hz.

19. **(b)** **20.** **(a)** **21.** **(c)** **22.** **(c)**
23. **(a)** **24.** **(b)** **25.** **(b)** **26.** **(d)**
27. **(c)** **28.** **(c)**

EXERCISE 2

1. **(c)** A neutral atom with Z > 1 can have neutron, proton and electron.

2. **(d)** Atomic orbitals are 4s, 3s, 3p and 3d. (n + *l*) values being 4, 3, 4 and 5. Hence 3d has highest energy.

3. **(a)** 19 + 1e⁻ = 20 electrons.

4. **(d)** Threshold frequency is not the same for all metals.

5. **(c)** incorrect. (see text).

6. **(a)** All positive ions are deposited at small part. (nucleus of atom).

7. **(b)** Ratio of mass of proton and electron is approx. $1837 = 1.8 \times 10^3$.

8. **(a)** Neutron being chargeless particle could not effect certain properties.

9. **(c)** ${}_{18}\text{Ar}^{40}$ contains 22 neutrons and ${}_{21}\text{Sc}^{40}$ contains 19 neutrons. The number of neutrons = (A – Z)

10. **(d)** Rutherford used doubly charged helium particle. (α - particle)

11. **(b)** Number of p = number of e^- = 89 and neutrons 231 – 89 = 142.

12. **(a)** Z = 11, A = 24. Hence protons = 11 the neutrons (24 – 11) = 13.

13. **(d)** For neutral atom . No. of p = No. of e^- = 18 and A = Z + No. of neutrons = 18 + 20 = 38.

14. **(c)** Hydride ion H^- contains two electrons and He contains two electrons.

15. **(c)**

16. **(c)** The species CO, NO^+, CN^- and C_2^{2-}. Contain 14 electrons each.

17. **(d)** Na^+, Mg^{++}, O^{2-} contain 10 electrons each Cl^- has 18 electrons.

18. **(b)** Nuclear charge of K^+ (19) is more than nuclear charge of Cl^- (17).

19. **(b)** $E \quad \frac{hc}{\lambda}; \frac{E_1}{E_2} \quad \frac{\lambda_2}{\lambda_1} \quad \frac{6000}{3000} \quad 2:1$

20. **(b)** $\Delta E = h\nu = \frac{hc}{\lambda}$;

$$\therefore \lambda = \frac{hc}{\Delta E} = \frac{6.63 \times 10^{-34}(3 \times 10^8)}{3.03 \times 10^{-19}} = 656 \text{ nm}$$

21. **(a)** $p = \frac{h}{\lambda} = \frac{6.63 \times 10^{-34}}{2.2 \times 10^{-11}} = 3 \times 10^{-23} \text{ kg/s}$

22. **(a)** It is in the lowest energy level, it can absorb and not emit energy.

23. **(c)** See text for Brackett $n_1 = 4$, $n_2 = 5, 6, 7$ etc.

24. **(d)** For Balmer $n_1 = 2$ and $n_2 = 3$; $\nu = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5R}{36} \text{ cm}^{-1}$

25. **(a)** 350-700 nm lies in visible region hence Balmer Series.

26. **(a)** For Balmer $n_1 = 2$ and $n_2 = 3, 4, 5$. For third line $n_1 = 2$ & $n_2 = 5$.

27. **(d)** Li^+ and He both have two electrons each.

28. **(a)** $KE = \frac{13.6Z^2}{n^2}$ eV when n = 2. $KE = \frac{13.6 \times 1}{2^2} = +3.4 \text{ eV}$.

29. **(a)** $KE = \frac{13.6Z^2}{n^2}$ eV and Total energy = $-\frac{13.6Z^2}{n^2}$ eV.

Hence ratio = –1.

30. **(c)**

31. **(c)** Angular momentum $mvr = \frac{nh}{2\pi}$

32. (b) Orbital angular momentum = $\sqrt{l(l+1)}\,\frac{h}{2\pi}$. For s the value of $l = 0$. Hence orbital angular momentum = 0.

33. (a) Total energy = $\frac{-13.6Z^2}{n^2}$ eV. Put n = 2, 3, 4 and get the value for subsequent orbits.

34. (c) Radius of nth orbit $r_n = \frac{a_0}{Z} \times n^2$; $\therefore r_3 = 9a_0$

35. (a) Angular momentum is quantised.

36. (c) The difference between the energy of adjacent energy levels decreases on moving away from nucleus.

37. (c) Wave number $\bar{\upsilon} = \frac{1}{2 \times 10^6} = 0.5 \times 10^{-6}\,\text{m} = 500\text{nm}$ (wave number $\bar{\nu}\quad \frac{1}{\lambda}$)

38. (c) He^{2+} does not contain any electron. Bohr's theory is applicalbe to species containing one electron.

39. (b) $E_n \propto Z^2$ increases rapidly.

40. (d) Ionisation energy = $E_\infty - E_1$
For H = 0 – (–13.6). For Be^{3+} = 0 – (–13.6 × 4^2).
Therefore Ratio is 1 : 16.

41. (d) $E_1 = \frac{-13.6}{1}$; $E_3 - E_1 = -1.5 - (-13.6)$; $= 12.1$ eV

$= 12.1 \times 1.6 \times 10^{-12}$ ergs

$= 0.1936 \times 10^{-10}$ ergs (1 ev = 1.6 × 10^{-12} ergs).

42. (a) $E_3 = -\frac{13.6}{9}$ eV = – 1.5 eV; $E_2 = \frac{-13.6}{4}$eV = –3.4 eV

$E_3 - E_2 = [-1.5 - (-3.4)] = 1.9 \text{ eV} = 3.04 \times 10^{-19}$ J / atom

43. (b) $E_2 = \frac{-13.6}{(2)^2} = -3.40$ eV

44. (a) $r_n = \frac{a_0 \times n^2}{Z} = \frac{0.53\text{Å} \times n^2}{Z}$;

For $Li^{++} = \frac{0.53\text{Å} \times (1)^2}{3} = 0.17$ Å

45. (d) First excited state means n = 2. $\therefore r_2 = \frac{0.53 \times (2)^2}{1} = 2.12$Å

46. (b) $r_n = \frac{a_0 n^2}{Z}, r_1 = \frac{a_0 (1)^2}{1}$ for hydrogen

$r_2 = \frac{a_0 (1)^2}{1}$ for deuterium $\therefore \frac{r_1}{r_2} = \frac{1}{1} = 1:1$

47. (b) $E_n = \frac{-13.6Z^2}{n^2}$; For He = –13.6 × $(2)^2$ = –54.4 eV.

48. (d) Sommerfield.

49. (c) $\lambda = \frac{h}{mv}$; $\quad \therefore \lambda \propto \frac{1}{v}$ hence answer (c).

50. (c) $\lambda = \frac{h}{p} = \frac{6.6 \times 10^{-34}}{3.3 \times 10^{-24}} = 2 \times 10^{-10} m = 2\text{Å}$

51. (b) $\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}}{9.11 \times 10^{-31} \times 10^6} = 0.727 \times 10^{-9}\text{m} = 0.727$ nm

52. (c) $\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}}{0.200 \times \frac{5}{3600}} = 2.4 \times 10^{-30}$ m

53. (c) $\Delta x \,.\, \Delta p = \frac{h}{4\pi}$ or $\Delta x \,.\, m\Delta v = \frac{h}{4\pi}$;

$\Delta v = \frac{0.011}{100} \times 3 \times 10^4 = 3.3 \text{ cms}^{-1}$

$\Delta x = \frac{6.6 \times 10^{-27}}{4 \times 3.14 \times 9.1 \times 10^{-28} \times 3.3} = 0.175$ cm

54. (c) $\Delta x = \frac{h}{4\pi \times \Delta p} = \frac{6.63 \times 10^{-34}}{4 \times 3.14 \times 10^{-5}} = 5.27 \times 10^{-30}$ m

55. (d) Azimuthal Quantum number represent quantised values of angular momentum $L = \sqrt{l(l+1)}\,.\,\frac{h}{2\pi}$.

56. (d) For $l = 2$ (d subshell) $n \geq 3$.

57. (b) $_5B = 1s^2, 2s^2, 2p_x{}^1p_y{}^0p_z{}^0$; n = 2, l = 1, m = –1

58. (c) Number of orbitals with principal quantum number n = n^2.

59. (b) Follow text.

60. (c) For 4p electron n = 4, l = 1, m = –1, 0 + 1 and s = +½ or –½

61. (d) l = 2 for d subshell hence 10 electrons.

62. (c) When n = 3 we have s,p and d sub-shells.
`Hence subshells = 3 and obitals 1 + 3 + 5 = 9.

63. (d) When m = – 3, l = 3, $\therefore n = 4$.

64. (b) Valence electron of K is $4s^1$. $\therefore$ n = 4, l = 0, m = 0, s = ½

65. (a) (n + l) rule the higher the value of (n + l), the higher is the energy. When (n + l) value is the same see value of n.

	I	II	III	IV
(n + l)	(4 + 1)	(4 + 0)	(3 + 2)	(3 + 1)
	5	4	5	4

$\therefore$ IV < II < III < I

66. (d) According to Bohr's model electrons follow definite path.

67. (c) Energy of subshells follow the order $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6$, 5s, 4d, 5p, 6s..... we can fill them by electrons upto 4p hence 36 electrons.

68. (b) Total number iof orbitals for principal quantum number n is n^2

69. (c) For $l = 0$, m cannot be -1.

70. (a) $m = +2$ signifies only one orbital.

71. (d) For 4d electron we have $n = 4$, $l = 2$, $m = -2, -1, 0, +1, +2$ & $s = ½$ or $-½$.

72. (b) For f orbital, the values of m are $-3, -2, -1, 0, +1, +2, +3$.

73. (b) $E = h\upsilon = \frac{ch}{\lambda}$; and $\upsilon = \frac{c}{\lambda}$

$$8 \times 10^{15} = \frac{3.0 \times 10^8}{\lambda}$$

$$\therefore\ \lambda = \frac{3.0 \times 10^8}{8 \times 10^{15}} = 0.37 \times 10^{-7} = 37.5 \times 10^{-9}\ \text{m} = 4 \times 10^1\ \text{nm}$$

74. (b) Number of nodal planes in d orbitals is 2.

75. (a) Degenerate orbitals have equal energy.

76. (a) One nodal plane in the YZ plane.

77. (a) Angular nodes $= l$, spherical nodes $(n - l - 1)$; Total $(n - 1)$. Hence spherical nodes for 5f orbits. $= (5 - 3 - 1) = 1$

78. (d) (follow text.)

79. (d) $Mg^{2+} = 1s^2, 2s^2p^6$, $Ti^{3+} = 1s^2\ 2s^2\ p^6\ 3s^2p^6d^1$, $V^{3+} = 1s^2, 2s^2p^6, 3s^2p^6d^2$, $Fe^{2+} = 1s^2, 2s^2p^6, 3s^2p^6d^6$ (4 unpaired electrons in d).

80. (c) Atomic number 9 is for F and ion is F^-.

81. (c) $1s^2, 2s^22p^5, 3s^1$. Total electrons (10) excited state of Ne.

82. (d) Heisenberg's uncertainty Principle is applicable to any moving object.

83. (d) Configuration contains 2 unpaired electrons hence most paramagnetic.

84. (d) For Cu^{2+} electronic configuration is $[Ar]3d^9$.

85. (c) Aufbau Principle.

86. (b) Zn^+ (1 unpaired electron); Fe^{++} (4); Ni^{3+} (3); Cu^+ (0).

87. (d) is correct.

88. (a) d subshell can accomodate 10 electrons.

89. (d) Atomic number 24 is for Cr $1s^2, 2s^2p^6, 3s^2p^6d^5, 4s^1$. Ans (d).

90. (a) Ni (28) $= 1s^2, 2s^2p^6, 3s^2p^6d^8, 4s^2$. Unpaired electrons 2.

91. (d) Cu. Ans (d).

92. (b) Write electronic configuration of Cu.

93. (c) In protium $_1H^1$. No neutron.

94. (b) M-shell means 3 principle energy level the element is Cr.

95. (b) Fe^{3+} and Mn^{2+} write and check the ans (b).

96. (b)

	5p	4f	6s	5d
(n + l)	5+1	4+3	6+0	5+2
	6	7	6	7

Hence the order is 5p < 6s < 4f < 5d

97. (d) Fe^{2+} $1s^2, 2s^2p^6, 3s^2p^6d^6$ hence 6 electrons.

98. (a) Pauli's exclusion principle.

99. (c) Write electronic configuration and find unpaired electrons. Cr (6), Fe (4), Mn (5), Cu (3), Zn (0), Hg (0).

The more the number of unpaired electrons the more is the paramagnetic character.

100.(c) Not more than two electrons can be present in same atomic orbital. This is Paulis exclusion principle.

101.(a) $_{11}Na = 1s^2, 2s^2p^6, 3s^1$ for $3s^1$, $l = 0$. Hence $m = 0$.

EXERCISE 3

1. (a) We know $\Delta p.\Delta x \geq \frac{h}{4\pi}$

since $\Delta p = \Delta x$ (given)

$\therefore\ \Delta p.\Delta p = \frac{h}{4\pi}$

or $m\Delta v\ m\Delta v.\ \frac{h}{4\pi}$ $[\therefore\ \Delta p = m\Delta v]$

or $(\Delta v)^2 = \frac{h}{4\pi m^2}$

or $\Delta v = \sqrt{\frac{h}{4\pi m^2}} = \frac{1}{2m}\sqrt{\frac{h}{\pi}}$

Thus option (a) is the correct option.

2. (a) $\Delta p = m\Delta v$

Substituting the given values of Δx and m, we get

1×10^{-18} g cm s^{-1} $= 9 \times 10^{-28}$ g $\times \Delta v$

or $\Delta v = \frac{1 \times 10^{-18}}{9 \times 10^{-28}}$

$= 1.1 \times 10^9$ cm s^{-1} $\simeq 1 \times 10^9$ cm s^{-1}

i.e. option (a) is correct.

3. (d) K.E per atom

$$= \frac{4.4 \times 10^{-19} - 4.0 \times 10^{-19}}{2}$$

$$= \frac{0.4 \times 10^{-19}}{2} = 2.0 \times 10^{-20}$$

4. (d) The number of sub shell is $(2l + 1)$. The maximum number of electrons in the sub shell is $2(2l + 1) = (4l + 2)$

5. (b) $m = -l$ to $+l$, through zero thus for $l = 2$, values of m will be $-2, -1, 0, +1, +2$.

Therefore for $l = 2$, m cannot have the value -3.

6. (d) $\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{0.66 \times 100} = 1 \times 10^{-35}$ m

7. (b) Total no. of atomic orbitals in a shell = n^2.
Given $n = 4$; Hence number of atomic orbitals in 4th shell will be 16.

8. (b) Given $E_1 = 25\text{eV} \quad E_2 = 50\text{ eV}$

$$E_1 \;\; \frac{hc}{\lambda_1} \;\; E_2 \;\; \frac{hc}{\lambda_2} \qquad \therefore \frac{E_1}{E_2} \;\; \frac{\lambda_2}{\lambda_1}$$

$$\therefore \frac{\lambda_2}{\lambda_1} \;\; \frac{25}{50} \;\; \frac{1}{2} \quad \therefore \lambda_1 = 2\lambda_2$$

9. (a) $ns \to (n-2)f \to (n-1)d \to np \;\; [n=6]$

10. (c) Energy of photon obtained from the transition $n = 6$ to $n = 5$ will have least energy.

$$\Delta E = 13.6Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

11. (c) $c = \nu\lambda$

$$\lambda = \frac{c}{\nu} = \frac{3\times10^{17}}{6\times10^{15}} = 50\text{ nm}$$

12. (c) n = 3 for 3rd shell
$l = 1$ for p sub shell.
m = – 1 is possible for two electrons present in an orbital.

13. (c) Energy of an electron at infinite distance from the nucleus is zero. As an electron approaches the nucleus, the electron attraction increases and hence the energy of electron decreases and thus becomes negative. Thus as the value of *n* decreases, *i.e.* lower the orbit is, more negative is the energy of the electron in it.

14. (a) 2nd excited state will be the 3rd energy level.

$$E_n = \frac{13.6}{n^2}\text{eV} \quad \text{or} \quad E = \frac{13.6}{9}\text{eV} = 1.51\text{ eV.}$$

15. (c) $\Delta x.\Delta p = \frac{h}{4\pi}$;

$$\therefore \Delta v = \frac{6.62\times10^{-34}}{4\times3.14\times0.025\times10^{-5}} = 2.1\times10^{-28}\text{ms}^{-1}$$

16. (c) $Fe^{+2} = 3d^6, 4s^0$

17. (a) For s-electron, $\ell = 0$ ∴ angular momentum = zero

18. (b) f-block elements show a regular decrease in atomic size due to lanthanide/actinide contraction.

19. (a) N^{3-}, F^- and Na^+ contain 10 electrons each.

20. (a) The lines falling in the visible region comprise Balmer series. Hence the third line would be n_1=2, n_2 = 5 i.e. $5 \to 2$.

21. (d) $\lambda = \frac{h}{mv} = \frac{6.6\times10^{-34}}{60\times10^{-3}\times10} = 10^{-33}\text{m}$

22. (a) The quantum numbers for 4f electron

$$n = 4, l = 3, m = -3, -2 -1, 0, 1, 2, 3 \text{ and } S = \pm\frac{1}{2}$$

23. (b) Electronic configuration of Cr atom (z = 24)

$$= 1s^2, 2s^2p^6, 3s^2p^6d^5, 4s^1$$

when $\ell = 1$, p - subshell,
Numbers of electrons = 12
when $\ell = 2$, d - subshell,
Numbers of electrons = 5

24. (c) $\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$$\frac{1}{\lambda} = 1.097\times10^7\left(\frac{1}{1} - \frac{1}{\infty}\right) = 1.097\times10^7$$

$$\lambda = 91.15\times10^{-9}\text{m} \approx 91\text{nm}$$

25. (c) ${}_{19}K^+, {}_{20}Ca^{2+}, {}_{21}Sc^{3+}, {}_{17}Cl^-$ each contains 18 electrons

26. (d) $(n\text{–}1)d^5ns^2$ attains the maximum O.S. of + 7

27. (a) The energy of an orbital is given by (n + *l*) in (d) and (c). (n + *l*) value is (3 + 2) = 5 hence they will have same energy.

28. (b) 1.
$$\left.\begin{array}{l} BO_3^{3-} \longrightarrow 5+8\times3 \;\; 3 \;\; 32 \\ CO_3^{2-} \longrightarrow 6+8\times3 \;\; 2 \;\; 32 \\ NO_3^{-} \longrightarrow 7+8\times3 \;\; 1 \;\; 32 \end{array}\right\} \text{iso electronic}$$

2.
$$\left.\begin{array}{l} SO_3^{2-} \longrightarrow 16+8\times3 \;\; 2 \;\; 42 \\ CO_3^{2-} \longrightarrow 32 \\ NO_3^{-} \longrightarrow 32 \end{array}\right\} \text{not iso electronic}$$

3.
$$\left.\begin{array}{l} CN^{-} \longrightarrow 6 \;\; 7 \;\; 1 \;\; 14 \\ N_2 \longrightarrow 7\times2 \;\; 14 \\ C_2^{2-} \longrightarrow 6\times2 \;\; 2 \;\; 14 \end{array}\right\} \text{iso electronic}$$

4.
$$\left.\begin{array}{l} PO_4^{3-} \longrightarrow 15+8\times4 \;\; 3 \;\; 50 \\ SO_4^{2-} \longrightarrow 16+8\times4 \;\; 2 \;\; 50 \\ ClO_4^{-} \longrightarrow 17+8\times4 \;\; 1 \;\; 50 \end{array}\right\} \text{iso electronic}$$

29. (b) Accroding to Bohr's theory angular momentum of an electron i in nth orbital is given by $mvr = \frac{nh}{2\pi}$

when n = 5

Angular momentum of electron $= \frac{5h}{2\pi} = \frac{2.5h}{\pi}$

30. (a) Given m = $9.1 \times 10^{-31 \text{kg}}$
h = 6.6×10^{-34}Js

$$\Delta V = \frac{300 \times .001}{100} = 0.003 \text{ms}^{-1}$$

From Heisenberg's uncertainity priciple

$$\Delta x = \frac{6.62 \times 10^{-34}}{4 \times 3.14 \times 0.003 \times 9.1 \times 10^{-31}} = 1.92 \times 10^{-2} \text{m}$$

31. (a) $N^{3-} = 7 + 3 = 10e^-$, $O^{--} \longrightarrow 8 + 2 = 10e$
$P^- = 9 + 1 = 10e^-$, $S^{--} \longrightarrow 16 + 2 = 18e^-$
(not iso electronic)

(b) $Li^+ = 3+1 = 4e^-$, $Na^+ = 11–1 = 10e^-$,
$Mg^{++} = 12–2 = 10e^-$
$Ca^{++} = 20 – 2 = 18e^-$ (not iso electronic)

(c) $K^+ = 19 – 1 = 18e^-$, $Cl^- = 17 + 1 = 18e^-$,
$Ca^{++} = 20 – 2 = 18e^-$, $Sc^{3+} = 21–3 = 18e^-$ (iso electronic)

(d) Ba^{++} $56 – 2 = 54e^-$, Sr^{++} $38–2 = 36e^-$
$K^+ = 19–1 = 18e^-$, $Ca^{++} = 20–2 = 18e^-$ (not iso electronic)

32. (c) (a) n = 3, $\ell = 0$ means 3s-orbital and n + 1 = 3
(b) n = 3, $\ell = 1$ means 3p-orbital n + 1 = 4
(c) n = 3, $\ell = 2$ means 3d-orbital n + 1 = 5
(d) n = 4, $\ell = 0$ means 4s-orbital n + 1 = 4

Increasing order of energy among these orbitals is
3s < 3p < 4s < 3d
∴ 3d has highest energy.

33. (a) (ΔE), The energy required to excite an electron in an atom of hydrogen from n = 1 to n = 2 is given by the following relation (difference in energy E_2 and E_1)

$$E_2 = \frac{-1.312 \times 10^6 \times (1)^2}{(2)^2} = -3.28 \times 10^5 \text{ J mol}^{-1}$$

$E_1 = – 1.312 \times 10^6$ J mol^{-1}
$\therefore \Delta E = E_2 – E_1$
$= [–3.28 \times 10^5] – [–1.312 \times 10^6]$ J mol^{-1}
$= (–3.28 \times 10^5 + 1.312 \times 10^6)$ J mol^{-1}
$= 9.84 \times 10^5$ J mol^{-1}

Thus the correct answer is (a)

34. (c) Species having same number of electrons are isoelectronic calculating the number of electrons in each species given here, we get.
CN^- (6 + 7 + 1 = 14); N_2 (7 + 7 = 14);
O_2^{2-}(8 + 8 + 2 = 18); C_2^{2-} (6 + 6 + 2 = 14);
O_2^- (8 + 8 + 1 = 17); NO^+ (7 + 8 – 1 = 14)
CO (6 + 8 = 14); NO (7 + 8 = 15)
From the above calculation we find that all the species listed in choice (c) have 14 electrons each so it is the correct answer.

35. (a) $$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}}{1.67 \times 10^{-27} \times 1 \times 10^3}$$

$= 3.97 \times 10^{-10}$ meter $= 0.397$ nanometer ≈ 0.40 nm

36. (b) According to Heisenberg uncertainty principle.

$$\Delta x . m \Delta v = \frac{h}{4\pi} \qquad \Delta x = \frac{h}{4\pi m \Delta v}$$

Here $\Delta v = \frac{600 \times 0.005}{100} = 0.03$

So, $\Delta x = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 0.03}$
$= 1.92 \times 10^{-3}$ meter

37. (d) Energy required to break one mole of Cl – Cl bonds in Cl_2

$$= \frac{242 \times 10^3}{6.023 \times 10^{23}} = \frac{hc}{\lambda}$$

$$\frac{6.626 \times 10^{-34} \times 3 \times 10^8}{\lambda}$$

$$\therefore \lambda = \frac{6.626 \times 10^{-34} \times 3 \times 10^8 \times 6.023 \times 10^{23}}{242 \times 10^8}$$

$= 0.4947 \times 10^{-6}$ m $= 494.7$ nm

38. (b) I. $E = \frac{Z^2}{n^2} \times 13.6 \text{eV}$ ...(i)

or $\frac{I_1}{I_2} = \frac{Z_1^2}{n_1^2} \times \frac{n_2^2}{Z_2^2}$ ...(ii)

Given $I_1 = – 19.6 \times 10^{-18}$, $Z_1 = 2$,
$n_1 = 1$, $Z_2 = 3$ and $n_2 = 1$
Substituting these values in equation (ii).

$$-\frac{19.6 \times 10^{-18}}{I_2} = \frac{4}{1} \times \frac{1}{9}$$

or $I_2 = -19.6 \times 10^{-18} \times \frac{9}{4}$
$= – 4.41 \times 10^{-17}$ J/atom

39. (a) For He^+

$$\bar{v} = \frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{2^2} - \frac{1}{4^2} \right)$$

$$= R_H (2)^2 \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = R_H \left(\frac{1}{(1)^2} - \frac{1}{(2)^2} \right)$$

For H

$$\bar{v} \quad \frac{1}{\lambda} \quad R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

For same frequency,

$$R_H \left(\frac{1}{(1)^2} - \frac{1}{(2)^2} \right) = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\therefore \quad \frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{1}{1^2} - \frac{1}{2^2}$$

$\therefore \quad n_1 = 1$ & $n_2 = 2$

40. (b) (A) 4*p* (B) 4*s*
(C) 3*d* (D) 3*p*
According to Bohr Bury's $(n + \ell)$ rule, increasing order of energy will be (D) < (B) < (C) < (A).
Note : If the two orbitals have same value of $(n + \ell)$ then the orbital with lower value of *n* will be filled first.

41. (c) Among isoelectronic species ionic radii increases as the charge increases.
Order of ionic radii $Ca^{2+} < K^{+} < Cl^{-} < S^{2-}$
The number of electrons remains the same but nuclear charge increases with increase in the atomic number causing decrease in size.

42. (a) $$\Delta E = 2.178\times10^{-18}\left(\frac{1}{1^2}-\frac{1}{2^2}\right) \quad \frac{hc}{\lambda}$$

$$\Rightarrow 2.178\times10^{-18}\times\frac{3}{4} \quad \frac{hc}{\lambda}$$

$$\frac{6.62\times10^{-34}\times3\times10^{8}}{\lambda}$$

$$\lambda \quad \frac{6.62\times10^{-34}}{2.178\times10^{-18}}\frac{3\times10^{8}\times4}{\times3}$$
$= 1.214 \times 10^{-7}$m

43. (c) As per Bohr's postulate,

$$mvr = \frac{nh}{2\pi}$$

So, $v \quad \frac{nh}{2\pi\, mr}$

$$KE = \frac{1}{2}mv^2$$

So, $KE = \frac{1}{2}m\left(\frac{nh}{2\pi\, mr}\right)^2$

Since, $r \quad \frac{a_o \times n^2}{z}$

So, for 2nd Bohr orbit

$$r \quad \frac{a_o \times 2^2}{1} \quad 4a_o$$

$$KE = \frac{1}{2}m\left(\frac{2^2h^2}{4\pi^2m^2 \times (4a_o)^2}\right)$$

$$KE = \frac{h^2}{32\pi^2 ma_o^2}$$

44. (b) Average atomic mass of Fe

$$\frac{(54\times5)+(56\times90)+(57\times5)}{100} \quad 55.95$$

EXERCISE 4

1. (d) All the statements are correct.

2. (d) In S.I. units the P.E. $\frac{-Ze^2}{4\pi\varepsilon_0 r}$. For Li^{2+}, Z = 3.

$\therefore$ P.E. $\frac{-3e^2}{4\pi\varepsilon_0 r}$.

3. (b) According to Pauli's exclusion principle the maximum number of electrons with opposite spin present in an atomic orbital is two.

4. (d) In photoelectric effect K.E., hence velocity is directly proportional to frequency of the incident light and independent of the intensity of light.

5. (a) Since K.E. $\frac{1}{2}mv^2$ and $\lambda \quad \frac{h}{mv}$.

$\therefore$ K.E. $\frac{1}{2}m.\frac{h^2}{m^2\lambda^2} \quad \frac{h^2}{2m\lambda^2}$. As λ is the same.

$\therefore$ K.E. $\frac{1}{m}$

6. (d) Angular speed is $\frac{V}{r}$. $V_n \quad \frac{1}{n}$ and $r_n \quad n^2$.
$\therefore$ Angular speed is inversely proportional to n

7. (d) The smallest value of energy of an electron in H atom in ground state can absorb is $= E_2 - E_1$.

$$= \frac{-13.58}{4} - \left(\frac{-13.58}{1}\right) \quad 10.19$$

8. (c) de-Broglie wavelength $\lambda \quad \frac{h}{mv} \quad \frac{6.6\times10^{-34}}{3.3\times10^{-24}} \quad 2$Å

9. (c) After absorbing 12.1 eV the electron in H atom is excited to 3 shell.

$$E_n - E_1 \quad \frac{-13.6}{n^2} - \ -13.6 \quad 12.1$$

$$\frac{-13.6}{n^2} \quad 13.6 \quad 12.1$$

$\therefore$ n = 3

The possible transitions are $\Sigma \quad (3-1) \quad 3$

10. (b) $\frac{1}{\lambda} \quad R_H\left[\frac{1}{2^2}-\frac{1}{4^2}\right] \quad 4.86\times10^{-7}$m $\quad$ 486 nm

11. (c) $E_{1_{He}} = E_{1H} \times Z^2$

$\therefore -871.6\times10^{-20} = E_{1H}\times4$

$\therefore E_{1H} = -217.9\times10^{-20}$ J

12. (c) $\bar{\upsilon} \quad \frac{1}{\lambda} \quad \frac{1}{500\times10^{-9}} \quad 2\times10^{6}\text{m}^{-1}$

13. (c) The ground state electronic configuration, of Cu^{+} ion is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}$
n = 3 (number of shells) ; Number of subshells occupied = 6, Number of filled orbitals = 14 ; There is no unpaired electron.

14. (d) Magnetic moment for an electron exists even if the orbital angular momentum is zero. This is explained by the spin magnetic because it is the spin which produces magnetic moment.

15. (a) $^{20}_{10}Ne$ contains 10 protons and 10 neutrons

$\therefore M_1 = 10\,m_p + 10m_n$

$^{40}_{20}Ca$ contains 20 protons and 20 neutrons

$\therefore M_2 = 20\,m_p + 20\,m_n$

$\therefore M_2 = 2M_1$

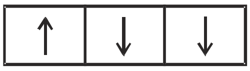
16. (c) Deuterium and an α-particle have identical values of e/m.

17. (b) $\frac{1}{\lambda} = R_\infty\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ for hydrogen atom.

For the Balmer series $n_1 = 2$ and $n_2 = 5$ for third line

$\therefore \frac{1}{\lambda} = R_\infty\left(\frac{1}{2^2} - \frac{1}{5^2}\right) = \frac{21}{100}R_\infty$ thus $\lambda = \frac{100}{21R_\infty}$

18. (c) Spin multiplicity is given by A = (2Σ S + 1). ↑ represent ½ and ↓ represent – ½ spin values. For

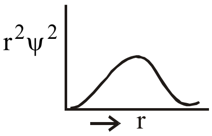


S = – ½

$\therefore A = (2 \times -½ + 1) = 0$

19. (a)

20. (c) $l = 2$ represent d orbital for which



21. (b) The point at which the radial function acquirs zero value is called a node. Examine the graph the answer is (b). (c) graph contains in nodes (a) and (d) none.

22. (b) $\lambda = \frac{h}{mv} = \frac{6.63\times10^{-34}}{10\times10^{-6}\times100} = 6.63 \times 10^{-31}$ m

23. (c) 1 amu $= \frac{1}{N_0}$ g $= N_0^{-1}$ or $\frac{1}{12}$ × mass of C-12 atom

24. (d) $\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

To calculate shortest wavelength take $n_2 = \infty$ and longest wavelength take nearest value of n_2.

For H-atom,

$\frac{1}{\lambda_{\text{shortest}}}$ $n_2 = \infty, Z = 1, n_1 = 1$

$\therefore \quad \frac{1}{x} = R_H$ (Lyman series)

For $\frac{1}{\lambda_{\text{longest}}}$ for Li^{2+}, $Z = 3$, $n_1 = 2$, $n_2 = 3$ (Balmer series)

$$\frac{1}{\lambda_{\text{longest}}} = \frac{1}{x} \times 3^2\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5}{4x}$$

$\therefore \quad \lambda_{\text{longest}} = \frac{4x}{5}$

25. (a) When $l = 4$, the number of degenrate orbitals $= 2l + 1 = 9$,

the maximum total spins $= 9 \times \frac{1}{2}$ and

minimum total spin $= \frac{1}{2}$

Maximum multiplicity $= 2s + 1 = 2 \times \frac{9}{2} + 1 = 10$

Minimum multiplicity $= 2 \times \frac{1}{2} + 1 = 2$

26. (a) From de-Broglie equation,

$\lambda = \frac{h}{\sqrt{2Vem}}$;

$\lambda = \frac{h}{\sqrt{2Vem_p}}$ (for proton)

$\lambda = \frac{h}{\sqrt{2V3em_{Li}}}$ (for Li^{3+})

$$\therefore \quad \frac{\lambda Li^{3+}}{\lambda p} = \frac{\sqrt{2Vem_p}}{\sqrt{6Vem_p \times 9}} = \frac{1}{3\sqrt{3}}$$

27. (c) One Bohr magneton $= \frac{he}{4\pi mc}$

28. (b) Energy of 1 mole of photons,

$E = N_0 \times h\upsilon$

$= \frac{N_0 \times h \times c}{\lambda}$

$= \frac{6.023\times10^{23}\times6.63\times10^{-34}\times3\times10^{8}}{253.7\times10^{-9}}$

= 472.2 kJ

Energy converted into KE = (472.2 – 430.53) kJ

% of energy converted into KE $= \frac{(472.2 - 430.53)}{472.2}$

= 8.76 %

29. (c) Magnetic moment

$\sqrt{n(n+2)} = \sqrt{15}$

$\therefore$ n = 3 number of unpaired electrons

$_{25}M = 3d^5, 4s^2$

$M^x \quad 3d^3$

$\therefore$ x = 4 for three unpaired electrons

30. (c) $\frac{(KE)_1}{(KE)_2} = \frac{\nu_1 - \nu_0}{\nu_2 - \nu_0}$

$= \frac{(1.5\times10^{15} - 1\times10^{15})}{(2.0\times10^{15} - 1\times10^{15})} = \frac{1}{2}$

31. (c) Fe (III) = [Ar] $3d^5$ unpaired electrons = 5;

Magnetic moment = $\sqrt{5(5+2)}$;

Ratio = $\sqrt{7}:\sqrt{3}$

Co(II) = [Ar] $3d^7$ unpaired electrons = 3;

Magnetic moment = $\sqrt{3(3+2)}$

Ratio = $\sqrt{7}:\sqrt{3}$

32. (a) Velocity of electron

$$v_n = 2.19\times 10^6 \frac{Z}{n} ms^{-1}$$

The distance travelled by electron in 10^{-8} s in Second Bohr's Orbit

$$= \frac{2.19\times 10^6 \times 1\times 10^{-8}}{2} m$$

$$= 1.095\times 10^{-2} \text{ m}$$

The circumference of second orbit = $2\pi r_2$

$$= 2\pi\times 0.529\times 10^{-10}\times 2^2$$

$$= 13.3\times 10^{-10} \text{m}$$

$$\therefore \quad \text{Number of revolutions} = \frac{1.095\times 10^{-2}}{13.3\times 10^{-10}} = 8.23\times 10^6$$

33. (b) The number of nodal surfaces is given by $n - l - 1 = 3 - 0 - 1 = 2$

34. (b) $E_1(He^+) = -IE_2(He) = -54.4 \text{ eV}$

The other energy states can be obtained from $\frac{-E_1}{n^2}$ where n = 1, 2, 3.

35. (a) $\Delta x.\Delta p = \frac{h}{4\pi}$ or $\Delta p^2 = \frac{h}{4\pi}$ or $\Delta(mv)^2$

$$\therefore \ \Delta v = \frac{1}{2m}\sqrt{\frac{h}{\pi}}$$

36. (a) $\lambda = \frac{h}{\sqrt{2eVm}} = \frac{1.23}{\sqrt{V}}$ nm

37. (a) Statement (a) is correct.

38. (b) $\lambda_p = \frac{h}{\sqrt{2eVm_p}}$;

$$\lambda_{He^{2+}} = \frac{h}{\sqrt{2\times 2eVm_{He^{2+}}}} = \frac{h}{\sqrt{2\times 2eV\times 4m_p}}$$

$$\therefore \quad \frac{\lambda_p}{\lambda_{He^{2+}}} = 2\sqrt{2}$$

39. (d) Isodiaphers have same difference of number of neutrons and protons or (A – 2Z) must be same.

40. (d) Quantum efficiency

$$= \frac{\text{Number of moles of substance reacted}}{\text{Number of Quanta absorbed}}$$

$$= \frac{3\times 10^{-3}\times 6\times 10^{23}}{3\times 10^{18}\times 60\times 10} = 1$$

41. (a) $r_n = a_0\times n^2$

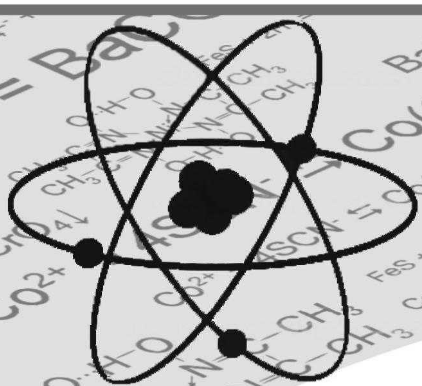
$$r_4 = a_0\times (4)^2 = 16a_0$$

$$mvr = \frac{nh}{2\pi};\ mv = \frac{4h}{2\pi\times 16a_0};$$

$$\lambda = \frac{h}{mv} = \frac{h}{h/8\pi a_0} = 8\pi a_0$$

42. (d) Isodiaphers since (A–2Z) value is the same for both.

43. (d) Apply de Broglie equation to solve.



3

Classification of Elements and Periodicity in Properties

THE PERIODIC TABLE OF THE ELEMENTS

periods (rows)

groups (columns)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
$_{1}$H																	$_{2}$He	1
$_{3}$Li	$_{4}$Be											$_{5}$B	$_{6}$C	$_{7}$N	$_{8}$O	$_{9}$F	$_{10}$Ne	2
$_{11}$Na	$_{12}$Mg											$_{13}$Al	$_{14}$Si	$_{15}$P	$_{16}$S	$_{17}$Cl	$_{18}$Ar	3
$_{19}$K	$_{20}$Ca	$_{21}$Sc	$_{22}$Ti	$_{23}$V	$_{24}$Cr	$_{25}$Mn	$_{26}$Fe	$_{27}$Co	$_{28}$Ni	$_{29}$Cu	$_{30}$Zn	$_{31}$Ga	$_{32}$Ge	$_{33}$As	$_{34}$Se	$_{35}$Br	$_{36}$Kr	4
$_{37}$Rb	$_{38}$Sr	$_{39}$Y	$_{40}$Zr	$_{41}$Nb	$_{42}$Mo	$_{43}$Tc	$_{44}$Ru	$_{45}$Rh	$_{46}$Pd	$_{47}$Ag	$_{48}$Cd	$_{49}$In	$_{50}$Sn	$_{51}$Sb	$_{52}$Te	$_{53}$I	$_{54}$Xe	5
$_{55}$Cs	$_{56}$Ba		$_{72}$Hf	$_{73}$Ta	$_{74}$W	$_{75}$Re	$_{76}$Os	$_{77}$Ir	$_{78}$Pt	$_{79}$Au	$_{80}$Hg	$_{81}$Tl	$_{82}$Pb	$_{83}$Bi	$_{84}$Po	$_{85}$At	$_{86}$Rn	6
$_{87}$Fr	$_{88}$Ra		$_{104}$Rf	$_{105}$Db	$_{106}$Sg	$_{107}$Bh	$_{108}$Hs	$_{109}$Mt	$_{110}$Ds	$_{111}$Rg	$_{112}$Cn	$_{113}$Uut	$_{114}$Fl	$_{115}$Uup	$_{116}$Lv	$_{117}$Uus	$_{118}$Uuo	7

lanthanoids	$_{57}$La	$_{58}$Ce	$_{59}$Pr	$_{60}$Nd	$_{61}$Pm	$_{62}$Sm	$_{63}$Eu	$_{64}$Gd	$_{65}$Tb	$_{66}$Dy	$_{67}$Ho	$_{68}$Er	$_{69}$Tm	$_{70}$Yb	$_{71}$Lu
actinoids	$_{89}$Ac	$_{90}$Th	$_{91}$Pa	$_{92}$U	$_{93}$Np	$_{94}$Pu	$_{95}$Am	$_{96}$Cm	$_{97}$Bk	$_{98}$Cf	$_{99}$Es	$_{100}$Fm	$_{101}$Md	$_{102}$No	$_{103}$Lr

PERIODIC TABLE :

It is a table of elements in which the elements with similar properties are placed together.

DOBEREINER'S LAW OF TRIADS :

This was the classification of elements into groups of three elements each with similar properties such that the atomic weight of the middle element was the arithmetic mean of the other two e.g. Ca, Sr, Ba; Cl, Br, I etc.

The difference between atomic weights of any two successive elements is nearly constant.

NEWLAND'S LAW OF OCTAVES :

This was an arrangement of elements in order of increasing atomic weights in which it was observed that every eighth element had properties similar to those of the first just like the eight node of an octave of music.

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl

Prouts Hypothesis : Atomic weight of an element is simple multiple of atomic weight of hydrogen.

MENDELEEV'S PERIODIC TABLE :

This is based upon Mendeleev's periodic law which states that the physical and chemical properties of the elements are a periodic function of their atomic weights.

Mendeleev named Gallium and Germanium elements as eka-aluminium and eka-silion respectively.

STRUCTURAL FEATURES OF THE MENDELEEV'S PERIODIC TABLE:

(i) Mendeleev's original periodic table consists eight vertical columns are called groups I-VIII & seven horizontal rows are called periods 1-7. But modified Mendeleev's periodic table contains nine groups, i.e., I-VIII and zero (of noble gases).

(ii) All groups except VII and zero have been further divided into two sub-groups called A and B. A groups of left hand side consist of ***normal elements*** while groups B of right hand side consist of ***transition elements***.

(iii) Elements of group IA are called ***alkali metals*** while those of group IB (i.e, Cu, Ag, Au) are called ***coinage metals***.

MODERN PERIODIC LAW :

Moseley formed the basis of the modern periodic law. He discovered that the square root of the frequency of the more prominent X-rays emitted by a metal was proportional to the atomic number and not the atomic weight of the atom of the metal. Hence atomic number should be the basis of classification of the elements.

Modern periodic law states, ***"that the physical and chemical properties of the elements are a periodic function of their atomic number."***

It was observed that the elements with similar properties reoccurred at regular intervals of 2, 8, 8, 18 or 32. These numbers (2, 8, 8, 18 and 32) are called ***magic numbers,*** and cause of periodicity in properties.

Structural features of the long form of the periodic table

(a) Groups -

(i) The 18 vertical columns, of the periodic table, are called groups

(ii) Elements of groups 1, 2, 13-17 are called ***normal*** or ***representative*** elements.

(iii) Elements of groups 3-12 are called ***transition elements***

(iv) The elements belonging to a particular group is known as a family and is usually named after the first element. For example, ***Boron*** family (group 13). In addition to this, some groups have typical names. For example,

Elements of group 1 are called ***alkali*** metals

Elements of group 2 are called ***alkaline*** earth metals

Elements of group 3 are called ***pnicogens***

Elements of group 16 are called ***chalcogens***

Elements of group 17 are called ***halogens***

Elements of group 18 are called ***noble gases***

(b) Periods - (i) The 7 horizontal columns (or rows) are called periods. The seven periods of periodic table are

Shortest period - 1st period ($_1H \rightarrow {}_2He$) contains 2 elements. It is the **shortest period**.

Short periods - 2nd period ($_3Li \rightarrow {}_{10}Ne$) and 3rd period ($_{11}Na \rightarrow {}_{18}Ar$) contains 8 elements each. These are **short periods**.

Long periods - 4th period ($_{19}K \rightarrow {}_{36}Kr$) and 5th period ($_{37}Rb \rightarrow {}_{54}Xe$) contain 18 elements each and are called long periods.

Longest period - 6th period ($_{55}Cs$ – $_{86}Rn$) contains 32 elements and is the longest period.

Incomplete period - 7th period ($_{87}Fr$ –) is, however, incomplete and contains at present only 26 elements.

(c) Blocks - The periodic table is divided into four main blocks (s, p, d and f) depending upon the subshell to which the valence electron enters into.

(i) **s-Block** - Elements of group 1 and 2 constitute **s-block**.

(ii) **p-Block -** Elements of group 13 to 18 constitute **p-block**.

(iii) **d-Block** - Elements of group 3 to 12 constitute **d-block**.

(iv) There are three complete series and one incomplete series of d-block elements. These are:

1st or 3d-transition series which contains ten elements with atomic number 21-30 ($_{21}Sc$–$_{30}Zn$).

2nd or 4d-transition series which contains ten elements with atomic number 39–48 ($_{39}Y$–$_{48}Cd$).

3rd or 5d-transition series which also contains ten elements with atomic number 57 and 72-80 ($_{57}La$, $_{72}Hf$–$_{80}Hg$).

4th or 6d-transition series which contains only ten elements.

(v) **The f-block** elements comprise two horizontal rows placed at the bottom of the periodic table to avoid its un-necessary expansion and make the symmetrial nature of periodic table. The two series of f-block elements containing 14 elements each. **Lanthanides -** The 14 elements from $_{58}Ce$–$_{71}Lu$ in which 4f-subshell is being progressively filled up are called **lanthanides** or **rare earth elements**. **Actinides -** Similarly, the 14 elements from $_{90}Th$ –$_{103}Lr$ in which 5f-subshell is being progressively filled up are called **actinides**.

(vi) Elements of s and p-blocks are called **normal** or **representative** elements, those of d-block are called **transition** elements while the f-block elements are called **inner transition** elements.

(vii) The 11 elements with Z = 93–103 ($_{93}Np$ – $_{103}Lr$) which occur in the periodic table after uranium and have been prepared by artificial means are called **transuranics**. These are all radioactive elements.

NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBER > 100

According to IUPAC the nomenclature can be derived using numerical roots for 0 and numbers 1-9 for atomic numbers of elements.

The roots are put together in order of digits which make the atomic number and 'ium' is added at the end. Use the following table

Digit	Name	Abbrevation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

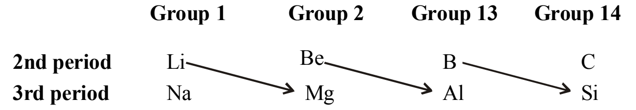
Example : Name the IUPAC name of the element of atomic number 108 : Name will be **Unniloctium** and **symbol** - UnO

(2) Example – Name the element with atomic number 115.

Name will be - **Ununpentium** and **symbol** UuP

DIAGONAL RELATIONSHIP:

Certain elements of 2nd period i.e., Li, Be, B. show similarity with their diagonal elements in the 3rd period i.e., Mg, Al, Si, as shown below:



This is called diagonal relationship and is due to the reason that these pairs of elements have almost identical ionic radii and polarizing power. (i.e. charge/size ratio).

PERIODIC PROPERTIES :

Properties which show a regular gradation when we move from left to right in a period or from top to bottom in a group are called periodic properties. These properties are atomic size, ionisation energy electron affinity etc.

(A) ***Atomic size:*** It refers to the distance between the centre of nucleus of atom to its outermost shell of electrons. The absolute value of atomic radius cannot be determined because

(i) It is not possible to locate the exact position of electrons in an atom as an orbital has no sharp boundaries.

(ii) It is not possible to isolate an individual atom.

(iii) In a group of atoms, the probability distribution of electrons is influenced by the presence of neighbouring atoms.

Since absolute value of atomic size cannot be determined, it is expressed in terms of the operational definitions such as covalent radius, vander waal's radius, ionic radius and metallic radius.

(a) ***Covalent radius :*** It is half of the distance between the nuclei of two like atoms bonded together by a single covalent bond, hence it is also known as single bond covalent radius (SBCR). Thus, covalent radius

$(r_{cov.}) = \frac{1}{2}d.$

where d = internuclear distance between two covalently bonded like atoms.

(b) ***Van-der Waal's radius :*** It is one-half of the distance between the nuclei of two adjacent atoms belonging to two neighbouring molecules of an element in the solid state.

The covalent radius is always smaller than the corresponding van der waal's radius.

(c) ***Metallic radius :*** It is half of the distance between two successive nuclei of two adjacent metal atoms in the metallic closed packed crystal lattice. Metallic radius of an element is always greater than its covalent radius.

(d) ***Ionic radius :*** It is the effective distance from the nucleus of the ion upto the electrons in the outer shell to which it can influence the ionic bond.

An atom can be changed into a **cation** (by loss of electron) which is always much smaller than the corresponding atom, or to an **anion** (by gaining of electrons) which is always larger than the corresponding atom.

(iv) Factors influencing covalent radius :

(a) ***Multiplicity of bond :*** Covalent radii depends on the multiplicity of bonds. e.g.,

	Bond length	*Radius of C-atom*
H_3C-CH_3	1.54Å	$\frac{1.54}{2}Å = 0.77Å$
$H_2C\ \ CH_2$	1.34Å	$\frac{1.34}{2}Å = 0.67Å$

(b) ***Percentage of ionic character:*** Covalent radius of H in HCl, HBr and HI are different.

(c) ***Effective nuclear charge :*** Greater the effective nuclear charge, more tightly is the hold with nucleus and hence smaller the radius.

(v) Periodic variation of atomic radii :

(a) On moving down the group the valence shells become far away from the nucleus and thus the atomic radius increases.

(b) On moving along the period, the effective nuclear charge increases and thus the electron cloud is attracted more strongly towards the nucleus resulting in the contraction of atomic radius.

(vi) Isoelectronic ions or ***species :*** These are ions of the different elements which have the same number of electrons but different magnitude of the nuclear charge. The size of isoelectronic ions decreases with the increase in the nuclear charge.

(B) Ionisation energy (I.E.) : The amount of energy (work) required to remove an electron from the last orbit of an isolated (free) atom in gaseous state is known as **ionisation potential** or **energy** or better **first ionisation potential** of the element,

i.e., $M(g) + I.E \longrightarrow M^{+}(g) + e^{-}$

(i) The amount of energies required to remove the subsequent electrons (2nd, 3rd, ...) from the monovalent gaseous cation of the element one after the other are collectively called successive ionisation energies. These are designated as $I.E_1$, $I.E_2$, $I.E_3$, $I.E_4$ and so on. It may be noted that. $I.E_4 > I.E_3 > I.E_2 > I.E_1$ (for a particular element)
IE is expressed in **eV/atom** or **kcal mol^{-1}** or **kJ mol^{-1}**
Note that eV $atom^{-1} = 23.06$ kcal $mol^{-1} = 96.3$ kJ mol^{-1}

(ii) In general, the first I.E. increases along the period from left to right. However there are some exceptions to the general trend -

(a) I.E. decreases from elements of group 2 $\rightarrow$ 3.

(b) I.E. decreases from elements of group 15 $\rightarrow$ 16.

(iii) In a group of the periodic table, the ionisation energy decreases from top to bottom.

(iv) **The factors which affect the ionisation energy are**

(a) Atomic size or radius : I.E. decreases as the atomic size increases so the attractive force decreases.

(b) Number of electrons in the inner shell (screening effect) : On moving down a group, the number of inner shells increases which increase the screening effect and hence the ionisation potential tends to decrease.

(c) Nuclear charge : On moving along the period, effective nuclear charge increases due to addition of electrons in same valence shell and hence ionisation energy increases.

(d) Stable cofiguration : Half filled or completely filled subshells possess extra stable nature and thus it is more difficult to remove electron and hence more is I.E.

(e) Penetration effect : More penetrating (i.e. more closes) are subshells of a shell to the nucleus, more tightly the electrons are held towards the nucleus and more is I.E.
I.E. : s > p > d > f for a given shell
Penetration power Surface area of a subshell

(v) In second period elements, the correct increasing order of ionisation energies is
$IE_1 : Li < B < Be < C < O < N < F < Ne$
$IE_2 : Be < C < B < N < F < O < Ne < Li$

(vi) In third period elements, the correct increasing order of ionisation is
$IE_1 : Na < Al < Mg < Si < S < P < Cl < Ar$
$IE_2 : Mg < Si < Al < P < S < Cl < Ar < Na$

(C) Electron affinity (EA): It is the amount of energy released when a gaseous atom accepts the electron to form gaseous anion .

$$X(g) + e^{-} \longrightarrow X^{-}(g) + EA$$

(i) EA values are expressed in **eV/atom** or **kcal/mol** or **kJ/mol**.

(ii) The energy change accompanying the addition of first, second, third etc. electrons to neutral isolated gaseous atoms are called successive electron affinities and are designated as EA_1, EA_2, EA_3 etc.

(iii) The first EA is always taken as positive. However, the addition of second electron to the negatively charged ion is opposed by coulombic repulsion and hence required (absorbed) energy for the addition of second electron. Thus, second electron affinity (EA_2) of an element is taken as negative. For example,

$$O(g) + e^{-} \longrightarrow O^{-}(g);\ EA_1 = +141 \text{KJ mol}^{-1}$$

(Exothermic)

$$O^{-}(g) + e^{-} \longrightarrow O^{2-}(g);\ EA_2 = -780 \text{KJ mol}^{-1}$$

(Endothermic)

(iv) Electron affinity increases in moving along the period from left to right due to increase in charge. But the values are unexpectedly low in elements of group 2, 15 and 18 due to stable electronic configurations of exactly half-filled and completely filled orbitals.

(v) Within a group of the periodic table the electron affinities decreases from top to bottom.

(vi) In general, electron affinity follows the following trend:
Halogens > Oxygen family > Nitrogen family > Metals of groups 1 and 13 and Non-metals of group 14 > Metals of group 2.

(vii)The electron affinities are indirectly measured with the help of Born-Haber Cycle, i.e.,

$$\Delta H_f = S + \frac{1}{2}D + IE + EA + U$$

Where, S, D, IE, EA and U are the heat of sublimation, bond dissociation energy, ionization energy, electron affinity and lattice energy respectively.

(viii)Electron affinity depends upon-

(a) Effective nuclear charge - Greater the effective nuclear charge, more is the attraction of nucleus towards the electron and hence higher will be the value of E.A.

(b) Atomic size - Greater the atomic radius of the atom, less will be the attraction of the nucleus to the electron to be added and hence lower will be the value of E.A.

(c) Penetrating power - Due to penetrating power, E.A. for addition of electron show the order
s > p > d > f

(d) Electronic configuration : Half filled and fully filled subshell are extra stable and thus oppose the addition of electron which leads to lower, E.A. value e.g. EA, of C > EA, of N.

(D) Electronegativity (EN) : It is the tendency of an atom in a molecule to attract the bonded shared pair of electrons, towards itself

(i) There are several electronegativity scales-

(a) **Mulliken scale:** On the Mulliken scale, electronegativity X is taken as average of IE and EA, i.e.,

$X \ \frac{IE \quad EA}{2}$ where IE and EA are expressed in electron volts

or $X \ \frac{IE \quad EA}{540}$ where IE and EA are expressed in kJ mol^{-1}

or $X \ \frac{IE \quad EA}{130}$ where IE and EA are expressed in kcal mol^{-1}

(b) **Pauling scale:** This is the most widely used scale and is based upon bond energy data. According to **Pauling**, the difference in electronegativity of two atoms A and B is given by the relationship as

$$X_A - X_B = 0.208\sqrt{\Delta E} = 0.088\sqrt{\Delta E} \text{ (in SI units)}$$

where X_A and X_B are electronegativities of the atoms A and B respectively while.

$$\Delta E = E_{A-B} - \sqrt{(E_{A-A} \times E_{B-B}}$$

where E_{A-B}, E_{A-A} and E_{B-B} represent bond dissociation energies of the bonds A-B, A-A and B-B respectively. The Pauling and the Mulliken scales are related to each other by the relation,

$$X_{Pauling} = \frac{X_{Mulliken}}{2.8}$$

(ii) In a period, EN increases from left to right due to decrease in size and increase in nuclear charge of atoms.

(iii) In a group, EN decreases from top to bottom due to increase in atomic size.

(iv) **Electronegativity depends on:**

(a) **Atomic size**

(b) **Nuclear charge**

(c) **Shielding effect**

(d) **Oxidation state** - EN increases as the positive oxidation state increases.

(e) **Hybridization** - Greater is the s-character in a hybrid orbital more is electronegativity.

(v) If electronegativity difference is greater than 1.7 the bond is ionic otherwise covalent.

(vi) In general, greater is difference of EN between two atoms smaller is the bond length.

(vii) Smaller the electronegativity, larger is the atomic size.

VALENCY :

Valency of an element is the number of electrons gained or lost or shared with other atoms in the formation of compounds.

Valency of group 1 and 2 elements is equal to the number of electrons in the outermost shell, while that for groups 13 to 14 is group number -minus 10 and that for group 15–18 is 8 -minus the number of electrons in the outermost shell.

ATOMIC VOLUME :

It may be defined as the volume occupied by one mole atoms of the element at its melting point in solid state.

(i) It is obtained by dividing the gram atomic mass of the element by its density.

(ii) It decreases along the period, reaches a minimum in the middle and then starts increasing, because of different packing arrangement of atoms in different elements in the solid state, i.e., P_4, S_8 etc.

(iii) In moving down the group atomic volume goes on increasing gradually

ACID-BASE BEHAVIOUR OF OXIDES AND HYDROXIDES :

The oxides or hydroxide of an element may act either as base or an acid depending upon its ionization energy.

(i) If the IE is low, it acts as a base and if the IE is high, it acts as an acid.

(ii) The IE of alkali metals is the lowest, therefore, their oxides and hydroxides are the strongest bases. The basic character of their hydroxides increases in the order:

$$CsOH > RbOH > KOH > NaOH > LiOH$$

(iii) The IE of halogens is quite high, therefore, their oxides are the strongest acids. The acidic character of their oxides and hydroxides decreases in the order:

$$HClO_4 > HBrO_4 > HIO_4$$

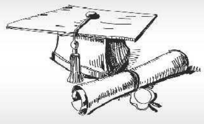
(iv) Within a period, the ionization energies of the elements usually increase and hence their oxides and hydroxides show a gradual variation from strongly basic through amphoteric to strongly acidic character. For example:

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10} SO_2	Cl_2O_7
Strongly basic	Basic	Amphoteric	Weakly acidic	Strongly acidic	Very strongly acidic

(v) The **non-metallic character, oxidising character** and **acidic nature** of oxides of the elements increases from left to right in a period and decrease from top to bottom in a group.

The stability of the metal increases and activity decreases from left to right in a period whereas the stability decreases and activity increases down the group.

Exercise-1 | NCERT BASED QUESTIONS



Very Short/Short Answer Questions

1. Name a species which is iso electronic with Al^{3+}.

2. Helium has a electronic configuration of $1s^2$ but it is placed in *p*-block in group 18. Explain.

3. Name the elements with the lowest and the highest ionisation energy.

4. Predict the position of the element in the Periodic Table satisfying the electronic configuration $(n-1)\ d^1\ ns^2$ for $n = 4$.

5. Write equations to demonstrate the difference between electron affinity and the reverse of ionization potential.

6. All the lanthanoid elements form stable compounds containing the +3 cation. Of the few other ionic forms known, Ce forms the stable + 4 series of ionic compounds and Eu the stable + 2 series. Account for these unusual ionic forms in terms of their electronic configurations.

7. Nitrogen has positive electron gain enthalpy whereas oxygen has negative. However, oxygen has lower ionisation enthalpy than nitrogen. Explain.

8. Explain the following :

(a) Electronegativity of elements increase on moving from left to right in the periodic table.

(b) Ionisation enthalpy decrease in a group from top to bottom.

9. Give the order in which the melting points of halides of sodium decrease and why ?

10. The first (IE_1) and second (IE_2) ionisation enthalpies (kJ mol^{-1}) of three elements I, II and III are given below :

	I	II	III
$1E_1$	403	549	1142
$1E_2$	2640	1060	2080

Identify the element which is likely to be (a) non-metal (b) an alkali metal (c) an alkaline earth metal.

11. Show by a chemical reaction with water that Na_2O is a basic oxide and Cl_2O_7 is an acidic oxide.

12. Consider the ground state electronic configuration of the five elements I to V given below :

Elements	Electronic Configuration
I	$1s^2\ 2s^2\ 2p^5$
II	$1s^2\ 2s^2\ 2p^4$
III	$1s^2\ 2s^2\ 2p^6\ 3s^2$
IV	$1s^2\ 2s^2\ 2p^6\ 3s^1$
V	$1s^2\ 2s^2\ 2p^6$

(i) Which of the above configuration is associated with the highest and which is associated with the lowest ionisation enthalpy ?

(ii) Arrange the above five elements is order of increasing electron gain enthalpy.

13. Predict the formula of a stable binary compound that would be formed by the following pairs of elements

(a) aluminum and phosphorous

(b) lithium and nitrogen

(c) calcium and sulphur

Long Answer Questions

14. Name the four blocks of elements in the periodic table and list the difference in their electronic configurations. Give examples of each type of elements. Write at least four characteristics of each block.

15. Find the best choice in the following list and give brief reason for your answer

(i) highest IE_1; Se, S, Te

(ii) smallest radius; Cl^-, Br^-, I^-

(iii) most parmagnetic; Fe, Co, Ni

(iv) smallest atom; Sn, I, Bi

(v) lowest IE_2 ; Ar, K, Ca

16. (i) Explain the terms (a) screening effect, (b) penetration effect, (c) metallic character.

(ii) Why are electron affinities of noble gases zero ? Arrange halogens in increasing order of electron affinity.

17. The second ionization enthalpy (IE_2) of the elements of the second period are given below :

Element :	**IE_2 (kJ/mol) :**
Li	7294
Be	1756
B	2430
C	2354
N	2856
O	3396
F	3377
Ne	3966

(i) Explain

(a) Why is IE_2 of Li so much higher than for all other elements of this period ?

(b) What is the general trend from Be to Ne of increasing IE_2?

(c) Why IE_2 of F is just about the same or very slightly less than that of oxygen ?

(ii) Would you predict the IE_2 of Na in kJ/mol is

(a) greater than 7294

(b) between 3966 and 7294 or

(c) less than 3966 ? Explain.

Multiple Choice Questions

18. Element A belongs to Group VII in p-block and element B belongs to Group I in s-block of the periodic table. Out of the following assumptions, the correct one is :

(a) A and B are metals
(b) A and B are non-metals
(c) A is a metal and B is a non-metal
(d) A is a non-metal and B is a metal

19. Examine the following elements :

N, O, F, Ne
P, S, Cl, Ar
Br, Kr
I, Xe

In modern periodic table, on which side these elements are placed

(a) Top left side (b) Bottom left side
(c) Top right side (d) Middle side

20. The screening effect of ‘d’ electrons is

(a) Much less than *s*-electrons
(b) Much more than *s*-electrons
(c) Equal to *s*-electrons
(d) Equal to *p*-electrons

21. Which of the following is not an actinoid ?

(a) Curium ($Z = 96$)
(b) Californium ($Z = 98$)
(c) Uranium ($Z = 92$)
(d) Terbium ($Z = 65$)

22. Electronic configurations of four elements A, B, C and D are given below :

(i) $1s^2\,2s^2\,2p^6$ (ii) $1s^2\,2s^2\,2p^4$
(iii) $1s^2\,2s^2\,2p^6\,3s^1$ (iv) $1s^2\,2s^2\,2p^5$

Which of the following is the correct order of increasing tendency to gain electron ?

(a) $A < C < B < D$ (b) $A < B < C < D$
(c) $D < B < C < A$ (d) $D < A < B < C$

23. The period number in the long form of the periodic table is equal to

(a) magnetic quantum number of any element of the period.
(b) atomic number of any element of the period.
(c) maximum Principal quantum number of any element of the period.
(d) maximum Azimuthal quantum number of any element of the period.

24. The lightest liquid metal is

(a) Hg (b) Ga
(c) Cs (d) Fr

25. Which of the following elements A, B, C, D and E with atomic number 3, 11, 15, 18 and 19 respectively belong to the same group?

(a) A, B, C (c) B, C, D
(c) A, D, E (d) A, B, E

26. Which of the following statement(s) about the Modern Periodic Table is/are incorrect ?

(i) The elements in the Modern Periodic Table are arranged on the basis of their decreasing atomic number
(ii) The elements in the Modern Periodic Table are arranged on the basis of their increasing atomic masses
(iii) Isotopes are placed in adjoining group(s) in the Periodic Table
(iv) The elements in the Modern Periodic Table are arranged on the basis of their increasing atomic number

(a) (i) only (b) (i), (ii) and (iii)
(c) (i), (ii) and (iv) (d) (iv) only

27. An element having electronic configuration

$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$ forms

(a) Acidic oxide (b) Basic oxide
(c) Amphoteric oxide (d) Neutral oxide

28. An element which is an essential constituent of all organic compounds belongs to

(a) group 1 (b) group 14
(c) group 15 (d) group 16

Exercise-2 | CONCEPTUAL MCQs

1. As per the modern periodic law, the physical and chemical properties of elements are periodic functions of their

(a) atomic volume
(b) electronic configuration
(c) atomic weight
(d) atomic size

2. Eka-aluminium and Eka-silicon are known as

(a) Gallium and Germanium
(b) Aluminium and Silicon
(c) Iron and Sulphur
(d) Manganese and Magnesium

3. The most significant contribution towards the development of periodic table was made by

(a) Mendeleev (b) Avogadro
(c) Dalton (d) Cavendish

4. Mendeleev’s periodic law is based on

(a) atomic number (b) atomic weight
(c) equivalent weight (d) valency

5. Which of these does not reflect the periodicity of the elements?

(a) Bonding behaviour (b) Electronegativity
(c) Ionization potential (d) Neutron/proton ratio

6. The statement that is not true for the long form of the periodic table is

(a) It reflects the sequence of filling electrons in the order of sub-energy levels s, p, d and f.

(b) It helps to predict the stable valence states of the elements

(c) It reflects trends in physical and chemical properties of the elements

(d) It helps to predict the relative ionicity of the bond between any two elements.

7. Which of the following pairs of atomic numbers represents elements belonging to the same group?

(a) 11 and 20 (b) 12 and 30

(c) 13 and 31 (d) 14 and 33

8. Which of the following sets of atomic number belong to that of alkali metals?

(a) 1, 12, 30, 4, 62 (b) 37, 19, 3, 55

(c) 9, 17, 35, 53 (d) 12, 20, 56, 88

9. What is the atomic number of the next halogen if discovered?

(a) 85 (b) 117

(c) 167 (d) 104

10. All the elements of a group in the periodic table have the same

(a) atomic weight

(b) number of protons

(c) mass number

(d) number of electrons for bonding

11. The elements in which 4f orbitals are progressively filled up are called as

(a) actinides (b) transition elements

(c) lanthanides (d) halogens

12. Which of the following is not a transition metal?

(a) Zr (b) Tc

(c) Re (d) Np

13. Which of the following have same number of electrons in the outermost orbit?

(a) Pb, Sb (b) N, O

(c) As, Bi (d) P, Ca

14. Representative elements belong to

(a) s- and p-blocks (b) p- and d-blocks

(c) f-block only (d) d- and f-blocks

15. Element with atomic number 56 belongs to which block?

(a) s (b) p

(c) d (d) f

16. Which of the following remains unchanged on descending in a group in the periodic table?

(a) Valence electrons (b) Atomic size

(c) Density (d) Metallic character

17. Which is true about the electronegativity order of the following elements?

(a) $P > Si$ (b) $C > N$

(c) $Br > Cl$ (d) $Sr > Ca$

18. Electronic configuration of most electronegative element is

(a) $1s^2\,2s^2\,2p^4\,3s^1$ (b) $1s^2\,2s^2\,2p^6\,3s^2\,3p^5$

(c) $1s^2\,2s^2\,2p^5$ (d) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$

19. Going from fluorine to chlorine, bromine and iodine, the electronegativity

(a) increases

(b) decreases

(c) first decrease then increases

(d) changes randomly

20. Which of the following is most electronegative?

(a) Lead (b) Silicon

(c) Carbon (d) Tin

21. On going from right to left in a period in the periodic table, the electronegativity of the elements

(a) increases

(b) decreases

(c) remains unchanged

(d) decreases first then increases

22. The electronegativity follows the order

(a) $F > O > Cl > Br$ (b) $F > Cl > Br > O$

(c) $O > F > Cl > Br$ (d) $Cl > F > O > Br$

23. Electronegativity values for the elements help in predicting

(a) polarity of bonds

(b) dipole moments

(c) valency of elements

(d) position in the electrochemical series

24. Which of the following is correctly matched?

(a) C—C bond length — 0.077 nm

(b) Ionic radius of Na^+ — 0.136 nm

(c) C—Cl bond length — 0.176 nm

(d) Ionic radius of F^- — 0.095 nm

25. The atomic radius increases as we move down in a group because

(a) effective nuclear charge increases

(b) atomic mass increases

(c) additive electrons are accommodated in new electron level

(d) atomic number increases

26. The correct order of radii is

(a) $N < Be < B$ (b) $F^- < O^{2-} < N^{3-}$

(c) $N < Li < K$ (d) $Fe^{3+} < Fe^{2+} < Fe^{4+}$

27. Which of the following is the smallest cation?

(a) Na^+ (b) Mg^{2+}

(c) Ca^{2+} (d) Al^{3+}

28. The ionic radii of N^{3-}, O^{2-}, F^- and Na^+ are in the order

(a) $N^{3-} > O^{2-} > F^- > Na^+$

(b) $N^{3-} > Na^+ > O^{2-} > F^-$

(c) $Na^+ > O^{2-} > N^{3-} > F^-$

(d) $O^{2-} > F^- > Na^+ > N^{3-}$

29. Ionic radii of

(a) $Ti^{4+} < Mn^{2+}$ (b) $^{35}Cl^{-} < ^{37}Cl^{-}$

(c) $K^{+} > Cl^{-1}$ (d) $P^{3+} > P^{5+}$

30. The radii of F, F^-, O and O^{2-} are in the order

(a) $O^{2-} > F^{-} > F > O$

(b) $F^{-} > O^{2-} > F > O$

(c) $O^{2-} > O > F^{-} > F$

(d) $O^{2-} > F^{-} > O > F$

31. Which stable nucleus has radius half than that of ^{54}Xe

(a) ^{40}Ca (b) ^{23}Na

(c) ^{32}S (d) ^{7}Li

32. For which of the following ionic species radius would be maximum?

(a) C^{4-} (b) N^{3-}

(c) O^{2-} (d) Mg^{2+}

33. The decreasing order of the size of the following ions is

(a) $Li^{+} > H^{+} > H^{-}$ (b) $H^{+} > H^{-} > Li^{+}$

(c) $H^{-} > Li^{+} > H^{+}$ (d) $H^{-} > H^{+} > Li^{+}$

34. Chloride ion and potassium ion are isoelectronic. Then

(a) their sizes are same

(b) Cl^- ion is bigger than K^+ ion

(c) K^+ ion is relatively bigger

(d) their sizes depend on either cation or anion

35. Which has the smallest size?

(a) Na^{+} (b) Mg^{2+}

(c) Al^{3+} (d) P^{5+}

36. Which of the following is isoelectronic with carbon atom?

(a) Na^{+} (b) Al^{3+}

(c) O^{2-} (d) N^{+}

37. Na^{+}, Mg^{++}, Al^{3+} and Si^{4+} are isoelectronic. The order of their ionic size is

(a) $Na^{+} > Mg^{++} < Al^{3+} < Si^{4+}$

(b) $Na^{+} < Mg^{++} > Al^{3+} > Si^{4+}$

(c) $Na^{+} > Mg^{++} > Al^{3+} > Si^{4+}$

(d) $Na^{+} < Mg^{++} > Al^{3+} < Si^{4+}$

38. Electron affinity depends on

(a) atomic size

(b) nuclear charge

(c) atomic number

(d) atomic size and nuclear charge both

39. The element with highest electron affinity among halogens is

(a) F (b) Cl

(c) Br (d) I

40. The correct order of electron affinity among the following is

(a) F > Cl > Br (b) Br > Cl > F

(c) Cl > F > Br (d) F > Br > Cl

41. Highest electron affinity is shown by

(a) O^{-} (b) F^{-}

(c) Cl_2 (d) F_2

42. Which of the following has least electron afinity?

(a) Oxygen (b) Argon

(c) Nitrogen (d) Boron

43. Which of the following has highest electron affinity?

(a) Li^{+} (b) Na^{+}

(c) F^{-} (d) Cl^{-}

44. The element having very high ionizaiton energy but zero electron affinity is

(a) H (b) F

(c) He (d) Be

45. The lower electron affinity of fluorine than that of chlorine is due to

(a) smaller size

(b) smaller nuclear charge

(c) difference in their electronic configurations

(d) its highest reactivity

46. Which of the following orders is correct for the first ionization potential of B, C and N?

(b) B > C > N (b) N > C > B

(c) N > C < B (d) N < C < B

47. Consider the following changes

$A \rightarrow A^{+} + e^{-} : E_1$ and $A^{+} \rightarrow A^{2+} + e^{-} : E_2$

The energy required to pull out the two electrons are E_1 and E_2 respectively. The correct relationship between two energies would be

(a) $E_1 < E_2$ (b) $E_1 = E_2$

(c) $E_1 > E_2$ (d) $E_1 \geq E_2$

48. Which of the following isoelectronic ions has the lowest ionization energy?

(a) K^{+} (b) Ca^{2+}

(c) Cl^{-} (d) S^{2-}

49. The decreasing order of the ionization potential of the following elements is

(a) Ne > Cl > P > S > Al > Mg

(b) Ne > Cl > P > S > Mg > Al

(c) Ne > Cl > S > P > Mg > Al

(d) Ne > Cl > S > P > Al > Mg

50. The electronic configuration of elements A, B and C are [He] $2s^1$, [Ne] $3s^1$ and [Ar] $4s^1$ respectively. Which one of the following order is correct for IE_1 (in kJ mol^{-1}) of A, B and C?

(a) A > B > C (b) C > B > A

(c) B > C > A (d) C > A > B

51. The set representing the correct order of first ionization potential is

(a) K > Na > Li (b) Be > Mg > Ca

(c) B > C > N (d) Ge > Si > C

52. The correct order of ionization energies is

(a) Zn < Cd < Hg (b) Hg < Cd < Zn

(c) Ar > Ne > He (d) Cs < Rb < Na

53. Which of the order for ionization energy is correct?

(a) Be < B < C < N < O (b) B < Be < C < O < N

(c) Be > B > C > N > O (d) B < Be < N < C < O

54. First ionization potential will be maximum for

(a) Uranium (b) Hydrogen

(c) Lithium (d) Iron

55. The incorrect statement among the following is

(a) the first ionization potential of Al is less than the first ionization potential of Mg

(b) the second ionization potential of Mg is greater than the second ionization potential of Na

(c) the first ionization potential of Na is less than the first ionization potential of Mg

(d) the third ionization potential of Mg is greater than the third ionization potential of Al.

56. The second ionization potential of an element M is the energy required to

(a) remove one mole of electrons from one mole of gaseous cations of the element

(b) remove one mole of electrons from one mole of gaseous anions

(c) remove one mole of electrons from one mole of monovalent gaseous cations of the element

(d) remove 2 moles of electrons from one mole of gaseous atoms

57. Highest ionization potential is shown by

(a) Alkali metals (b) Transition elements

(c) Halogens (d) Inert gases

58. With reference to ionization potential which one of the following sets is correct?

(a) Li > K < Cs (b) B > Li > K

(c) Cs > Li > B (d) Cs < Li < K

59. Which of the following species has lowest ionization potential?

(a) O (b) O_2

(c) O_2^+ (d) O_2^-

60. The factor not affecting the ionization energy is

(a) size of atom

(b) charge in the nucleus

(c) type of bonding in the crystalline lattice

(d) type of electron involved

61. The screening effect of inner electrons of the nucleus causes

(a) decrease in the ionization energy

(b) increase in the ionization energy

(c) no effect on the ionization energy

(d) increases the attraction of the nucleus for the electrons

62. Consider the following statements

I. The radius of an anion is larger than that of the parent atom.

II. The ionization energy generally increases with increasing atomic number in a period.

III. The electronegativity of an element is the tendency of an isolated atom to attract an electron.

Which of the above statements is/are correct?

(a) I alone (b) II alone

(c) I and II (d) II and III

63. Which of the following order is wrong?

(a) $NH_3 < PH_3 < AsH_3$ — Acidic

(b) $Li < Be < B < C$ — IE_1

(c) $Al_2O_3 < MgO < Na_2O < K_2O$ — Basic

(d) $Li^+ < Na^+ < K^+ < Cs^+$ — Ionic radius

64. Gradual addition of electronic shells in the noble gases causes a decrease in their

(a) ionization energy (b) atomic radius

(c) boiling point (d) density

65. Which of the following elements represents highly electropositive as well as highly electronegative character in its period?

(a) Hydrogen (b) Nitrogen

(c) Fluorine (d) None of these

66. The cause of diagonal relationship is

(a) similar electronegativities

(b) similar ionic or atomic radii

(c) similar polarizing power of ions

(d) All the three

67. Variable valency is generally exhibited by

(a) representative elements

(b) transition elements

(c) non-metallic elements

(d) metallic elements

68. Which of the following elements does not belong to first transition series?

(a) Fe (b) V

(c) Ag (d) Cu

69. In the periodic table, with the increase in atomic number, the metallic character of an element

(a) decreases in a period and increases in a group

(b) increases in a period and decreases in a group

(c) increases both in a period and the group

(d) decreases both in a period and the group

Exercise-3 | PAST COMPETITION MCQs

1. Identify the correct order of the size of the following: **[CBSE-PMT 2007]**
(a) $Ca^{2+} < K^+ < Ar < Cl^- < S^{2-}$
(b) $Ar < Ca^{2+} < K^+ < Cl^- < S^{2-}$
(c) $Ca^{2+} < Ar < K^+ < Cl^- < S^{2-}$
(d) $Ca^{2+} < K^+ < Ar < S^{2-} < Cl^-$

2. In which of the following electronic configuration an atom has the lowest ionisation enthalpy? **[CBSE-PMT 2007]**
(a) $1s^2\,2s^2\,2p^3$ (b) $1s^2\,2s^2\,2p^5\,3s^1$
(c) $1s^2\,2s^2\,2p^6$ (d) $1s^2\,2s^2\,2p^5$

3. Which one of the following ionic species has the greatest proton affinity to form stable compound? **[CBSE-PMT 2007]**
(a) NH_2^- (b) F^-
(c) I^- (d) HS^-

4. The stability of + 1 oxidation state increases in the sequence: **[CBSE-PMT 2009]**
(a) Tl < In < Ga < Al (b) In < Tl < Ga < Al
(c) Ga < In < Al < Tl (d) Al < Ga < In < Tl

5. Amongst the elements with following electronic configurations, which one of them may have the highest ionization energy? **[CBSE-PMT 2009]**
(a) Ne $[3s^23p^2]$ (b) Ar $[3d^{10}4s^24p^3]$
(c) Ne $[3s^23p^1]$ (d) Ne $[3s^23p^3]$

6. Which of the following represents the correct order of increasing electron gain enthalpy with negative sign for the elements O, S, F and Cl ? **[CBSE-PMT 2010]**
(a) Cl < F < O < S (b) O < S < F < Cl
(c) F < S < O < Cl (d) S < O < Cl < F

7. Among the elements Ca, Mg, P and Cl, the order of increasing atomic radii is : **[CBSE-PMT 2010]**
(a) Ca < Mg < P < Cl (b) Mg < Ca < Cl < P
(c) Cl < P < Mg < Ca (d) P < Cl < Ca < Mg

8. What is the value of electron gain enthalpy of Na^+ if IE_1 of Na = 5.1 eV ? **[CBSE-PMT 2011 M]**
(a) –5.1 eV (b) –10.2 eV
(c) +2.55 eV (d) +10.2 eV

9. According to the Periodic Law of elements, the variation in properties of elements is related to their **[AIEEE 2003]**
(a) nuclear masses
(b) atomic numbers
(c) nuclear neutron-proton number ratios
(d) atomic masses

10. Which is the correct order of ionic sizes (At. No. : Ce = 58, Sn = 50, Yb = 70 and Lu = 71) ? **[AIEEE 2003]**
(a) Ce > Sn > Yb > Lu (b) Sn > Ce > Yb > Lu
(c) Lu > Yb > Sn > Ce (d) Sn > Yb > Ce > Lu

11. Which one of the following ions has the highest value of ionic radius ? **[AIEEE 2004]**
(a) O^{2-} (b) B^{3+}
(c) Li^+ (d) F^-

12. Among Al_2O_3, SiO_2, P_2O_3 and SO_2 the correct order of acid strength is **[AIEEE 2004]**
(a) $Al_2O_3 < SiO_2 < SO_2 < P_2O_3$
(b) $SiO_2 < SO_2 < Al_2O_3 < P_2O_3$
(c) $SO_2 < P_2O_3 < SiO_2 < Al_2O_3$
(d) $Al_2O_3 < SiO_2 < P_2O_3 < SO_2$

13. Beyllium and aluminium exhibit many properties which are similar. But, the two elements differ in **[AIEEE 2004]**
(a) forming covalent halides
(b) forming polymeric hydrides
(c) exhibiting maximum covalency in compounds
(d) exhibiting amphoteric nature in their oxides

14. Which of the following oxides is amphoteric in character? **[AIEEE 2005]**
(a) SnO_2 (b) SiO_2
(c) CO_2 (d) CaO

15. In which of the following arrangements, the order is NOT according to the property indicated against it? **[AIEEE 2005]**
(a) Li < Na < K < Rb :
Increasing metallic radius
(b) I < Br < F < Cl :
Increasing electron gain enthalpy (with negative sign)
(c) B < C < N < O
Increasing first ionization enthalpy
(d) $Al^{3+} < Mg^{2+} < Na^+ < F^-$
Increasing ionic size

16. The increasing order of the first ionization enthalpies of the elements B, P, S and F (Lowest first) is **[AIEEE 2006]**
(a) B < P < S < F (b) B < S < P < F
(c) F < S < P < B (d) P < S < B < F

17. Following statements regarding the periodic trends of chemical reactivity of the alkali metals and the halogens are given. Which of these statements gives the correct picture? **[AIEEE 2006]**
(a) Chemical reactivity increases with increase in atomic number down the group in both the alkali metals and halogens
(b) In alkali metals the reactivity increases but in the halogens it decreases with increase in atomic number down the group
(c) The reactivity decreases in the alkali metals but increases in the halogens with increase in atomic number down the group
(d) In both the alkali metals and the halogens the chemical reactivity decreases with increase in atomic number down the group

18. The charge/size ratio of a cation determines its polarizing power. Which one of the following sequences represents the increasing order of the polarizing power of the cationic species, K^+, Ca^{2+}, Mg^{2+}, Be^{2+}? **[AIEEE 2007]**
(a) $Ca^{2+} < Mg^{2+} < Be^+ < K^+$
(b) $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$
(c) $Be^{2+} < K^+ < Ca^{2+} < Mg^{2+}$
(d) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$.

19. In which of the following arrangements, the sequence is *not* strictly according to the property written against it? **[AIEEE 2008]**
(a) $HF < HCl < HBr, HI$: increasing acid strength
(b) $NH_3 < PH_3 < AsH_3 < SbH_3$: increasing basic strength
(c) $B < C < O < N$: increasing first ionization enthalpy
(d) $CO_2 < SiO_2 < SnO_2 < PbO_2$: increasing oxidising power

20. The correct sequence which shows decreasing order of the ionic radii of the elements is **[AIEEE 2010]**
(a) $Al^{3+} > Mg^{2+} > Na^+ > F^- > O^{2-}$
(b) $Na^+ > Mg^{2+} > Al^{3+} > O^{2-} > F^-$
(c) $Na^+ > F^- > Mg^{2+} > O^{2-} > Al^{3+}$
(d) $O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$

21. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I, having atomic number 9, 17, 35 and 53 respectively, is : **[AIEEE 2011 RS]**
(a) $F > Cl > Br > I$ (b) $Cl > F > Br > I$
(c) $Br > Cl > I > F$ (d) $I > Br > Cl > F$

22. The increasing order of the ionic radii of the given isoelectronic species is : **[AIEEE 2012]**
(a) $Cl^-, Ca^{2+}, K^+, S^{2-}$ (b) $S^{2-}, Cl^-, Ca^{2+}, K^+$
(c) $Ca^{2+}, K^+, Cl^-, S^{2-}$ (d) $K^+, S^{2-}, Ca^{2+}, Cl^-$

23. Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar ? **[JEE M 2013]**
(a) $Ca < S < Ba < Se < Ar$ (b) $S < Se < Ca < Ba < Ar$
(c) $Ba < Ca < Se < S < Ar$ (d) $Ca < Ba < S < Se < Ar$

Exercise-4 | Applied MCQs

1. An element X occurs in short period having configuration $ns^2\, np^1$. The formula and nature of its oxide is
(a) XO_3, basic (b) XO_3 acidic
(c) X_2O_3, amphoteric (d) X_2O_3 basic

2. The law of triads is applicable to a group of
(a) Cl, Br, I (b) C, N, O
(c) Na, K, Rb (d) H, O, N

3. Elements of IA group give flame colour due to
(a) low IP
(b) low m.pt.
(c) softness
(d) one electron in outermost shell.

4. The ionic radii of N^{3-}, O^{2-} and F^- are respectively given by
(a) 1.36, 1.40, 1.71 (b) 1.36, 1.71, 1.40
(c) 1.71, 1.40, 1.36 (d) 1.71, 1.36, 1.40

5. The first ionisation potential of aluminium is smaller than that of magnesium because
(a) Atomic size of Al > Atomic size of Mg.
(b) Atomic size of Al < Atomic size of Mg.
(c) Al has one electron in p - orbital
(d) None of these

6. Which of the following halides is not oxidized by MnO_2
(a) F^- (b) Cl^-
(c) Br^- (d) I^-

7. Which species has the maximum ionic radius
(a) Na^+ (b) O^{2-}
(c) F^- (d) Mg^{2+}

8. The valence shell of element A contains 3 electrons while the valence shell of element B contains 6 electrons . If A combines with B, the probable formula of the compound formed will be
(a) AB_2 (b) A_2B
(c) A_2B_3 (d) A_3B_2

9. Pauling scale of electronegativity of elements helps to determine
(a) covalent nature of an element
(b) position of an element in EMF series
(c) dipole moment of molecules
(d) polarity of bond.

10. The statement that is not correct for the periodic classification of elements is
(a) The properties of elements are the periodic functions of their atomic number
(b) Non-metallic elements are lesser in number than metallic elements
(c) The first ionization energies of elements along a period do not vary in a regular manner with increase in atomic number.
(d) For transition elements the d-sub shells are filled with electrons monotonically with increase in atomic number

11. Which is coloured ion
(a) $[Cu(NH_3)_4]^+$ (b) $[Cu(NH_3)_4]^{2+}$
(c) $[Zn(H_2O)_6]^{2+}$ (d) $[Ca(H_2O)_6]^{2+}$

12. Considering the elements from left to right in the second period of the periodic table, the gram atomic volume of the elements.

(a) first increases then decreases
(b) decreases
(c) increases at constant rate
(d) remains unchanged

13. Atomic radii of fluorine and neon in angstrom units are respectively given by

(a) 0.72 ; 1.60 (b) 1.60 ; 1.60
(c) 0.72 ; 0.72 (d) None of these

14. The screening effect of 'd' electrons is

(a) much less than s- electrons
(b) much more than s- electrons
(c) equal to s- electrons
(d) equal to p- electrons

15. An element having electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ forms

(a) acidic oxide (b) basic oxide
(c) amphoteric oxide (d) neutral oxide

16. Which pair of elements belongs to same group

(a) Elements with atomic no. 17 and 38
(b) Elements with atomic no. 20 and 40
(c) Elements with atomic no. 17 and 53
(d) Elements with atomic no. 11 and 33

17. Which transition involves maximum amount of energy

(a) $M^-(g) \longrightarrow M(g) + e$
(b) $M^-(g) \longrightarrow M^+(g) + 2e$
(c) $M^+(g) \longrightarrow M^{2+}(g) + e$
(d) $M^{2+}(g) \longrightarrow M^{3+}(g) + e$

18. A sudden jump between the values of second and third ionization energies of an element would be associated with the electronic configuration

(a) $1s^2 2s^2 2p^6 3s^1$ (b) $1s^2 2s^2 2p^6 3s^2 3p^1$
(c) $1s^2 2s^2 2p^6 3s^2 3p^2$ (d) $1s^2 2s^2 2p^6 3s^2$

19. The element with outer electronic configuration $3d^6 4s^2$ is a

(a) metalloid (b) non-metal
(c) transition metal (d) noble gas

20. In the process, $Cl(g) + e^- \xrightarrow{\Delta H} Cl^-(g); \Delta H$ is

(a) positive (b) negative
(c) zero (d) unpredictable

21. Among the following the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by

(a) $MnSO_4.4H_2O$ (b) $CuSO_4.5H_2O$
(c) $FeSO_4.6H_2O$ (d) $NiSO_4.6H_2O$

Hints & Solutions

EXERCISE 1

1. Mg^{2+}
3. Cs, He.
4. It lies in the 4th period and III B (or 13th) group.
5. Electron affinity : $A + e^- \rightarrow A^-$
   Reverse of ionization potential; $A^+ + e^- \rightarrow A$
8. (a) Decrease in size of atom and increase in nuclear charge.
   (b) Increase in atomic size.
9. NaF > NaCl > NaBr > NaI high melting point is due to high lattice energy.
10. (a) III is non-metal.
    (b) I is an alkali metal.
    (c) II is alkaline earth metal.
11. $$\underset{\text{Sod. oxide}}{Na_2O} + H_2O \longrightarrow \underset{\text{Sod. hydroxide}}{2NaOH}$$
    $$Cl_2O_7 + H_2O \longrightarrow \underset{\text{perchloric acid}}{2HClO_4}$$
12. (i) Highest ionisation enthalpy → element V Lowest ionisation enthalpy → element IV
    (ii) The correct order of increasing electron gain enthalpy is
    V < III < IV < II < I.
13. (a) AlP (aluminum phosphide)
    (b) Li_3N (lithium nitride)
    (c) CaS (calcium sulphide)

18. **(d)** **19.** **(c)** **20.** **(a)** **21.** **(d)** **22.** **(a)**
23. **(c)** **24.** **(c)** **25.** **(d)** **26.** **(b)** **27.** **(b)**
28. **(b)**

EXERCISE 2

1. **(b)** **2.** **(a)** **3.** **(a)** **4.** **(b)**
5. **(d)** **6.** **(b)** **7.** **(c)** **8.** **(b)**

9. (b) The atomic number 85 lies in the sixth period and since the next halogen, if discovered, will lie in the 7th period. Hence, its atomic number must be 85+32=117.

10. (d) All the elements in a group have the same valence shell electrons.

11. (c)

12. (d) Np is an-inner-transition element.

13. **(c)** **14.** **(a)** **15.** **(a)** **16.** **(a)**
17. **(a)** **18.** **(c)** **19.** **(b)** **20.** **(c)**

21. (b)

22. (a) F and O belong to 2nd period whereas Cl and Br belong to 3rd and 4th periods respectively. Hence the sequence of the E.N. is F > O > Cl > Br

23. (a) Higher the value of electronegativity difference, more polar is the bond.

24. **(c)** **25.** **(c)** **26.** **(b)** **27.** **(d)**

28. (a)

29. (d) P^{5+} has more effective nuclear charge and smaller size than P^{3+}.

30. **(d)** **31.** **(c)**

32. (a) Among the isoelectronic species, the anion having more negative charge would be the largest.

33. **(c)** **34.** **(b)** **35.** **(d)** **36** **(d)**

37. (c) Among the isoelectronic species, the cation having more positive charge would be the smaller in size.

38 **(d)** **39.** **(b)** **40.** **(c)**

41. (a) Due to inert gas configuration molecules F_2, Cl_2 and anion F^- have almost zero electron affinity.

42. (b)

43. (a) Addition of an electron to F^- and Cl^- ions will involve repulsions whereas in case of Na^+ ion, hence EA of Li^+ is highest among these.

44. (c) He has zero EA because of its completely filled subshells ($1s^2\,2s^2$).

45. (a) Since F has small size and its relatively compact 2 p-subshell's electron-electron repulsion, do not allow the addition of an extra electron whereas Cl has bigger size than F, allows the addition of an extra electron more easily.

46. (b) Due to stable electronic configuration and effective nuclear charge. IE_1 of N > C > B

47. (a) IE_1 is always less than IE_2.

48. (d) Amongst the isoelectronic species, the size of S^{2-} is largest hence its IE will be the lowest.

49. (b) Closed shell (Ne), half filled (P) and completely filled configuration (Mg) are the cause of higher value of I.E.

50. **(a)** **51.** **(b)** **52.** **(d)** **53.** **(b)**

54. (b) Due to presence of most penetrating one s-electron, hydrogen (1s) shows maximum IP out of list.

55. (b) IE_2 of Mg is lower than that of Na because in case of Mg^+, 3s-electron has to be removed where as in case of Na^+, an electron is removed from the stable inert gas configuration which is difficult.

56. (c)

57. (d) Inert gases due to completely filled and stable. s^2p^6 configuration show highest I.E.

58. (b)

59. (d) The additional π -molecular electron in O_2^- is added to the less stable antibonding orbital. Hence, it is easy to remove that electron from O_2^- ion. Thus I.E. (I.P.) of O_2^- is lowest.

60. (c)

61. (a) Higher the screening effect, lower is the I.E.

62. (c)

63. (b) The right sequence of I.E$_1$ of $Li < B < Be < C$.

64. (a)

65. (a) First period has H and He only out of which He is inert, hence, H behaves as a highly electropositive as well as electronegative.

66. (c) **67. (b)** **68. (c)** **69. (a)**

EXERCISE 3

1. (a) For isoelectronic species, size of anion increases as negative charge increases whereas size of cation decreases with increase in positive charge. Further ionic radii of anions is more than that of cations. Thus the correct order is

$$Ca^{++} < K^+ < Ar < Cl^- < S^{--}$$

2. (b)

3. (a) Proton affinity decreases in moving across the period from left to right due to increase in charge, within a group the proton affinities decreases from top to bottom.

Nitrogen family > Oxygen family > Halogens

4. (d) The stability of +1 oxidation state increases from aluminium to thallium i.e.

$Al < Ga < In < Tl$

5. (d) The smaller the atomic size, larger is the value of ionisation potential. Further the atoms having half filled or fully filled orbitals are comparitively more stable, hence more energy is required to remove the electron from such atoms.

6. (b) $O < S < F < Cl$

Electron gain enthalpy – 141, –200, – 333, – 349 kJ mol^{-1}

7. (c)

$_{12}Mg$	$_{15}P$	$_{17}Cl$	$_{20}Ca$
160_p	110	99	197 (pm)

$Cl < P < Mg < Ca$

$\therefore$ **Correct choice : (c)**

8 (a) IE$_1$ of Na = – Electron gain enthalpy of Na^+

= – 5.1 eV.

9. (b) The properties of elements change with a change in atomic number.

10. (b) Correct order of ionic size is Sn > Ce > Yb > Lu.

11. (a) The ionic radii follows the order

$$O^{2-} > F^- > Li^+ > B^{3+}$$

12. (d) $\underset{\text{Acidic}}{SO_2 > P_2O_3} > \underset{\text{Weak acidic}}{SiO_2} > \underset{\text{Amphoteric}}{Al_2O_3}$

13. (c) The valency of beryllium is +2 while that of aluminium is +3

14. (a) CaO is basic as it form strong base $Ca(OH)_2$ on reaction with water.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

CO_2 is acidic as it dissolve in water forming unstable carbonic acid.

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

Silica (SiO_2) is insoluble in water and acts as a very weak acid.

SnO_2 is amphoteric as it reacts with both acid and base.

$$SnO_2 + 2H_2SO_4 \longrightarrow Sn(SO_4)_2 + 2H_2O$$
$$SnO_2 + 2KOH \longrightarrow K_2SnO_3 + H_2O$$

15. (c) In a period the value of ionisation potential increases from left to right with breaks where the atoms have some what stable configuration. In this case N has half filled stable orbital. Hence has highest ionisation energy. Thus the correct order is

$$B < C < O < N \text{ not } B < C < N < O$$

16. (b) On moving along a period ionization enthalpy increases from left to right and decreases from top to bottom in a group. But this trend breaks in case of atoms having fully or half filled stable orbitals. In this case P has a stable orbitals filled electronic configuration hence its ionisation enthalpy is greater in comparision to S. Hence the correct order is $B < S < P < F$.

17. (b) The alkali metals are highly reactive because their first ionisation potential is very low and hence they have great tendency to loses electron to form unipositive ion. On moving down group- I from Li to Cs ionisation enthalpy decreases hence the reactivity increases. The halogens are most reactive elements due to their low bond dissociation energy, high electron affinity and high enthalpy of hydration of halide ion. However their reactivity decreases with increase in atomic number

18. (d) Smaller the size and higher the charge more will be polarising power of cation. Since the order of the size of cation is $K^+ > Ca^{++} > Mg^{++} > Be^{++}$. So the correct order of polarising power is

$K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

19. (b) In hydrides of 15th group elements, basic character decreases on descending the group i.e.

$NH_3 > PH_3 > AsH_3 > SbH_3$.

20. (d) All the given species contains 10 e^- each i.e. isoelectronic.
For isoelectronic species anion having high negative charge is largest in size and the cation having high positive charge is smallest.

21. (b) As we move down in a group electron gain enthalpy becomes less negative because the size of the atom increases and the distance of added electron from the nucleus increases. Negative electron gain enthalpy of F is less than Cl. This is due to the fact that when an electron is added to F, the added electron goes to the smaller n = 2 energy level and experiences significant repulsion from the other electrons present in this level. In Cl, the electron goes to the larger n = 3 energy level and consequently occupies a larger region of space leading to much less electron–electron repulsion. So the correct order is $Cl > F > Br > I$.

22. (c)

23. (c) On moving along a period from left to right I.E. increases and on moving down a group I.E. decreases.
hence correct order is : $Ba < Ca < Se < S < Ar$

EXERCISE 4

1. (c) $ns^2\ np^1$ is the electronic configuration of III A period. Al_2O_3 is amphoteric oxide

2. (a) According to the law of triads the atomic wt of the middle element is arithmatic mean of I and III. At wt of Br $\frac{\text{At.wt of Cl} \quad \text{At wt of I}}{2}$

3. (a) Due to low value of IP, valence electrons are. migrated to higher energy levels

4. (c) The ionic radii must follow the order $N^{3-} > O^{2-} > F^-$

5. (c) Al ($3s^2\ p^1$) and Mg ($3s^2$). Lower energy is required to remove $3p^1$ electron than $3s^1$ electron (penetrating effect is $s > p > d > f$) . Secondly Mg has stable electronic configuration than Al

6. (a) F_2 is strongest oxidising agent. F^- is not oxidised by MnO_2

7. (b) O^{2-} has minimum effective nuclear charge, hence has maximum ionic radius

8. (c) The element A is ns^2p^1 and B is ns^2p^4. They can form compound of the type A_2B_3

9. (d) Pauling scale of electronegativity helps to determine polarity of bond

10. (d)

11. (b) Due to presence of one unpaired electron $(Cu^{2+} = 3p^6d^9)$ the complex $[Cu(NH_3)_4]^{2+}$ is coloured

12. (a)

13. (a) In inert gases we have van der waal's radii which is always higher than atomic radii

14. (a) The screening effect follows the order $s > p > d > f$

15. (b) It is electronic configuration of alkali metal. Hence it will form basic oxide

16. (c) Atomic no. 17 (Cl) and 53 (I) are present in the same group

17. (d) The energy involved is ionisation energy (I.E.). Further the 3rd ionisation energy will be greater than the 2nd and 1st.

18. (d) There is a sudden jump in the value of IP when there is change of principal energy level

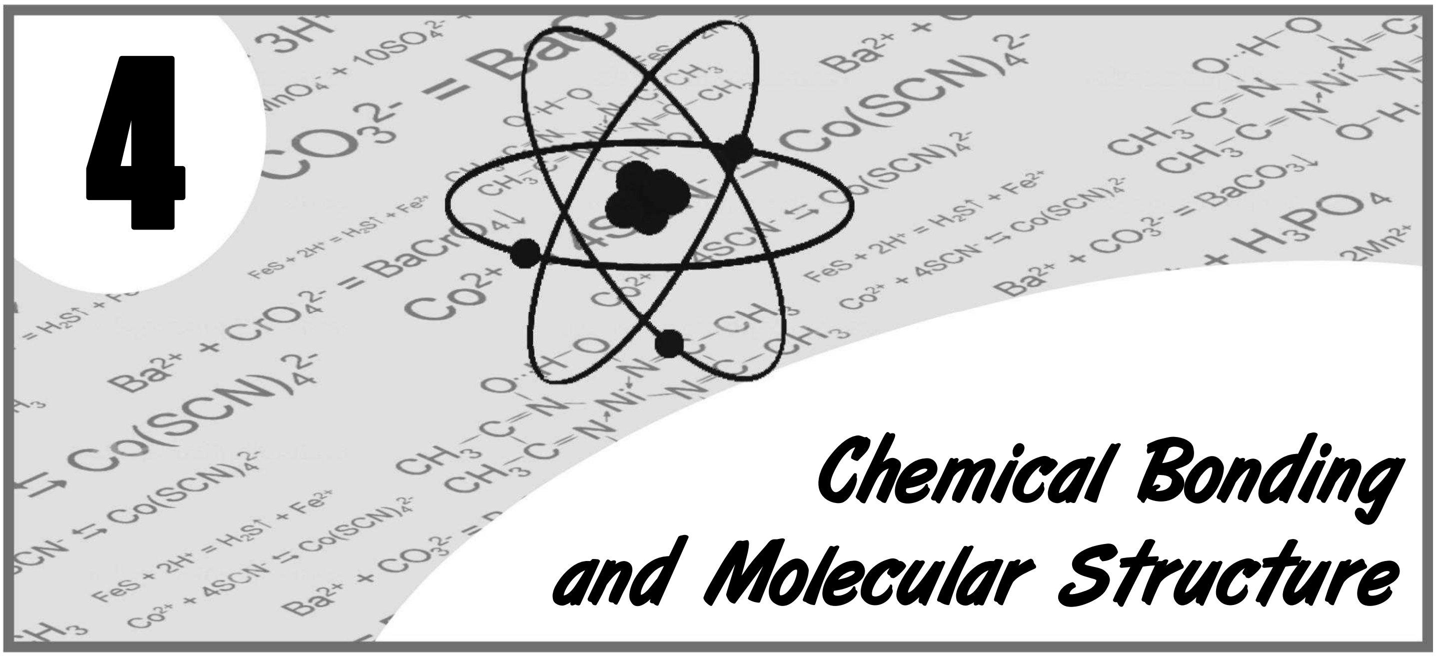
19. (c) In $3d^6 4s^2$ the differentiating electron enters d sub shell, Hence it represents transition metal, Fe.

20. (b) The process represents the first electron affinity which is always exothermic. Hence ΔH is negative

21. (b)

Ion =	Mn^{2+}	Cu^{2+}	Fe^{2+}	Ni^{2+}
EC=	$3d^5$	$3d^9$	$3d^6$	$3d^8$
Number of unpaired electrons =	5	1	4	2

Hence lowest paramagnetism is shown by $CuSO_4.5H_2O$



4

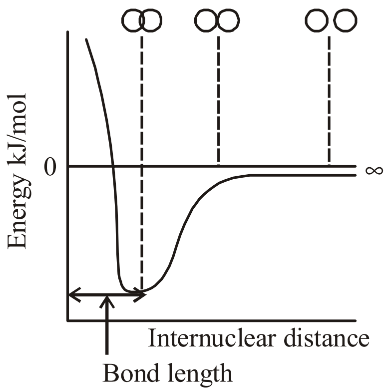
Chemical Bonding and Molecular Structure

CHEMICAL BOND :

A chemical bond is a sort of attraction which keeps the two atoms together. Thus depending upon the variety of force, there may be variety of chemical bonds.

REASONS FOR THE FORMATION OF A CHEMICAL BOND :

(i) **Energy concept :** When two atoms approach each other, the attractive and repulsive forces operate between them. The distance at which the attractive forces overweigh the repulsive forces is known as the bond distance, the potential energy of the system is minimum and the bond is said to be formed.



(ii) **Lewis and Langmuir (octet rule) :** Concept of stable electronic configuration.

Atoms enter into chemical bonding to acquire the stable inert gas electronic configuration. They can do so by losing, gaining or shairing of electrons.

Lewis symbols : The electrons present in the outermost energy level of an atoms and known as **valence electrons.** Only valence electrons are involved in the combilation of two atoms. The representation of valence electrons on an atom called **Lewis Symbol** eg.

(Second Period elements)

TYPES OF CHEMICAL BOND : (By Kossel and Lewis)

Depending upon the mode of acquiring the stable electronic configuration, the chemical bonds may be

i) Ionic or electrovalent bond
ii) Covalent bond
iii) Coordinate or dative bond
iv) Metallic bond
v) Hydrogen bond
vi) Weak van der Waal's forces of attraction

IONIC BOND (By Kossel and Lewis)

Ionic bond is formed by the complete transference of one or more valence electrons of one atom to the valence shell of the other atom. Both atoms are converted into ions and have the electronic configuration of nearest noble gases. The electrostatic attraction between these oppositely charged ions, which always tends to decrease the potential energy of the system is known as the ionic bond. Consider the formation of KCl. The electronic configuration of K, Cl and their ions (K^+ and Cl^-) are given below

K (19) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
K^+(18) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$ Inert gas (Ar) configuration
Cl (17) $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$
Cl^- (18) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$ Inert gas (Ar) configuration
$K^+ + Cl^- \rightarrow KCl$

The number of electrons lost or gained by an atom represent the electrovalency of the atom.

FACTORS AFFECTING THE FORMATION OF IONIC BOND :

There are three main factors

(i) **Ionisation energy (I) :** The lower the value of the ionisation energy of an atom greater will be the ease of formation of cation from it.
Note: the size of the cation is always smaller than the atom from which it is derived

(ii) **Electron affinity (E) :** The higher the electron affinity of an atom the greater will be the ease of formation of anion from it. The size of the anion is always larger than the atom from which it is derived.

(iii) **Lattice structure :** The electrostatic field of cations and anions extends in all directions, their union is not limited to form a single molecule, rather a cluster of ions, having three dimensional orderly arrangement, known as the lattice structure is formed.

(iv) **Lattice energy (U) :** The amount of heat evolved when one mole of ionic compound is formed from positive and negative ions in the crystalline form is known as the lattice energy.

BORN HABER CYCLE :

The formation of ionic compounds in terms of energy can be seen by Born Haber cycle *eg.* formation of NaCl is as follows

$$Na(s) \xrightarrow[S]{\text{sublimation}} Na(g) \xrightarrow[I]{\text{ionisation}} Na\ \ (g)\ \ \bar{e}$$

$$\frac{1}{2}Cl_2(g) \xrightarrow[\frac{1}{2}D]{\text{Dissociation}} Cl(g) \xrightarrow[-E]{\text{Addition of } e^-} Cl^-\ (g)$$

$$Na\ \ (g)\ \ Cl^-\ (g) \xrightarrow[-U]{\text{crystal formation}} NaCl(s)$$

where S = Heat of sublimation of Na metal
I = Ionisation energy of Na
D = Heat of dissociation of molecular chlorine
E = Electron affinity of chlorine atom
U = Lattice energy of NaCl

The amount of heat liberated (Q) in the overall reaction is the heat of formation of NaCl.

Thus $Q = S + I + 1/2\,D - E\ - U$

(The negative sign indicates heat is evolved or liberated)

The important energy terms are I, E and U. The more the negative value of Q, the greater will be the stability of ionic compound. Hence formation of ionic compound is favoured by

(i) **Low ionisation** energy (I) of the metal

(ii) **High electron** affinity (E) of the non-metal.

(iii) **Higher lattice** energy (U) of the compound
In general the alkali metals have low values of ionisation energy and halogens have high values of electron affinity. Hence they form the stable ionic compounds.

FACTORS AFFECTING LATTICE ENERGY (U) :

The force of attraction between two oppositely charged ions is given by well known Coulombs law as, $F \quad \dfrac{q_1q_2}{(4\pi\varepsilon_0)r^2}$

Where q_1 and q_2 are the charges of ions in coulombs, $4\pi\varepsilon_0$ is the permitivity factor and r is the distance between ions. Hence lattice energy depends upon

i) **Charge on ions :** The higher the charge on ions, the greater will be the force of attraction between them and greater will be the lattice energy. The order of lattice energy for different solids is as follows

bi - bivalent solids	>	uni - bivalent solids	>	uni - univalent solids
MgO	>	$CaCl_2$	>	NaCl

ii) **Size of ions :** The smaller the size of the ions, the lesser will be distance between them, the greater will be the force of attraction and so greater will be the lattice energy.

FAJAN'S RULE :

This rule is for **covalent character of an ionic bond.** Covalent character of an ionic bond is favoured by

i) Small positive ion
ii) Large negative ion
iii) Large charge on ions

Thus for a fixed cation, the larger the size of anion, the more the magnitude of the charge, the more is covalent character eg. covalent character of sodium halides follows the order

$$NaI > NaBr > NaCl > NaF$$

For fixed anion, the smaller the size of cation, the more the magnitude of the charge, the more is the covalent character eg.

$$BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$$

It has been observed that a cation having 18 ($s^2p^6d^{10}$) electrons in outermost shell (**pseudo noble gas configuration**) can polarise the anion more than cation having 8 (s^2p^6) noble gas electronic configuration. Hence CuCl is more covalent than NaCl. Similarly AgCl is more covalent than KCl.

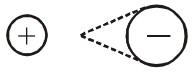
POLARISING POWER OF CATION :

It is generally represented by φ and also known as ionic potential charge density. It can be represented as

$$\varphi \quad \frac{\text{charge on cation}}{\text{radius of cation}}$$

POLARISATION :

When cation and anion come closer to each other, the electron cloud of anion is attracted towards the cation, some partial sharing of electrons take place, the anion is distorted and the effect is known as polarisation.

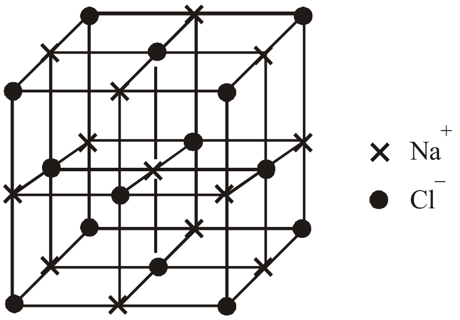


More the effect of polarisation, more is the sharing of electrons and the more is covalent character of ionic bond.

PROPERTIES OF IONIC COMPOUNDS :

The important properties are as follows

i) **Crystal structure :** The crystalline ionic compounds have well defined crystal structure or crystal lattice eg in NaCl each Na^+ is surrounded by six Cl^- ions and vice versa



Cubical structure of sodium chloride crystal

ii) **Melting and boiling points :** ionic compounds have high m.pt and b.pt due to powerful electrostatic force between ions.

iii) **Solubility :** They are generally soluble in polar solvents (having high value of dielectric constant). The solubility of ionic compounds decreases with increase in covalent character of ionic compounds. It is also governed by

- a) **Lattice energy :** More the lattice energy, lesser is the solubility, eg. sulphates and phosphates of Ba and Sr are insoluble in water due to high lattice energy.
- b) **Heat of hydration :** More the heat of hydration, more is the solubility. eg $AlCl_3$ though covalent in nature is soluble in water due to high value of heat of hydration.

iv) **Electrical conductivity :** In solid state they do not conduct electricity since there is no free movement of electrons but in molten state and in solution they conduct electricity.

v) **Isomorphism -** NaF and MgO are isomorphous due to similar electronic structure

Na	F^-	Mg	O^{--}
2,8	2,8	2,8	2,8

Similarly K_2S and $CaCl_2$ are isomorphous

K^+	S^{2-}	K^+	Cl^-	Ca^{++}	Cl^-
2,8,8	2,8,8	2,8,8	2,8,8	2,8,8	2,8,8

VARIABLE ELECTROVALENCY :

It is due to unstable atomic core and inert pair effect. When valence electrons from a metal atom are removed it leaves behind the atomic core or atomic kernel. The latter with 2 or 8 electrons are stable. In case of transition elements the atomic cores are not very stable. They may lose one or more electrons thus exhibiting variable electrovalency eg. iron and copper etc.

Fe (2, 8, 14, 2)	$1s^2, 2s^2p^6, 3s^2p^6\,d^6, 4s^2$
Fe^{++} (2, 8, 14)	$1s^2, 2s^2p^6, 3s^2p^6\,d^6$
Fe^{+++} (2, 8, 13)	$1s^2, 2s^2p^6, 3s^2p^6\,d^5$

The energy difference between 4s and 3d subshell is not very large.

INERT PAIR EFFECT :

The reluctance of s electron pair of some heavy elements (p - block elements present at the bottom of group) to take part in bonding is known as inert pair effect. Thus Tl ($6s^2, 6p^1$) show +1 electrovalence. Similarly Sn($5s^2p^2$) and Pb ($6s^2p^2$) show + 2 oxidation state commonly. In such elements the lower oxidation state is more stable than higher oxidation state.

COVALENT BOND : (By lewis and Langley)

According to **G. N. Lewis** atoms may also combine by sharing of electrons present in their outermost shells and attain noble gas electronic configuration. One shared pair of electrons constitute a single bond, two electron pairs constitute a double bond and so on. The bonds thus formed ore known as covalent bonds.

COVALENCY :

It is the number of electron pairs shared by one atom of the element in combination with other atoms in a molecule.

Variable Covalency :

Generally the covalency of an element is equal to the total number of unpaired electrons in s– and p– orbitals of the valence shell. For example

$_6C \quad 1s^2, 2s^1, 2p^1{}_x, 2p^1{}_y, 2p^1{}_z$ covalency of carbon = 4

$_8O \quad 1s^2, 2s^2, 2p^2{}_x, 2p^1{}_y, 2p^1{}_z$ covalency of oxygen = 2

The variable covalency is shown by elements having vacant d-orbitals in their valence shell. The unpairing of the s- and p-electrons is possible by promoting them to d- orbitals. For example

Ground state Covalency of sulphur = 2

$_{16}S \quad 1s^2, 2s^2, 2p^6, 3s^2, 3p^2{}_x, 3p^1{}_y, 3p^1{}_z$

First excited state Covalency of sulphur = 4

$= 3s^2, 3p^1{}_x, 3p^1{}_y, 3p^1{}_z, 3d^1{}_{xy}$

Second excited state Covalency of sulphur = 6

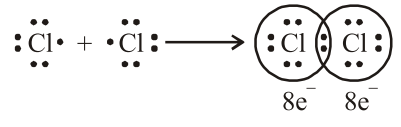
$= 3s^1, 3p^1{}_x, 3p^1{}_y, 3p^1{}_z, 3d^1{}_{xy}, 3d^1{}_{yz}$

Similarly, other than fluorine, the halogens have high covalencies equal to 3, 5 and 7. Phosphorous shows covalencies equal to 3 and 5.

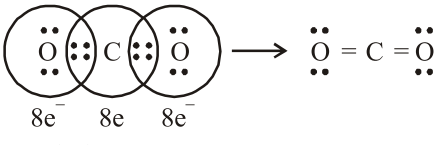
The elements having no d-orbitals do not exhibit variable covalency

EXAMPLES OF COVALENT COMPOUNDS :

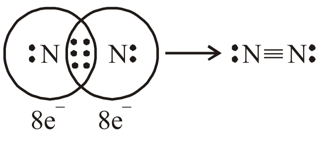
(i) Chlorine (Cl_2)



(ii) Carbon dioxide (CO_2)



(iii) Nitrogen (N_2)



NATURE OF COVALENT BOND :

The nature of covalent bond is explained by

(i) **Heitler - london theory** Valence bond theory
(ii) **Pauling - slater theory**
(iii) **Hund - mulliken theory** } Molecular orbital theory

VALENCE BOND THEORY :

A covalent bond is formed by the overlapping between two half filled atomic orbitals having electrons with opposite spin.

i) Sigma bond (σ bond) - The following overlappings result in the formation of sigma bond

a) s - s overlapping
b) s - p overlapping
c) p - p head on overlapping

ii) pi - bond (π - bond) - It is formed by the sidewise or lateral overlapping between unhybridised *p* - atomic orbitals

p - p side wise or lateral overlapping.

- π bond is a weaker bond than σ - bond.
- The strength of σ bond depends upon the extent of overlapping between atomic orbitals. Greater the overlapping stronger the σ - bond is. It follows the following order

  s – s > s – p > p – p
- Single bond is always σ bond.
- In multiple bonds only one is σ bond, others are π - bonds
- π - bond is not formed by hybrid orbitals.

LIMITATIONS OF VALENCE BOND THEORY :

i) It fails to explain the magnetic properties of some molecules
ii) Bonding in electron deficient compounds.

MOLECULAR ORBITAL THEORY OR HUND-MULLIKEN THEORY :

According to this theory the atomic orbitals combine to form the molecular orbitals. The number of molecular orbitals formed are equal to the number of atomic orbitals involved and they belong to the molecule.

i) The molecular orbitals are formed by LCAO method (linear combination of atomic orbitals) *i.e.* by addition or subtraction of wave functions of individual orbitals thus

$$\Psi_{MO} = \Psi_A \quad \Psi_B$$

$$\Psi_b = \Psi_A + \Psi_B$$

$$\Psi_a = \Psi_A - \Psi_B$$

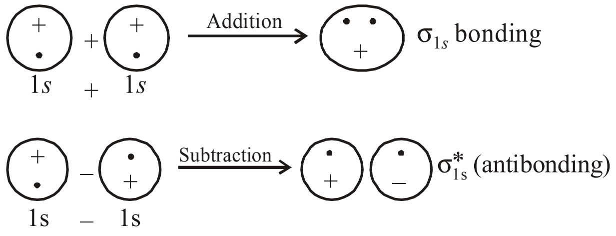
ii) Molecular orbital of lower energy is known as bonding molecular orbital and of higher energy is known as antibonding molecular orbital.

iii) Molecular orbitals are characterised by a set of quantum numbers.

iv) Aufbau rule, Pauli's exclusion principle and Hund's rule are applicable to molecular orbitals.

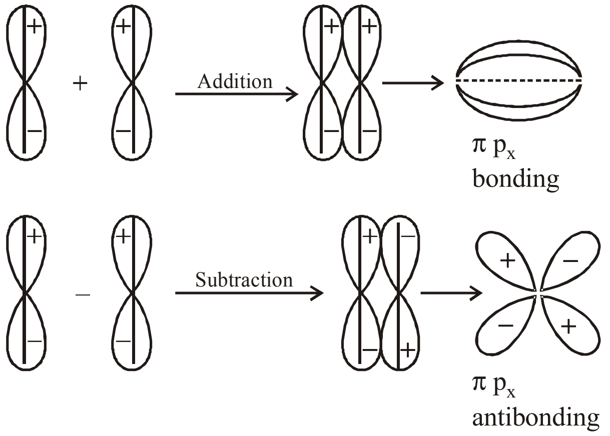
v) Their shape is governed by the shape of atomic orbitals eg by s - s and *p* - *p* overlapping we have

(a)

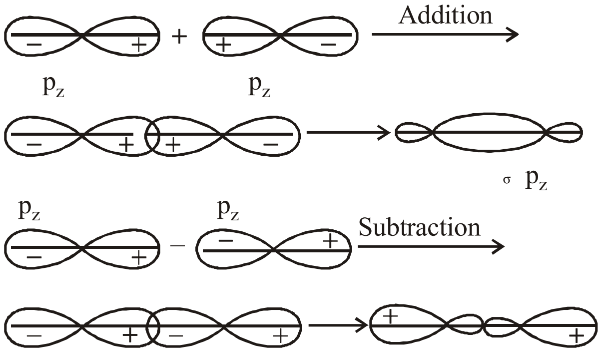


(b) $p_x + p_x$ or $p_x - p_x$ and $p_y + p_y$ or $p_y - p_y$ overlap to form π bond.

p_x p_x



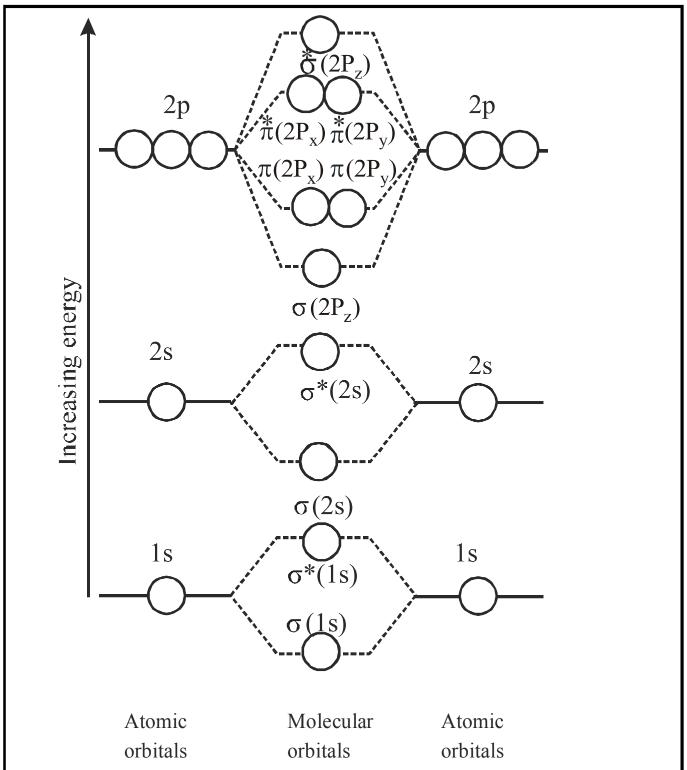
(c) p_z p_z form σ bond and their combination is according to inter nuclear distance.



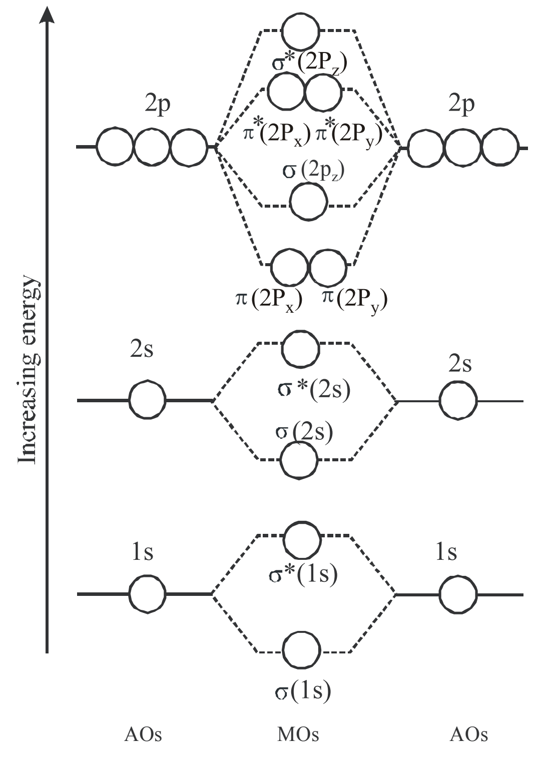
ENERGY LEVEL DIAGRAM :

When two atoms A and B are brought nearer to one another, the atomic orbitals present in atom A undergo overlapping with atomic orbitals present in atom B, having the same energy and molecular orbitals are formed. There are two types of energy level diagrams

i) for molecules upto N_2 (here the energy difference between 2s and 2p orbitals is small)
ii) for molecules after N_2 (here the energy difference between 2s and 2p orbitals is large and they cannot interact)



Molecular orbital energy level diagram for molecules after N_2



Molecular orbital energy level diagram for molecules upto N_2

Simply we can write

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < [\pi 2p_x = \pi 2p_y]$$

$$< [\pi^* 2p_x = \pi^* 2p_y] < \sigma^* 2p_z$$

ELECTRONIC CONFIGURATION / BOND ORDER OF SIMPLE DIATOMIC MOLECULES :

The electronic configuration and the bond order in case of simple diatomic molecules can be obtained by filling the molecular orbitals by applying Aufbau principle and Hund's rule

Bond order $= \frac{1}{2}$ [Number of bonding electrons - Number of antibonding electrons]

The magnetic properties of molecules can also be ascertained

BONDING IN SOME DIATOMIC MOLECULES AND IONS :

(a) **Hydrogen molecule (H_2)** - Total number of electrons = 2, filling in molecular orbitals we have

$\sigma 1s^2$

$$\text{Bond order} = \frac{(N_b - N_a)}{2} = \frac{2-0}{2} = \frac{2}{2} = 1$$

Hence there is a single bond between two hydrogen atoms (H - H). Since there is no unpaired electron, H_2 is diamagnetic

(b) **Helium molecule (He_2)** - The total number of electrons = 4 and filling in molecular orbitals we have

$\sigma 1s^2 < \sigma^* 1s^2$

$$\text{Bond order} = \frac{(N_b - N_a)}{2} = \frac{2-2}{2} = 0$$

Hence He_2 molecule cannot exist

(c) **Nitrogen molecule (N_2)** - The total number of electrons = 14 and filling in molecular orbitals we have

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \pi 2p_x^2 = \pi 2p_y^2 < \sigma 2p_z^2$$

$$\text{Bond order} = \frac{(N_b - N_a)}{2} = \frac{10-4}{2} = \frac{6}{2} = 3 \quad \therefore \ddot{N} \equiv \ddot{N}$$

(d) **Oxygen molecule (O_2)** - Total number of electrons = 16 and electronic configuration is

$$\sigma 1s^2 \quad \sigma^* 1s^2 \quad \sigma 2s^2 \quad \sigma^* 2s^2 \quad \sigma 2p_z^2$$

$$\pi 2p_x^2 = \pi 2p_y^2 < \pi^* 2p_x^1 = \pi^* 2p_y^1$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-6}{2} = \frac{4}{2} = 2$$

As shown by electronic configuration the O_2 molecule contains two unpaired electrons, hence it is **paramagnetic in** nature

(e) O_2^+ ion - Total number of electrons (16 – 1) = 15. Electronic configuration

$$\sigma 1s^2 \quad \sigma^* 1s^2 \quad \sigma 2s^2 \quad \sigma^* 2s^2 \quad \sigma 2p_z^2$$

$$\pi 2p_x^2 = \pi 2p_y^2 < \pi^* 2p_x^1$$

$$\text{Bond order } \frac{N_b - N_a}{2} = \frac{10-5}{2} = \frac{5}{2} = 2\frac{1}{2}$$

It is paramagnetic

(f) O_2^- (Super oxide ion) Total number of electrons $(16 \quad 1) \quad 17$.
Electronic configuration

$$\sigma 1s^2 \quad \sigma^* 1s^2 \quad \sigma 2s^2 \quad \sigma^* 2s^2 \quad \sigma 2p_z^2$$

$$\pi 2p_x^2 \quad \pi 2p_y^2 \quad \pi^* 2p_x^2 \; \pi^* 2p_y^1$$

Bond order

$$\frac{(N_b - N_a)}{2} \quad \frac{10 - 7}{2} \quad \frac{3}{2} \quad 1\frac{1}{2}$$ It is paramagnetic

(g) **Peroxide ion** O_2^{2-} **-** Total number of electrons $(16 \quad 2) \quad 18$. The electronic configuration is

$$\sigma 1s^2 \quad \sigma^* 1s^2 \quad \sigma 2s^2 \quad \sigma^* 2s^2 \quad \sigma 2p_z^2 \quad \pi 2p_x^2$$

$$\pi 2p_y^2 \quad \pi^* 2p_x^2 \quad \pi^* 2p_y^2$$

Bond order $\frac{N_b - N_a}{2} \quad \frac{10 - 8}{2} \quad \frac{2}{2} \quad 1$

It is diamagnetic

(h) **Carbon monoxide (CO)** - Total number of electrons $= (6 + 8) = 14$

The electronic configuration is

$$\sigma 1s^2 \quad \sigma^* 1s^2 \quad \sigma 2s^2 \quad \sigma^* 2s^2 \quad \sigma 2p_z^2 \quad \pi 2p_x^2 \quad \pi 2p_y^2$$

Bond order $\frac{N_b - N_a}{2} \quad \frac{10 - 4}{2} \quad \frac{6}{2} \quad 3$

It is diamagnetic

(i) **Nitric Oxide (NO)** - Total number of electrons $= (7 + 8) = 15$

$$\sigma 1s^2 \quad \sigma^* 1s^2 \quad \sigma 2s^2 \quad \sigma^* 2s^2 \quad \sigma 2p_z^2$$

$$\pi 2p_x^2 \quad \pi 2p_y^2 \quad \pi^* 2p_x^1$$

Bond order $\frac{N_b - N_a}{2} \quad \frac{10 - 5}{2} \quad \frac{5}{2} \quad 2\frac{1}{2}$

It is paramagnetic.

TABLE : M.O. CONFIGURATION OF SOME MOLECULES

Molecule or ion	*total no. of electrons*	*MO configuration*	*Bond order*	*Magnetic behaviour*
He_2	4	$(\sigma 1s^2), (\sigma^* 1s)^2$	0	Diamagnetic
N_2	14	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2$	3	Diamagnetic
O_2	16	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2$ $(\pi^* 2p_x)^1(\pi^* 2p_y)^1$	2	Paramagnetic
O_2^+	15	Remove one electron from $\pi^* 2p_y$ from O_2	2.5	Paramagnetic
O_2^-	17	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2$ $(\pi^* 2p_x)^2(\pi^* 2p_y)^1$	1.5	Paramagnetic
O_2^{2-}	18	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2$ $(\pi^* 2p_x)^2(\pi^* 2p_y)^2$	1	Diamagnetic
F_2	18	Same as above	1	Diamagnetic
Ne_2	20	18 as above and $(\sigma^* 2p_z)^2$	0	Diamagnetic
CO	14	Same as in N_2	3	Diamagnetic
NO	15	Same as in O_2^+	2.5	Paramagnetic
NO^+	14	Same as in N_2	3	Diamagnetic
NO^{2+}	13	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^1$	2.5	Paramagnetic
NO^-	16	Same as in O_2	2	Paramagnetic
CN	13	Same as in NO_2^+	2.5	Paramagnetic
CN^-	14	Same as in N_2	3	Diamagnetic

IONIC CHARACTER OF A COVALENT BOND :

i) ***By electronegativity difference -*** It is determined by the electronegativity difference of the participating atoms. The higher the electronegativity difference between the two atoms, more is the percentage ionic character of a covalent bond. The mathematical equations for calculating, the % ionic character are

a) Pauling equation % ionic character

$$= 100\left[1 - \exp^{-\frac{1}{4}(X_A - X_B)}\right]$$

b) Hannay and smith equation

$$= 16\,(x_A - x_B) + 3.5\,(x_A - x_B)^2$$

where x_A and x_B are the electronegativities of atoms

Percentage ionic character and the electronegativity difference

x_A - x_B value	***% ionic character***	***x_A - x_B value***	***%ionic character***
0.1	0.5	1.7	51.0
0.4	4.0	2.0	63.0
0.7	12.0	2.3	74.0
1.0	22.0	2.6	82.0
1.4	39.0	2.9	88.0

ii) ***By dipole moment -*** By dipole moment the % ionic character of a covalent bond can be obtained from the following equation

% ionic character

$$\frac{\text{observed dipole moment of bond}}{\text{calculated dipole moment of bond}} \times 100$$

Example : Calculate the percentage ionic character of HCl molecule. The bond length is 1.275 A° and observed dipole moment is 1.03 D

Solution - For 100% ionic character the dipole moment should be

$$\mu = e \times d = 4.8 \times 10^{-10} \times 1.275 \times 10^{-8} = 6.12\text{ D}$$

The observed dipole moment is = 1.03 D

$$\therefore\ \%\text{ ionic character}\quad \frac{1.03}{6.12} \times 100 \quad 16.83\%$$

CHARACTERISTICS OF COVALENT COMPOUNDS :

i) **Physical state** - They may be gases, liquids or solids

ii) **Crystal structure** - They may exist as simple molecules held together by weak forces, giant molecules united by covalent link eg diamond, silicon carbide, alumina, aluminium nitride etc and can have layer structure. eg graphite.

iii) **Solubility** - Generally soluble in non polar solvents.

iv) **Melting/ boiling points -** Low as compared to ionic compounds.

v) **Electrical conductivity -** Being non electrolytes they do not conduct electricity, graphite does due to presence of free electrons.

vi) **Stereo isomerism** - They exhibit structural and stereo - isomerism both

HYBRIDISATION :

Hybridisation is the redistribution of energy levels at the time of formation of molecules. It may also be defined as intermixing of atomic orbitals of nearly the same energy and resulting in the formation of new atomic orbitals same in number and identical in all respects (shape, energy and size). The new atomic orbitals are known as hybrid atomic orbitals.

The completely filled or half filled atomic orbials can take part in hybridisation and hybrid atomic orbitals form stronger bonds.

Shape of molecules / ions having only bond pair of electrons

No. of bp of electrons at the central atom	***Hybridisation***	***Bond angle***	***Shape of molecule***	***Examples***
2	sp	180°	Linear	BeH_2, BeX_2 (X = F, Cl, Br, I), CO_2, $HgCl_2$, $ZnCl_2$, HCN, $MgCl_2$, C_2H_2 (alkynes), $[Ag(NH_3)_2]^+$ $[Ag(CN)_2]^-$
3	sp^2	120°	Trigonal planar	$[BeF_3]^-$, BF_3, BCl_3, BBr_3, BH_3, $AlCl_3$, SO_3, C_2H_4 (alkenes), NO^- , CO^- , C_6H_6
4.	sp^3	109.5°	Tetrahedral	SiX_4, $SnCl_4$, CH_4 (alkanes), CX_4, $[BeF_4]^{2-}$, SO^- , ClO_4^- , NH , BF^- , PO^-
4.	dsp^2	90°	Square planar	$[Ni(CN)_4]^{2-}$, $[PtCl_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$
5.	sp^3d	90°, 120°	Trigonal bipyramidal	PCl_5, PF_5, $SbCl_5$
6.	sp^3d^2	90°	Octahedral	SF_6, SeF_6, TeF_6, PF^- , $SnCl^-$ $[CrF_6]^{3-}$, $[Co(NH_3)_6]^{3+}$, $[SiF_6]^{2-}$, $[Co(CN)_6]^{3-}$, $W(CO)_6$
7.	sp^3d^3	90°, 72°	Pentagonal bipyramidal	IF_7

Geometry of molecules/ions having bond pair as well as lone pair(s) of electrons

Type of molecule	*Bond pairs*	*No. of lone pairs of electrons*	*Hybridi- sation*	*Bond angle*	*Expected geometry*	*Actual geometry*	*Examples*
AX_3	2	1	sp^2	120°	Trigonal planar	V-shape, Bent, Angular	SO_2, $SnCl_2$, NO^-
AX_4	2	2	sp^3	109° 28'	Tetrahedral	V-shape	H_2O, H_2S, SCl_2, $PbCl_2$, OF_2, NH^- , ClO^-
AX_4	3	1	sp^3	109° 28'	Tetrahedral	Pyramidal	NH_3, NF_3, PCl_3, PH_3, AsH_3, ClO^- , H_3O^+
AX_5	3	2	sp^3d	90°	Trigonal bipyramidal	T- shape	ICl_3, IF_3, ClF_3
AX_5	2	3	sp^3d	180°	Trigonal bipyramidal	Linear	XeF_2, I_3^-, ICl_2^-
AX_6	5	1	sp^3d^2	90°	Octahedral Pyramidal	Square	ICl_5, BrF_5, IF_5
AX_6	4	2	sp^3d^2	-	Octahedral	Square planar	XeF_4, ICl_4^-
AX_7	6	1	sp^3d^3	-	Pentagonal bipyramidal	Distorted octahedral	XeF_6

METHOD FOR FINDING THE TYPE OF HYBRIDISATION :

Apply the following formula to find the hybridisation of central atom.

$$\frac{1}{2}\left\{\begin{array}{l}\text{Number of valence electrons of central atom}\\ \text{number of monovalent atoms attached to it}\\ \text{negative charge if any} - \text{positive charge if any}\end{array}\right\} \quad z$$

Value of z	2	3	4	5	6	7
Hybridisation	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

Examples :

i) Hybridisation of $NH_3 = \frac{1}{2}[5+3+0-0] = 4; sp^3$

ii) Hybridisation of $H_2O = \frac{1}{2}[6+2+0-0] = 4; sp^3$

iii) Hybridisation of $SO_3 = \frac{1}{2}[6+0+0-0] = 3; sp^2$

iv) Hybridisation of $SO_4^{2-} = \frac{1}{2}[6+0+2-0] = 4; sp^3$

v) Hybridisation of $CO_3^{2-} = \frac{1}{2}[4+0+2-0] = 3; sp^2$

vi) Hybridisation of $PCl_5 = \frac{1}{2}[5+5+0-0] = 5; sp^3d$

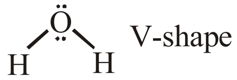
vii) Hybridisation of $SF_6 = \frac{1}{2}[6+6+0-0] = 6; sp^3d^2$

Note : Species having same hybridisation are isostructral in nature.

VSEPR THEORY VALENCE SHELL ELECTRON PAIR REPULSION THEORY :

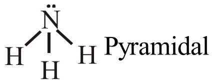
The following types of repulsions between different pair of electrons change the regular geometry of the molecule. Lone pair - lone pair repulsion > Lone pair - bond pair repulsion > Bond pair - bond pair repulsion or **lp - lp > lp - bp > bp - bp eg:**

(i) ***Shape of H_2O molecule -*** The hybridisation of oxygen is sp^3 and angle should be 109° 28'. But actually the ∠ HOH angle is 104.5°. The VSEPR theory explains this fact

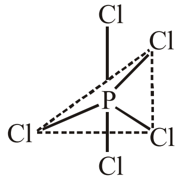


All types of repulsions (lp–lp, lp–bp, bp–bp) are present in H_2O.

(ii) ***Shape of NH_3 molecule -*** The hybridisation of nitrogen is sp^3. The H–N–H angle is 107.5° instead of 109°28'. Due to **lp–bp** and **bp–bp** repulsions the value of angle change



(iii) ***Structure of PCl_5 :*** The phosphorous is in sp^3d hybridised form. The five hybrid orbitals are not equivalent. The bonds pointing towards the three corners of equilateral triangle are known as **equatorial bonds** making an angle of 120° between them. The remaining two bonds are at right angle to the plane of three make an angle of 90° and are called **axial bonds.** The axial bonds are slightly longer and weaker then equatorial bonds. Since they suffer more repulsive interaction from the later. Consequently PCl_5 is very reactive molecule.



CO-ORDINATE COVALENT BOND OR DATIVE BOND :

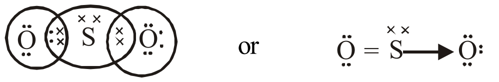
When both the elctrons for sharing between two atoms are contributed by one atom only the bond formed is known as coordinate bond or dative bond.

In terms of orbital theory the co-ordinate covalent bond is formed by overlapping between empty and completely filled atomic orbitals.

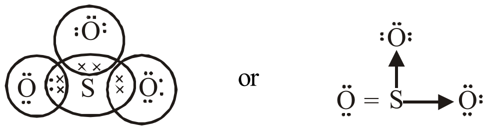
The atom donating the pair of electrons is called donor and the atom which accepts the pair of electrons is called acceptor. The compounds containing coordinate bonds are known as co-ordination compounds. The bond is represented by an arrow (→) pointing head towards the acceptor.

Once the coordinate bond is formed it is indistinguishable from a covalent bond. Examples

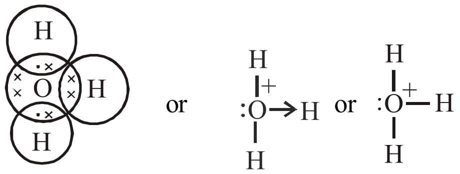
(i) Formation of SO_2



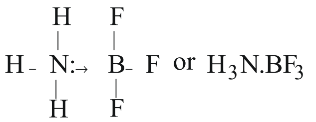
ii) Formation of SO_3



iii) Formation of Hydroxonium ion



iv) NH_3 and BF_3 form addition product by Co-ordinate covalent bond



$H_3N \rightarrow BF_3$ or $H_3N.BF_3$

CHARACTERITICS OF CO-ORDINATE COMPOUNDS

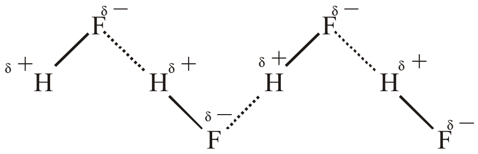
Co-ordinate compounds have volatile character in between ionic and covalent compounds. Other properties like solubility, electrical conductivity and stereo isomerism are similar to covalent compounds.

HYDROGEN BOND :

It may be defined as the force of attraction existing between hydrogen atom covalently bonded to highly electronegative atom (N, O or F) and the electronegative atom belonging to another molecule of the same or different substance. It is represented by dotted lines

H–F .... H–F .... H–F

The chains possess a **Zig-Zag** structure



Hydrogen bond is purely electrostatic in nature. It is a weak bond, the strength of the strongest being about 5 - 10 kcal per mole. The more the electronegativity of atom involved in H - bonding, the more is the bond strength eg.

H···F > H···O > H···N
10 kcal/mole > 7 kcal/mole > 2.0 kcal/mole

Types of hydrogen bonds - Hydrogen bond is of two types

(i) Intermolecular H-bonding (Association). H–bonding involving two or more molecules.

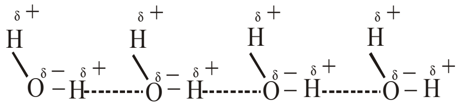
(ii) Intramolecular H-bonding (chelation). H–bonding taking place within single molecule.

(i) Applications of intermolecular H-bonding.

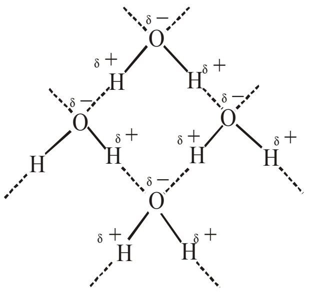
(a) Water - Water has the lowest molecular weight among the hydrides of group 16 elements yet it has the highest melting and boiling points

	H_2O	H_2S	H_2Se	H_2Te
Melting point	0ºC	-85.5ºC	-66ºC	-51.2ºC
Boiling point	100ºC	-60.4ºC	-41.5ºC	+2ºC

It is due to intermolecular H - bonding through which water molecules associate



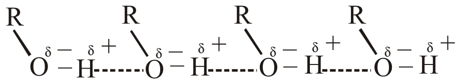
(b) Ice has less density than water - In crystal structure of ice every water molecule is associated with four other water molecules by H-bonding in a tetrahedral fashion



It gives rise to cage likes tetrahedral structure of ice with large empty spaces. On melting the ice H-bonds are broken and space between water molecules decreases and density of water increases upto 4ºC. Above 4ºC more H - bonds are broken, the water molecules move apart from each other and the density again decreases. Thus water has maximum density at 4ºC.

(c) Alcohols - The marked difference between the melting and boiling points of alcohols and corresponding mercaptans is also due to association.

	CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH
Boiling point	64.4ºC	78ºC	97ºC	117ºC
	CH_3SH	C_2H_5SH	C_3H_7SH	C_4H_9SH
Boiling point	5.8ºC	37ºC	67ºC	97ºC

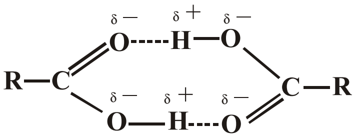


(d) Amides - Amides associate and have higher melting and boiling points

$$H_2N-\overset{R}{\overset{|}{C}}\;\overset{\delta-}{O}\cdots\cdots\overset{\delta}{H}-\overset{H}{\overset{|}{N}}-\overset{R}{\overset{|}{C}}\;\overset{\delta-}{O}\cdots\cdots\overset{\delta}{H}-\overset{H}{\overset{|}{N}}-\overset{R}{\overset{|}{C}}\;O$$

(e) Amines - Primary and secondary amines are associated and have higher boiling points than isomeric tertiary amines.

(f) Fatty acids - In organic solvents, fatty acids form a dimer

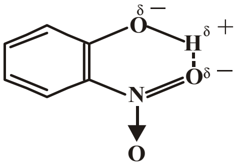


It is confirmed by electron diffraction method.

(ii) Applications of Intramolecular H - bonding.

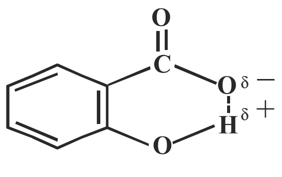
When the H - bonding takes place within a single molecule this is known as intramolecular H - bonding. It also effects the physical and chemical properties of compound.

(a) Volatile character of nitrophenols - o-nitrophenol is more volatile (b.pt 214ºC) as compared to meta (b.pt 290ºC) and para (b.pt 279ºC). It is due to chelation

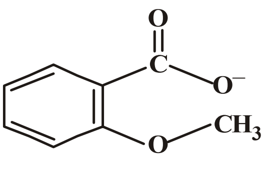


In meta and para isomer chelation is not possible due to the formation of desired size of ring. They therefore associate to some extent and have higher B.P

(b) Salicylic acid is stronger acid than *o* - methoxy benzoic acid

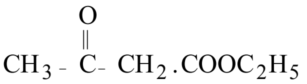


H-bonding in salicylate ion



No-H-bonding in o-methoxy benzoate ion

(c) Ethyl aceto acetate - It exists in two forms



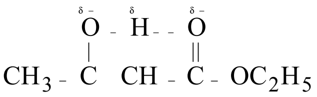
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2.COOC_2H_5$$

Keto form

$$CH_3-\overset{OH}{\overset{|}{C}}\;CH.COOC_2H_5$$

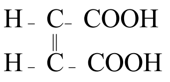
Enol form

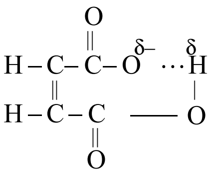
Enolic form is more volatile due to chelation



$$CH_3-\overset{\overset{\delta-}{O}}{\overset{|}{C}}\;\overset{\overset{\delta}{H}}{CH}-\overset{\overset{\delta-}{O}}{\overset{\|}{C}}-OC_2H_5$$

(d) Maleic acid is stronger acid than fumaric acid



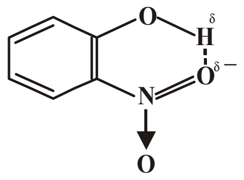


Maleic acid Chelation in maleate ion

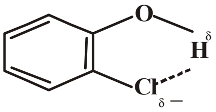
(e) Acid character of nitrophenols. It follows the following order

p - nitrophenol > o - nitrophenol > m - nitrophenol

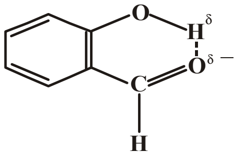
Acid character of o - nitrophenol is suppressed by chelation



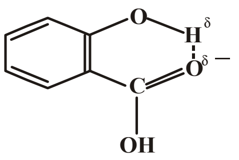
(f) Other compounds showing intramolecular H - bonding



o-Chlorophenol



o-hydroxy benzaldehyde



o-hydroxy benzoic acid

METALLIC BOND :

It has been found that metals have generally low ionisation energies indicating that valence electrons are weakly bound to the atomic kernel (or core).

Metals contain few valence electrons and valence orbitals which are empty. Thus valence electrons are completely delocalised and are frequently exchanged between atoms. The atoms thus acquire a positive charge and are arranged in a regular fashion (lattice structure).

⊕ $\bar{e}$ ⊕ $\bar{e}$ ⊕ $\bar{e}$ ⊕
⊕ $\bar{e}$ ⊕ $\bar{e}$ ⊕ $\bar{e}$ ⊕
⊕ $\bar{e}$ ⊕ $\bar{e}$ ⊕ $\bar{e}$ ⊕

The valence electrons form an “electron gas” or "sea of electrons". The attractive interaction between the mobile electrons and a number of ⊕ ions constitutes a weak bond known as metallic bond.

CONSEQUENCES OF METALLIC BOND :

1. ***Electrical conductivity* -** It is due to presence of mobile valence electrons.
2. ***Thermal conductivity* -** On heating one part of metal, the K.E. of electrons is increased and they conduct heat to the other parts of the metal.
3. ***Metallic lustre*-** The mobile elctrons are promoted to excited states by absorption of light and on coming back from the excited state light of all wavelengths in the visible region is emitted. The surface, therefore emits metallic lustre.
4 ***Malleability* -** Metals can be made thin sheets
5. ***Ductility* -** Metals can be drawn into wires since metal kernels can easily be shifted.
6. ***Electrical conductivity decreases with temperature* -** It is due to random motion of mobile electrons which increases with increase of temperature.

van der Waal's Forces :

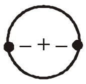
Attractive forces between uncharged molecules are known as van der Waals forces. These forces may be divided into three groups

(i) ***Dispersion or London forces***. These are due to transient polarisation.

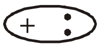
(ii) ***Dipole - dipole attraction.*** These are due to permanent polarisation.

(iii) ***Dipole-Induced fipole forces***

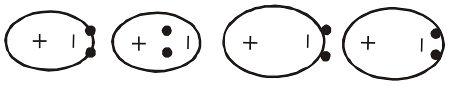
London forces - The negative electrons in a neutral molecule are balanced by the positive charges on the nuclues. Since the electrons are in motion the centre of density of the electrons does not coincide continuously with the centre of density of positively charged nuclei, the molecules acquire an electric dipole. Polarised molecules exert an attraction for other molecules having a dipole. Consider the case of helium.



Non polar atom



Polarised atom



Attraction between polarised atom

- The greater the polarizability of a molecule, the stronger are the London forces.
- The polarizability increases with number of electrons and their distance from the nucleus.
- These forces are operative over a very short range.
- The inert gases have weak van der Waals forces of attraction
- The striaght chain hydrocarbons boil at higher temperature than isomeric branched chain hydrocarbons due to greater magnitude of van der Waal's forces of attraction.

Dipole - dipole attraction

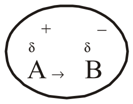
It is the attraction between the positive end of the one molecule and negative end of the another molecule

$\overset{\delta}{H}-\overset{\delta-}{Cl}\ \ \overset{\delta}{H}-\overset{\delta-}{Cl}$ or $\overset{\delta-}{Cl}-\overset{\delta}{H}\ \ \overset{\delta-}{Cl}-\overset{\delta}{H}$

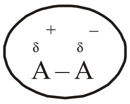
This type of interaction is called dipole - dipole interaction. The force of dipole - dipole attraction is inversely proportional to fourth power of their separation of distance r. $F \quad \frac{1}{r^4}$. The dipole dipole attractions in gaseous molecules are particularly small since the gas molecules are in continuous motion. This attraction increases the m.pt. and b.pt. of substances and makes their liquification easy.

Dipole-induced dipole attraction

The attractive forces operate between polar molecules having permanent dipole and non-polar molecules. The polarity in the non-polar molecules is induced by the polar molecule



Polar molecules



Non-polar molecules

DIPOLE MOMENT :

If a covalent bond is formed between two disimilar atoms, eg. A and B, one of the atoms (A or B) must be more electronegative than the other. If A is more electronegative than the shared pair of electrons is drawn near A leaving a positive charge on B and hence making the molecule dipolar (A^-B^+). The percentage of polar character is given in terms of dipole moment (μ).

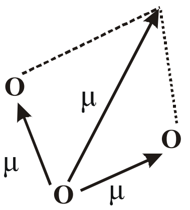
The dipole moment is defined as the product of electric charge q and the distance r between the two atoms of a polar molecule. ($\mu = e \times d$) Dipole moment is a vector quantity with direction same as that of the line joining positive and negative centres.

Thus molecules having dipole moment ($\mu = 0$) are called non polar molecules and molecules with $\mu > 0$ are polar. Greater is μ, greater is the polarity.

For polyatomic molecules with two or more bonds, net dipole moment is the resultant of vector addition of individual moments.

For e.g. in the figure shown, the resultant dipole moment,

$\vec{\mu}$ $\vec{\mu}$ $\vec{\mu}$



While expressing dipole moments, generally charge is given in electrostatic units (esu) and distance in angstrom units (1A° = 10^{-10} m). Thus dipole moment of an electron separated from unit positive charge by a distance 1A° would be (4.80×10^{-10} esu) × (10^{-8} cm) = 4.8×10^{-18} esu cm = 4.8 Debye.

Some compounds and their dipole moments are

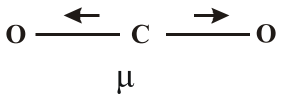
Substance	***Moment***	***Substance***	***Moment***
(Debye)			***(Debye)***
CO_2	0.00		
HBr	0.78		
CH_3Cl	1.85	CH_2F_2	1.96
NH_3	1.48	O_3	0.52
H_2O	1.85	CO	1.11
CH_3I	1.35	CH_3OH	1.68
$C_6H_5NO_2$	4.08	C_2H_5OH	1.65
CH_4	0.00	N_2O	0.17
HF	1.91	H_2S	0.92
SO_2	1.61	H_2O_2	1.84
NF_3	0.24	PH_3	0.59
C_6H_5OH	1.70	HCN	2.93
HCl	1.03	CCl_4	0.0
HI	0.38	CS_2	0.0
H_2	0.95	PCl_5	0.0

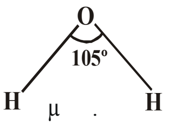
Applications of dipole moment

(1) Dipole moment is helpful in predicting the geometry of the molecule.

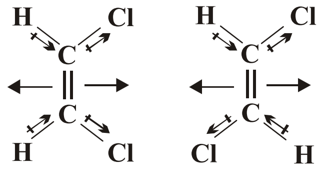
(2) Dipole moment helps in determining the polarity.

(3) Dipole moment can distinguish between symmetrical and non symmetrical molecules. eg. CO_2 has 0 dipole moment as it is symmetrical whereas H_2O has a dipole moment of 1.85D.





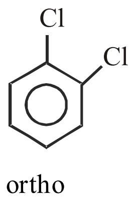
(4) Cis and trans isomers can be distinguished by dipole moments, usually cis isomers have higher dipole moment and hence higher polarity e.g.



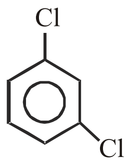
Cis (μ ≠) trans (μ)

(5) Dipole moment is greatest for ortho isomer, zero for para isomer and less than that of ortho for meta isomer.

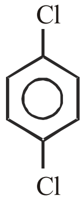
o > m > p. e.g.



ortho



meta



para

μ 2.53 Debye μ 1.48 Debye μ

(6) Ionic character can be determined by using dipole moment

For e.g. experimental dipole moment for HCl is 1.03 and

μ r × e

as r = 1.26 and, e = 4.8×10^{-10} esu,

⇒ μ = 6.05 Debye.

$$\text{Thus the ionic character } \frac{1.03}{6.05} \approx \frac{1}{6} \times 100\%$$

Thus we can say % ionic character

$$\frac{\text{experimental dipole moment}}{\text{theoretical dipole moment}} \times 100$$

(7) Hybridisation can be determined by dipole moment for eg.

(i) If a molecule AB_2 has μ =0, the σ orbitals used by A (z < 21) must be sp hybridised e.g. BeF_2

(ii) If a molecule AB_3 has μ =0, the σ orbitals used by A (z < 21) must be sp^2 hybridised e.g. BF_3

(iii) If a molecule AB_4 has μ =0, the σ orbitals used by A (z < 21) must be sp^3 hybridised e.g. CCl_4

BOND LENGTH :

It is the distance between the nuclei of two atoms between which the bond is formed. Other names for bond length are interatomic distance or bond distance. It is usually expressed in angstrom unit (1Å=10^{-10}m). Pauling's rule states that for covalently bonded atoms, bond length is sum of covalent radii. Thus for a covalent compound AB, the bond length is $r_A + r_B$. where r_A and r_B are covalent radii of A and B

Bond length depends on:-

i) Bond order - Bond length decreases with bond order. For e.g. C - C length in $CH_3 - CH_3$ is 1.54 Å, C = C length in $CH_2 = CH_2$ is 1.34 Å and C ≡ C length in CH ≡ CH is 1.20 Å. Larger the s character, smaller is bond length.

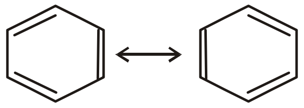
ii) ***Electronegativity*** - If one of the atoms is more electronegative than other, the bond length is found to be smaller than expected value. The relation that holds true for most compounds is

$$r_{AB} = r_A + r_B - 0.09\,(x_A - x_B)$$

where x_A and x_B are electronegativities of A and B

iii) ***Hybridisation -*** Larger is *s* character, shorter is orbital and hence shorter is the length of bond formed by it.

iv) ***Resonance and delocalisation -*** C-C bond length is 1.54Å and C = C bond length is 1.34 Å but in benzene, due to resonance, the carbon-carbon bond is neither single nor double but intermediate between single and double and same holds for bond length and is equal to 1.39 Å.



Average Bond Distance of Covalent Bonds

Bond	*Bond length (Å)*	*Bond*	*Bond length (Å)*	*Bond*	*Bond length (Å)*
C - C	1.54	C - H	1.12	H - H	0.74
C = C	1.34	C - F	1.42	F - F	1.42
$C \equiv C$	1.20	C - Cl	1.77	Cl - Cl	1.99
C - N	1.47	C - Br	1.91	Br - Br	2.28
C = N	1.28	C – I	2.13	I – I	2.67
$C \equiv N$	1.15	O - H	0.97	H - F	0.92
C - O	1.43	N - H	1.03	H - Cl	1.27
C = O	1.20	S - H	1.35	H - Br	1.41
O = O	1.21	N = N	1.09	H - I	1.61

BOND ENERGY :

Bond strength or bond energy is the amount of energy required to break a bond in one gram mole of a substance in gaseous state. Bond energy is also called bond dissociation energy. Its units are $kJmol^{-1}$. Bond dissociation energy and (average) bond energy are same in diatomic molecules as they have only one bond. But in molecules having many bonds, bond dissociation energy of the bonds are different and bond energy is the average value of bond dissociation energy

Factors affecting the bond energy

1) ***Atomic size*** - Strength of shorter bond is more e.g. atomic size of Cl, Br, I has the order Cl < Br < I and their bond energies, Cl - Cl (243 kJ mol^{-1}) > Br - Br (192 kJ mol^{-1}) > I - I(151 $kJmol^{-1}$)

2) ***Bond order*** - Higher bond order implies higher energy e.g. bond energies for C—C, C=C and $C \equiv C$ are 347.2, 610.0 and 835.1 kJ mol^{-1} respectively.

3) ***Electronegativity***-Larger the difference in electronegativities of bonded atoms, more is the attraction, shorter is bond length and hence higher is bond energy.

4) ***Hybridisation*** - Due to directional character of hybridised orbitals, extent of overlapping increases and hence stronger bonds are formed.

5) ***Type or extent of overlapping*** - Coaxial overlappings (s-s, s-p, p-p) have higher extents and hence are stronger than collateral overlappings. Thus sigma bond (coaxial overlapping) is stronger than pi bond (collateral overlapping).As p orbitals are more directional, p - p coaxial overlapping gives stronger bond in comparison to s - s overlapping.

6) ***Repulsion between lone pair*** - In a bonding atom having lone pair the bond formed is weaker due to non localisation of lone pair. Mutual repulsion takes place between lone pair clouds of two atoms, decrease the strength and hence the bond energy. For e.g. as lone pair at each C - C is 0, N - N is one, O - O is two, so values of their bond energies are in order C - C > N - N > O - O.

Determination of bond energy

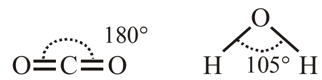
Bond energy is determined by thermochemical methods by determining either the heat of atomisation i.e. heat required to break the molecule into its atoms or by the heat of formation of compound.

Some average Bond Energies (kcal/mole)

Bond	*Energy*	*Bond*	*Energy*	*Bond*	*Energy*
H – H	103.4	C – N	69.3	C – F	107.0
C – H	98.4	$C \equiv N$	135.0	C – Cl	78.0
C – C	81.6	O – O	34.9	C – Br	65.0
C = C	146.1	O = O	119.0	C – I	57.0
$C \equiv C$	192.1	N – N	39.0	H – F	132.4
C – O	81.5	N = N	97.6	H – Cl	102.7
C = O	173.0	$N \equiv N$	225.0	H – Br	87.3
$C \equiv O$	256.0	N – H	92.9	H – I	71.4
C = S	114.0	S – H	87.5	F – F	37.0
N = O	146.0	O – H	110.2	Cl – Cl	58.0

BOND ANGLE :

Bond angle is the angle between two adjacent bonds in a molecule.



Thus bond angles in CO_2 and H_2O are 180° and 105°.

Factors affecting bond angle

1) ***Electronegativity*** - Cl - O- Cl bond angle in Cl_2O is more than F - O - F bond angle in OF_2 because in Cl_2O, O atom is more electronegative compared to Cl atom due to which shared electrons are attracted towards O. This makes bonded electrons of two Cl-O bonds to come close and hence more repulsion resulting in wider bond angle. Whereas in OF_2, F is more electronegative than O thus bonded electrons of F-O bond are closer to F atom. This makes bonded electrons of two O - F bonds to go apart, feeling less repulsion and hence a lower value for bond angle.

2) ***Hybridisation*** - sp^3 hybridisation at central atom implies a bond angle of 109° 28′ each e.g. CH_4, CH_3CH_3 etc. sp^2 hybridisation leads to 120° bond angle as in BF_3. sp hybridisation makes angle 180° e.g. $BeCl_2$.

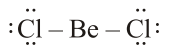
3) ***Lone pair repulsions*** - Presence of lone pair at central atom results in repulsion of shared pair of electrons. Thus bonds at central atom are displaced inside making the value of bond angle smaller e.g. bond angle in ammonia is 107° even though hybridisation at nitrogen is sp^3. It is due to presence of lone pair of electrons at nitrogen atom which causes more repulsion between N and H and hence decreasing the bond angle. Bond angle can be measured by X-ray techniques or by I.R. spectroscopy.

Baeyer's strain theory states that any shift in normal bond angle causes strain over the molecule making it less stable and more reactive. Thus CH_4, C_2H_6 are quite stable while ethylene is less stable (bond angle 120°).

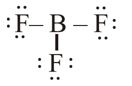
OCTET RULE :

During formation of a covalent bond, the atoms attain an intert gas electronic configuration (ns^2p^6 configuration). This is known as **Octet rule**. There are exceptions of octet rule.

(1) **Incomplete octet** : Consider the following molecules



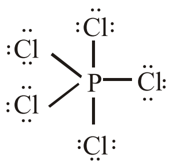
(4 electrons around Be)



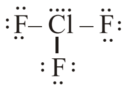
(6 electrons around B)

(7 electrons around N)

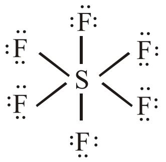
(2) **Expansion of octet** : Consider the following molecules



(10 electrons around P)



(10 electrons around Cl)

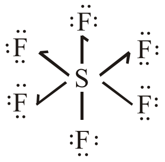


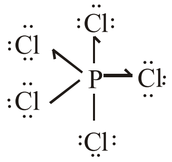
(12 electrons around S)

Explanation for the failure of Octet rule : The concepts given below explain the failure of the octet rule :

(a) **Sidwick's rule of maximum covalency** : The maximum covalency of an element depends on the period to which it belongs and octet can be exceeded for n = 1 it is 2, for n = 2 it is 4, for n = 3 it is 6 and for n > 4 it is 8.

(b) **Sugden's view of singlet linkage** : According to Sugden the octet rule is never violated. There can be one electron bond known as **Singlet linkage, Singlet** or **half bond** is formed by sharing of one electron between two atoms. It is represented by half arrow (⇀). Thus SF_6 and PCl_5 have the structures :





Exercise-1 | NCERT BASED QUESTIONS

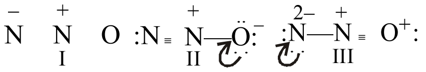
Very Short/Short Answer Questions

1. Out of bonding and antibonding molecular orbitals which one has lower energy and which one has higher stability?

2. The H—S—H bond angle in H_2S is 92.2° whereas the H—O—H bond angle in H_2O is 104.5°, why?

3. Out of NaCl and MgO, which has higher value of lattice energy?

4. Which of the following structures contributes least towards resonance hybrid?



5. Which of the following has higher dipole moment $H_3C-CH_2-CH=CH_2$(1–butene) or

$H_3C-CH_2-C\equiv CH$(1–butyne)?

6. Predict the dipole moment of

(i) A molecule AX_4 with tetrahedral geometry

(ii) A molecule AX_2 with linear geometry

(iii) A molecule AX_3 with distorted tetrahedral geometry.

7. Three elements have the following Lewis symbols:

(a) Assign groups of the periodic table to these elements.

(b) Which elements are expected to form ions and what is the expected charge over these ions?

(c) Write the formulae and Lewis structures of the covalent compounds formed between

(i) A and B

(ii) A and C

8. Why are lone pair-lone pair repulsions stronger than lone pair-bond pair?

9. Account for the following :

(i) N_2 has a higher bond dissociation energy than NO.

(ii) N_2 and CO both have the same bond order but CO is more reactive than N_2.

10. Account for the following :

(i) He_2 is not found to exist in nature

(ii) N_2^+ is not a diamagnetic substance

(iii) The dissociation energy of H_2 is almost the same as that of He_2^+.

11. Which is more covalent and why : $BeCl_2$ or $MgCl_2$?

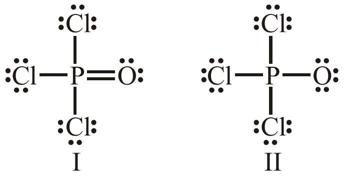
12. Why does Pauli's exclusion principle permit bonding only if the electrons are of different spins?

Long Answer Questions

13. Give difference between Bonding Molecular orbital and Anti–bonding molecular orbital.

14. What are the characteristics of resonance?

15. Determine the formal charges on the atoms in the two structures shown below for the molecule $POCl_3$. Which of these two structures is the better structure (i.e., which is preferred)?



16. Draw all possible resonance structures for the sulfate ion, SO_4^{2-} on the basis of formal charge

17. State the hybridization and draw the molecular structure of the following

(a) PF_5 (b) I_3^- (c) NH_3 (d) XeO_3 (e) CH_4

18. Give reasons for following :

(i) What is the decreasing order of lattice energy of various ions?

(ii) $PbSO_4$, $BaSO_4$, AgCl, AgBr, AgI are insoluble in water, why?

(iii) Which is more ionic and why? $FeCl_2$ or $FeCl_3$?

(iv) What is the decreasing order of strengths of bonds between sp^3, sp^2 and sp hybrid orbitals?

(v) What is the order of dipole moment of ortho, meta and para disubstituted derivatives?

Multiple Choice Questions

19. Sodium chloride is an ionic compound whereas hydrogen chloride is mainly covalent because

(a) sodium is less reactive

(b) hydrogen is non-metal

(c) hydrogen chloride is a gas

(d) electronegativity difference in the case of hydrogen and chlorine is less than 2.1.

20. Which one of the following molecules will have unequal M – F bond lengths ?

(a) NF_3 (b) BF_3

(c) PF_5 (d) SF_4

21. Match List I (Molecules) with List II (Bond order) and select the correct answer using the codes

List I		**List II**	
I.	Li_2	A.	3
II	N_2	B.	1.5
III	Be_2	C.	1.0
IV	O_2	D.	0
		E.	2

Codes

(a) I - B, II - C, III - A, IV - E
(b) I - C, II - A, III - D, IV - E
(c) I - D, II - A, III - E, IV - C
(d) I - C, II - B, III - E, IV - A

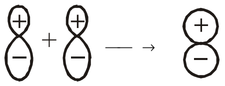
22. Polarity in a molecule and hence the dipole moment depends primarily on electronegativity of the constituent atoms and shape of a molecule. Which of the following has the highest dipole moment?

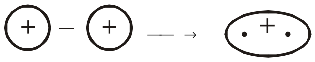
(a) CO_2 (b) HI
(c) H_2O (d) SO_2

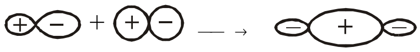
23. Which does not show resonance ?

(a) Benzene (b) Aniline
(c) Ethylamine (d) Toluene

24. Which of the following overlap is correct ?

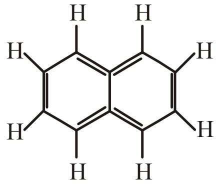
(a)


(b)


(c)


(d) None of the above

25. Number of π bonds and σ bonds in the following structure is



(a) 6, 19 (b) 4, 20
(c) 5, 19 (d) 5, 20

26. The states of hybridisation of boron and oxygen atoms in boric acid (H_3BO_3) are respectively

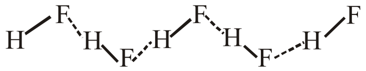
(a) sp^3 and sp^2 (b) sp^2 and sp^3
(c) sp^2 and sp^2 (d) sp^3 and sp^3

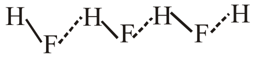
27. Which of the following statement is not correct from the view point of molecular orbital theory?

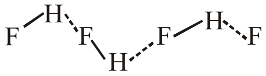
(a) Be_2 is not a stable molecule.
(b) He_2 is not stable but He_2 is expected to exist.
(c) Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules belonging to the second period.
(d) The order of energies of molecular orbitals in N_2 molecule is
$\sigma 2s < \sigma * 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y)$
$< (\pi *2p_x = \pi *2p_y) < \sigma *2p_z$

28. The correct representation of H-bond in solid HF

(a) H – F- - - - - H – F- - - - - H – F

(b)


(c)


(d)


Exercise-2 | CONCEPTUAL MCQs

1. Chemical bond implies
(a) repulsion
(b) attraction
(c) attraction and repulsion balanced at a particular distance
(d) attraction and repulsion

2. The bonding is electrovalent in
(a) NaCl (b) Br_2
(c) PF_5 (d) XeF_4

3. Bonding in ferric chloride is
(a) covalent (b) ionic
(c) co-ordinate (d) None of the above

4. Which of the following species has lowest ionization potential?
(a) O (b) O_2
(c) O (d) O^-

5. Polarization power of a cation increases when
(a) charge on the cation increases
(b) size of the cation increases
(c) charge on the cation decreases
(d) has no relation to its size or charge

6. The correct order of decreasing polarisability of following ions is
(a) Cl^-, Br^-, I^-, F^- (b) F^-, I^-, Br^-, Cl^-
(c) F^-, Cl^-, Br^-, I^- (d) I^-, Br^-, Cl^-, F^-

7. Which of the following statements regarding covalent bond is not true ?
(a) The electrons are shared between atoms
(b) The bond is non - directional
(c) The strength of the bond depends upon the extent of overlapping
(d) The bond formed may or may not be polar

8. Among the following, electron deficient compound is
(a) CCl_4 (b) PCl_5
(c) $BeCl_2$ (d) BCl_3

9. Consider the following statements:
(i) A sigma (σ) bond is formed when two s - orbitals overlap
(ii) A pi (π) bond is formed when two p- orbitals axially overlap
(iii) A σ -bond is weaker than π -bond.
Which of the above statements is/are correct ?
(a) i and ii (b) ii and iii
(c) i alone (d) ii alone

10. Number of π bonds in naphthalene are
(a) 6 (b) 3
(c) 4 (d) 5

11. Ground state electronic configuration of valence shell electrons in nitrogen molecule (N_2) is written as $(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$. Hence the bond order of nitrogen molecule is
(a) 2 (b) 3
(c) 0 (d) 1

12. The bond order of NO molecule is
(a) 1.5 (b) 2.0
(c) 2.5 (d) 3.0

13. Which of the following cannot be formed ?
(a) He^{2+} (b) He^+
(c) He (d) He_2

14. N_2 and O_2 are converted into monoanions, N_2^- and O_2^- respectively. Which of the following statements is wrong ?
(a) In N^-, N – N bond weakens
(b) In O^-, O - O bond order increases
(c) In O^-, O - O bond order decreases
(d) N^- becomes paramagnetic

15. N_2 and O_2 are converted into monocations, N and O respectively. Which of the following statements is wrong?
(a) In N , N - N bond weakens
(b) In O , the O - O bond order increases
(c) In O , paramagnetism decreases
(d) N becomes diamagnetic

16. Which of the following molecule is paramagnetic?
(a) CO_2 (b) SO_2
(c) NO (d) H_2O

17. In PO_4^{3-}, the formal charge on each oxygen atom and the P - O bond order respectively are
(a) –0.75, 0.6 (b) –0.75, 1.0
(c) –0.75, 1.25 (d) –3, 1.25

18. Which of the following ion has not bond order of 2.5 ?
(a) O^- (b) O
(c) N (d) N^-

19. Oxygen molecule is
(a) diamagnetic with no unpaired electrons
(b) diamagnetic with two unpaired electrons
(c) paramagnetic with two unpaired electrons
(d) paramagnetic with no unpaired electrons

20. The number of electrons that are paired in oxygen molecule is
(a) 16 (b) 12
(c) 7 (d) 8

21. Which of the following pairs have identical bond order ?
(a) N ,O (b) N ,O^-
(c) N^-,O (d) O ,N

22. Which one of the following should be most stable?
(a) H (b) H^+
(c) H (d) H^-

23. The number of antibonding electron pairs in O^{-} molecular ion on the basis of molecular orbital theory are (at. no. O = 8)
(a) 2 (b) 3
(c) 4 (d) 5

24. Which of the following is not paramagnetic ?
(a) N (b) CO
(c) O^- (d) NO

25. Which of the following molecular species has unpaired electron (s) ?
(a) N_2 (b) F_2
(c) O^- (d) O^{-}

26. Which of the following has least covalent P–H bond?
(a) PH_3 (b) P_2H_6
(c) P_2H_5 (d) PH_6^+

27. Which contains both polar and non - polar bonds?
(a) NH_4Cl (b) HCN
(c) H_2O_2 (d) CH_4

28. Which of the following has least polarity in bond?
(a) H – F (b) H – Cl
(c) H – O (d) H – S

29. Which of the following substances has the least ionic character ?
(a) $FeCl_2$ (b) $ZnCl_2$
(c) $CdCl_2$ (d) $MgCl_2$

30. The correct order of increasing ionic character is
(a) $BeCl_2 < MgCl_2 < CaCl_2 < BaCl_2$
(b) $BeCl_2 < MgCl_2 < BaCl_2 < CaCl_2$
(c) $BeCl_2 < BaCl_2 < MgCl_2 < CaCl_2$
(d) $BaCl_2 < CaCl_2 < MgCl_2 < BeCl_2$

31. Which of the following contains both covalent and ionic bond?
(a) NH_4Cl (b) H_2O
(c) CCl_4 (d) $CaCl_2$

32. The values of electronegativity of atoms A and B are 1.20 and 4.0 respectively. The percentage of ionic character of A - B bond is
(a) 50% (b) 72.24%
(c) 55.3% (d) 43%

33. The electronegativities of F, Cl, Br and I are 4.0, 3.0, 2.8, 2.5 respectively. The hydrogen halide with a high percentage of ionic character is
(a) HF (b) HCl
(c) HBr (d) HI

34. Covalent compounds have low melting point because
(a) covalent molecules have definite shape
(b) covalent bond is weaker than ionic bond
(c) covalent bond is less exothermic
(d) covalent molecules are held by weak van der Waal's forces of attraction

35. The number of sigma (σ) bonds in 1-butene is
(a) 8 (b) 10
(c) 11 (d) 12

36. The structure of PF_5 molecule is
(a) tetrahedral
(b) square planar
(c) trigonal bipyramidal
(d) pentagonal bipyramidal

37. Which of the following has sp^2-hybridization?
(a) C_2H_6 (b) C_2H_4
(c) $BeCl_2$ (d) C_2H_2

38. The structure and hybridization of $Si(CH_3)_4$ is
(a) bent, sp (b) trigonal, sp^2
(c) octahedral, sp^3d (d) tetrahedral, sp^3

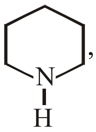
39. Which of the following molecule is not linear in shape
(a) $HgCl_2$ (b) Hg_2Cl_2
(c) CO_2 (d) $SnCl_2$

40. Among the following compounds the one that is polar and has the central atom with sp^2 hybridisation is
(a) H_2CO_3 (b) SiF_4
(c) BF_3 (d) $HClO_2$

41. Which one of the following compounds has sp^2 hybridisation?
(a) CO_2 (b) SO_2
(c) N_2O (d) CO

42. The AsF_5 molecule is trigonal bipyramidal. The hybrid orbitals used by the As atoms for bonding are :
(a) $d_{x^2-y^2}, d_{z}^{2}, s, p_x, p_y$ (b) d_{xy}, s, p_x, p_y, p_z
(c) $s, p_x, p_y, p_{z,} d_{z}^{2}$ (d) $d_{x^2-y^2}, s, p_x, p_y$

43. The hybridization of S atom in SO_4^{2-} is
(a) sp (b) sp^2
(c) sp^3 (d) sp^3d

44. In piperidine , the hybrid state assumed by N is

(a) sp (b) sp^2

(c) sp^3 (d) dsp^2

45. Which of the following will be octahedral ?

(a) SF_6 (b) BF_4^-

(c) PCl_5 (d) $BO^{\ \ -}$

46. The hybridization of atomic orbitals of nitrogen in NO_2 , NO_2^- and NH_4 are

(a) sp^2, sp^3 and sp^2 respectively

(b) sp, sp^2 and sp^3 respectively

(c) sp^2, sp and sp^3 respectively

(d) sp^2, sp^3 and sp respectivley

47. The compound MX_4 is tetrahedral. The number of $\angle$ XMX formed in the compound are

(a) three (b) four

(c) five (d) six

48. The shape of gaseous $SnCl_2$ is

(a) tetrahedral (b) linear

(c) angular (d) t-shape

49. Which of the following molecule is linear ?

(a) SO_2 (b) NO

(c) NO^- (d) SCl_2

50. Each carbon in carbon suboxide (C_3O_2) is

(a) sp^2 - hybridized

(b) sp^3 - hybridized

(c) sp - hybridized

(d) sp^2 - hybridized but linked with one co-ordinate bond

51. In XeF_2, XeF_4 and XeF_6, the number of lone pairs on Xe are respectively

(a) 2, 3, 1 (b) 1, 2, 3

(c) 4, 1, 2 (d) 3, 2, 1

52. In which of the following species is the underlined carbon having sp^3 - hybridisation ?

(a) $CH\ \ -\underline{C}OOH$ (b) $CH\ \ \underline{C}H\ \ OH$

(c) $CH\ \ \underline{C}OCH$ (d) $CH\ \ \ \ \underline{C}H-CH$

53. A square planar complex is formed by hybridisation of which atomic orbitals ?

(a) s, p_x, p_y, d_{yz} (b) $s, p_x, p_y, d_{x^2-y^2}$

(c) s, p_x, p_y, d_z (d) s, p_x, p_z, d_{xy}

54. According to VSEPR theory, the most probable shape of the molecule having 4 electron pairs in the outershell of the central atom is

(a) linear (b) tetrahedral

(c) hexahedral (d) octahedral

55. The geometry of ClO^- ion according to Valence Shell Electron Pair Repulsion (VSEPR) theory will be

(a) planar triangular (b) pyramidal

(c) tetrahedral (d) square planar

56. Among the following ions, the $p\pi - d\pi$ overlap could be present in

(a) NO^- (b) $PO^{\ \ -}$

(c) $CO^{\ \ -}$ (d) NO^-

57. In NO^- ion, number of bond pairs and lone pairs of electrons on nitrogen atom are

(a) 2, 2 (b) 3, 1

(c) 1, 3 (d) 4, 0

58. In OF_2, number of bond pairs and lone pairs of electrons are respectively

(a) 2, 6 (b) 2, 8

(c) 2, 10 (d) 2, 9

59. The compound containing co-ordinate bond is

(a) H_2SO_4 (b) O_3

(c) SO_3 (d) All of these

60. Sulphuric acid provides a simple example of

(a) co-ordinate bonds

(b) non-covalent compound

(c) covalent ion

(d) non - covalent ion

61. Which of the following does not contain coordinate bond ?

(a) BH^- (b) NH_4

(c) CO_3^{2-} (d) H_3O

62. The maximum number of water molecules that one water molecule can hold through hydrogen bonding is

(a) 2 (b) 4

(c) 6 (d) 8

63. NH_3 has abnormally high boiling point because it has

(a) alkaline nature (b) distorted shape

(c) sp^3 - Hybridization (d) hydrogen bonding

64. In which of the following pairs hydrogen-bonding is not possible ?

(a) NH_3, NH_3 (b) NH_3,CH_4

(c) H_2O, CH_3OCH_3 (d) CH_3OH,CH_3OCH_3

65. The high density of water compared to ice is due to

(a) H - bonding interactions

(b) dipole - dipole interactions

(c) dipole-induced dipole interactions

(d) induced dipole-induced dipole interactions

66. Two ice cubes are pressed over each other until they unite to form one block. Which one of the following forces dominate for holding them together?

(a) Dipole-dipole interaction

(b) Van der waals' forces

(c) Hydrogen bond formation

(d) Covalent attraction

67. Which of the following molecules will form a linear polymeric structure due to hydrogen bonding ?

(a) HCl (b) HF

(c) H_2O (d) NH_3

68. Among H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is

(a) H_2O because of hydrogen bonding

(b) H_2Te because of higher molecular weight

(c) H_2S because of hydrogen bonding

(d) H_2Se because of lower molecular weight

69. Which of the following is soluble in water ?

(a) CS_2 (b) C_2H_5OH

(c) CCl_4 (d) $CHCl_3$

70. A metallic bond is

(a) ionic (b) polar covalent

(c) non-polar covalent (d) electrostatic in nature

71. Type of forces between molecules of C_6H_6 are

(a) dipole-dipole interaction (b) dispersive forces

(c) H-bonding (d) van der Waals' forces

72. Which of the following has the highest dipole moment?

(a) AsH_3 (b) SbH_3

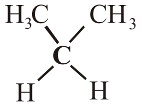
(c) PH_3 (d) NH_3

73. The molecule having non-zero dipole moment is

(a) H_2O_2 (b) CH_4

(c) C_2H_6 (d) BF^-

74. Which of the following hydrocarbons has the lowest dipole moment ?

(a) 

(b) CH C $\equiv$ CCH

(c) CH CH C $\equiv$ CH (d) CH_2 CH $-$ C $\equiv$ CH

75. Which of the following has zero dipole moment?

(a) ClF (b) PCl_3

(c) SiF_4 (d) $CFCl_3$

76. Dipole moment is shown by

(a) 1, 4-dichlorobenzene

(b) cis 1,2-dichlorobenzene

(c) trans 1, 3-dichlorobenzene

(d) trans 2, 3-dichloro -2- butene

77. Which one of the following molecules will have unequal M – F bond lengths ?

(a) NF_3 (b) BF_3

(c) PF_5 (d) SF_4

78. The bond length in LiF will be

(a) less than that of NaF (b) equal to that of KF

(c) more than that of KF (d) equal to that of NaF

79. Which has the least bond angle ?

(a) NH_3 (b) BeF_2

(c) H_2O (d) CH_4

80. The correct sequence of decrease in the bond angles of the following hydrides is

(a) $NH_3 > PH_3 > AsH_3 > SbH_3$

(b) $NH_3 > AsH_3 > PH_3 > SbH_3$

(c) $SbH_3 > AsH_3 > PH_3 > NH_3$

(d) $PH_3 > NH_3 > AsH_3 > SbH_3$

81. The sulphate of a metal has the formula $M_2(SO_4)_3$. The formula of its phosphate will be

(a) $M(HPO_4)_2$ (b) $M_3(PO_4)_2$

(c) $M_2(PO_4)_3$ (d) MPO_4

82. KF combines with HF to form KHF_2. The compound contains the species

(a) K^+, F^- and H^+ (b) K^+, F^- and HF

(c) K^+, and $[HF_2]^-$ (b) $[KHF]^+$ and F_2

83. Which of the following molecular orbitals has two nodal planes ?

(a) σ 2s (b) π $2p_y$

(c) π $*2p_y$ (d) σ $*2p_x$

84. The electronic configuration of metal M is $1s^2\ 2s^2\ 2p^6\ 3s^1$. The formula of its oxide will be

(a) MO (b) M_2O

(c) SO_3 (d) All of these

85. The number of possible resonance structure for $CO^{\ -}$ is

(a) 2 (b) 3

(c) 6 (d) 9

86. Match List I (Molecules) with List II (Bond order) and select the correct answer using the codes

List I	***List II***
I. Li_2	A. 3
II N_2	B. 1.5
III Be_2	C. 1.0
IV O_2	D. 0
	E. 2

Codes

(a) I - B, II - C, III - A, IV - E

(b) I - C, II - A, III - D, IV - E

(c) I - D, II - A, III - E, IV - C

(d) I - C, II - B, III - E, IV - A

87. An ether is more volatile than an alcohol having the same molecular formula. This is due to

(a) dipolar character of ethers

(b) alcohols having resonance structures

(c) inter-molecular hydrogen bonding in ethers

(d) inter-molecular hydrogen bonding in alcohols

88. The reason for double helical structure of DNA is operation of

(a) van der Waal's forces (b) dipole-dipole interaction

(c) hydrogen bonding (d) electrostatic attraction

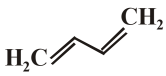
89. Among the following, the molecule with the highest dipole moment is

(a) CH_3Cl (b) CH_2Cl_2

(c) $CHCl_3$ (d) CCl_4

90. Which of the following represents the given mode of hybridisation $sp^2 - sp^2 - sp - sp$ from left to right ?

(a) H C CH $-$ C $\equiv$ N (b) HC $\equiv$ C $-$ C $\equiv$ CH

(c) H C C C CH (d) 

Exercise-3 | PAST COMPETITION MCQs

1. In which of the following pairs, the two species are iso-structure? **[CBSE-PMT 2007]**

(a) SO_3^{2-} and NO_3^- (b) BF_3 an NF_3
(c) BrO_3^- and XeO_3 (d) SF_4 and XeF_4

2. The *correct* order of increasing bond angles in the following triatomic species is : **[CBSE-PMT 2008]**

(a) NO_2^- NO_2 NO_2 (b) NO_2^- NO_2 NO_2
(c) NO_2^+ NO_2 NO_2^- (d) NO_2^+ NO_2^- NO_2

3. Four diatomic species are listed below in different sequences. Which of these presents the *correct* order of their increasing bond order ? **[CBSE-PMT 2008]**

(a) O_2^- NO C_2^{2-} He_2 (b) NO C_2^{2-} O_2^- He_2
(c) C_2^{2-} He_2^+ NO O_2^- (d) He_2^+ O_2^- NO C_2^{2-}

4. What is the dominant intermolecular force or bond that must be overcome in converting liquid CH_3OH to a gas?

(a) Dipole-dipole interactions **[CBSE-PMT 2009]**
(b) Covalent bonds
(c) London dispersion forces
(d) Hydrogen bonding

5. In which of the following molecules / ions BF_3, NO_2^-, NH_2^- and H_2O, the central atom is sp^2 hybridized ? **[CBSE-PMT 2009]**

(a) NH_2^- and H_2O (b) NO_2^- and H_2O
(c) BF_3 and NO_2^- (d) NO_2^- and NH_2^-

6. According to MO theory which of the following lists ranks the nitrogen species in terms of increasing bond order? **[CBSE-PMT 2009]**

(a) N_2^{2-} N_2^- N_2 (b) N_2 N_2^{2-} N_2^-
(c) N_2^- N_2^{2-} N_2 (d) N_2^- N_2 N_2^{2-}

7. In which one of the following species the central atom has the type of hybridization which is not the same as that present in the other three? **[CBSE-PMT 2010]**

(a) SF_4 (b) I_3^- (c) $SbCl_5^{2-}$ (d) PCl_5

8. Some of the properties of the two species, NO_3^- and H_3O^+ are described below. Which one of them is correct? **[CBSE-PMT 2010]**

(a) Similar in hybridization for the central atom with different structures.
(b) Dissimilar in hybridization for the central atom with different structures.
(c) Isostructural with same hybridization for the central atom.
(d) Isostructural with different hybridization for the central atom.

9. In which of the following molecules the central atom does not have sp^3 hybridization? **[CBSE-PMT 2010]**

(a) NH_4^+ (b) CH_4 (c) SF_4 (d) BF_4^-

10. Which one of the following species does not exist under normal conditions? **[CBSE-PMT 2010]**

(a) Be_2 (b) Be_2 (c) B_2 (d) Li_2

11. Considering the state of hybridization of carbon atoms, find out the molecule among the following which is linear ?

(a) $CH_3-CH=CH-CH_3$ **[CBSE-PMT 2011]**
(b) $CH_3-C\equiv C-CH_3$
(c) $CH_2=CH-CH_2-C\equiv CH$
(d) $CH_3-CH_2-CH_2-CH_3$

12. Which of the two ions from the list given below have the geometry that is explained by the same hybridization of orbitals, NO_2^-, NO_3^-, NH_2^-, NH_4^+, SCN^-? **[CBSE-PMT 2011]**

(a) NO_2^- and NO_3^- (b) NH_2^- and NO_3^-
(c) SCN^- and NH_2^- (d) NO_2^- and NH_2^-

13. Which of the following has the minimum bond length ? **[CBSE-PMT 2011]**

(a) O_2^+ (b) O_2^-
(c) O_2^{2-} (d) O_2

14. The pairs of species of oxygen and their magnetic behaviours are noted below. Which of the following presents the correct description ? **[CBSE-PMT 2011 M]**

(a) O_2^-, O_2^{2-} – Both diamagnetic
(b) O_2^+, O_2^{2-} – Both paramagnetic
(c) O_2^+, O_2 – Both paramagnetic
(d) None of these

15. Which one of the following pairs is isostructural (i.e., having the same shape and hybridization) ? **[CBSE-PMT 2012]**

(a) $\left[BCl_3 \text{ and } BrCl_3^-\right]$ (b) $\left[NH_3 \text{ and } NO_3^-\right]$
(c) NF_3 and BF_3 (d) $\left[BF_4^- \text{ and } NH_4\right]$

16. Bond order of 1.5 is shown by : **[CBSE-PMT 2012]**

(a) O_2 (b) O_2^- (c) O_2^{2-} (d) O_2

17. Which of the following species contains three bond pairs and one lone pair around the central atom ? **[CBSE-PMT 2012]**

(a) H_2O (b) BF_3 (c) NH_2^- (d) PCl_3

18. The pair of species with the same bond order is : **[CBSE-PMT 2012]**

(a) O_2^{2-}, B_2 (b) O_2^+, NO^+

(c) NO, CO (d) N_2, O_2

19. Which of the following is electron - deficient ? **[NEET 2013]**

(a) $(SiH_3)_2$ (b) $(BH_3)_2$

(c) PH_3 (d) $(CH_3)_2$

20. Which one of the following molecules contains no π bond? **[NEET 2013]**

(a) H_2O (b) SO_2

(c) NO_2 (d) CO_2

21. Which of the following is paramagnetic ? **[NEET 2013]**

(a) O_2^- (b) CN^-

(c) NO^+ (d) CO

22. Dipole-induced dipole interactions are present in which of the following pairs : **[NEET 2013]**

(a) Cl_2 and CCl_4

(b) HCl and He atoms

(c) SiF_4 and He atoms

(d) H_2O and alcohol

23. In which of the following species the interatomic bond angle is 109° 28'? **[AIEEE 2002]**

(a) $NH_3, (BF_4)^{1-}$ (b) $(NH_4)^+, BF_3$

(c) NH_3, BF_4 (d) $(NH_2)^{1-}, BF_3$.

24. Which one of the following pairs of molecules will have permanent dipole moments for both members ? **[AIEEE 2003]**

(a) NO_2 and CO_2 (b) NO_2 and O_3

(c) SiF_4 and CO_2 (d) SiF_4 and NO_2

25. Which one of the following compounds has the smallest bond angle in its molecule ? **[AIEEE 2003]**

(a) OH_2 (b) SH_2

(c) NH_3 (d) SO_2

26. The pair of species having identical shapes for molecules of both species is **[AIEEE 2003]**

(a) XeF_2, CO_2 (b) BF_3, PCl_3

(c) PF_5, IF_5 (d) CF_4, SF_4

27. The correct order of bond angles (smallest first) in H_2S, NH_3, BF_3 and SiH_4 is **[AIEEE 2004]**

(a) $H_2S < NH_3 < SiH_4 < BF_3$

(b) $NH_3 < H_2S < SiH_4 < BF_3$

(c) $H_2S < SiH_4 < NH_3 < BF_3$

(d) $H_2S < NH_3 < BF_3 < SiH_4$

28. The bond order in NO is 2.5 while that in NO^+ is 3. Which of the following statements is true for these two species ? **[AIEEE 2004]**

(a) Bond length in NO^+ is equal to that in NO

(b) Bond length in NO is greater than in NO^+

(c) Bond length in NO^+ is greater than in NO

(d) Bond length is unpredictable

29. The states of hybridization of boron and oxygen atoms in boric acid (H_3BO_3) are respectively **[AIEEE 2004]**

(a) sp^3 and sp^2 (b) sp^2 and sp^3

(c) sp^2 and sp^2 (d) sp^3 and sp^3

30. Which one of the following has the regular tetrahedral structure ? **[AIEEE 2004]**

(a) BF_4^- (b) SF_4

(c) XeF_4 (d) $[Ni(CN)_4]^{2-}$

(Atomic nos. : B = 5, S = 16, Ni = 28, Xe = 54)

31. The maximum number of 90° angles between bond pair-bond pair of electrons is observed in **[AIEEE 2004]**

(a) dsp^2 hybridization (b) sp^3d hybridization

(c) dsp^3 hybridization (d) sp^3d^2 hybridization

32. Which of the following species is diamagnetic in nature? **[AIEEE 2005]**

(a) H_2^- (b) H_2

(c) H_2 (d) He_2

33. Lattice energy of an ionic compound depends upon

(a) Charge on the ion and size of the ion **[AIEEE 2005]**

(b) Packing of ions only

(c) Size of the ion only

(d) Charge on the ion only

34. The molecular shapes of SF_4, CF_4 and XeF_4 are **[AIEEE 2005]**

(a) different with 1, 0 and 2 lone pairs of electrons on the central atom, respectively

(b) different with 0, 1 and 2 lone pairs of electrons on the central atom, respectively

(c) the same with 1, 1 and 1 lone pair of electrons on the central atoms, respectively

(d) the same with 2, 0 and 1 lone pairs of electrons on the central atom, respectively

35. Which of the following molecules/ions does not contain unpaired electrons? **[AIEEE 2006]**

(a) N_2 (b) O_2 (c) O_2^{2-} (d) B_2

36. Among the following mixtures, dipole-dipole as the major interaction, is present in **[AIEEE 2006]**

(a) KCl and water

(b) benzene and carbon tetrachloride

(c) benzene and ethanol

(d) acetonitrile and acetone

37. In which of the following molecules/ions are all the bonds **not** equal? **[AIEEE 2006]**

(a) XeF_4 (b) BF_4^-

(c) SF_4 (d) SiF_4

38. Which of the following species exhibits the diamagnetic behaviour ? **[AIEEE 2007]**

(a) NO (b) O_2^{2-} (c) O_2^+ (d) O_2

39. The charge/size ratio of a cation determines its polarizing power. Which one of the following sequences represents the increasing order of the polarizing power of the cationic species, K^+, Ca^{2+}, Mg^{2+}, Be^{2+}? **[AIEEE 2007]**

(a) $Ca^{2+} < Mg^{2+} < Be^{2+} < K^+$
(b) $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$
(c) $Be^{2+} < K^+ < Ca^{2+} < Mg^{2+}$
(d) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

40. In which of the following ionization processes, the bond order has increased and the magnetic behaviour has changed? **[AIEEE 2007]**

(a) $N_2 \rightarrow N_2$ (b) $C_2 \rightarrow C_2$
(c) $NO \rightarrow NO$ (d) $O_2 \rightarrow O_2$

41. Which of the following hydrogen bonds is the strongest? **[AIEEE 2007]**

(a) O – H - - - F (b) O – H - - - H
(c) F – H - - - F (d) O – H - - - O

42. Which one of the following pairs of species have the same bond order? **[AIEEE 2008]**

(a) CN^- and NO^+ (b) CN^- and CN^+
(c) O_2^- and CN^- (d) NO^+ and CN^+

43. The bond dissociation energy of B – F in BF_3 is 646 kJ mol^{-1} whereas that of C – F in CF_4 is 515 kJ mol^{-1}. The correct reason for higher B – F bond dissociation energy as compared to that of C – F is **[AIEEE 2008]**

(a) stronger σ bond between B and F in BF_3 as compared to that between C and F in CF_4.
(b) significant $p_\pi - p_\pi$ interaction between B and F in BF_3 whereas there is no possibility of such interaction between C and F in CF_4.
(c) lower degree of $p_\pi - p_\pi$ interaction between B and F in BF_3 than that between C and F in CF_4.
(d) smaller size of B– atom as compared to that of C– atom.

44. The number of types of bonds between two carbon atoms in calcium carbide is **[AIEEE 2011 RS]**

(a) One sigma, One pi
(b) Two sigma, one pi
(c) Two sigma, two pi
(d) One sigma, two pi

45. The molecule having smallest bond angle is : **[AIEEE 2012]**

(a) NCl_3 (b) $AsCl_3$
(c) $SbCl_3$ (d) PCl_3

46. In which of the following pairs the two species are not isostructural ? **[AIEEE 2012]**

(a) CO_3^{2-} and NO_3^-
(b) PCl_4^+ and $SiCl_4$
(c) PF_5 and BrF_5
(d) AlF_6^{3-} and SF_6

47. Which one of the following molecules is expected to exhibit diamagnetic behaviour ? **[JEE Main 2013]**

(a) C_2 (b) N_2 (c) O_2 (d) S_2

48. Which of the following is the wrong statement ? **[JEE Main 2013]**

(a) ONCl and ONO^- are not isoelectronic.
(b) O_3 molecule is bent
(c) Ozone is violet-black in solid state
(d) Ozone is diamagnetic gas.

49. In which of the following pairs of molecules/ions, both the species are not likely to exist ? **[JEE Main 2013]**

(a) H_2^+, He_2^{2-} (b) H_2^-, He_2^{2-}
(c) $H_2^2\ , He_2$ (d) H_2^-, He_2^2

50. Stability of the species Li_2, Li_2^- and Li_2 increases in the order of : **[JEE Main 2013]**

(a) $Li_2 \quad Li_2^+ \quad Li_2^-$ (b) $Li_2^- \quad Li_2 \quad Li_2$
(c) $Li_2 \quad Li_2^- \quad Li_2$ (d) $Li_2^- \quad Li_2 \quad Li_2$

51. Among the following, the paramagnetic compound is **[IIT-JEE 2007]**

(a) Na_2O_2 (b) O_3
(c) N_2O (d) KO_2

52. The species having bond order different from that in CO is **[IIT-JEE 2007]**

(a) NO^- (b) NO^+
(c) CN^- (d) N_2

53. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is : **[IIT-JEE 2010]**

(a) 1 and diamagnetic (b) 0 and dimagnetic
(c) 1 and paramagnetic (d) 0 and paramagnetic

54. The species having pyramidal shape is : **[IIT-JEE 2010]**

(a) SO_3 (b) BrF_3
(c) SiO_3^{2-} (d) OSF_2

55. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^-, CN^- and H_2O, respectively, are **[IIT-JEE 2011]**

(a) octahedral, tetrahedral and square planar
(b) tetrahedral, square planar and octahedral
(c) square planar, tetrahedral and octahedral
(d) octahedral, square planar and octahedral

56. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is (are) : **[IIT-JEE 2012]**

(a) *sp* and sp^3 (b) *sp* and sp^2
(c) only sp^3 (d) sp^2 and sp^3

Exercise-4 | Applied MCQs

1. Sodium chloride is an ionic compound whereas hydrogen chloride is mainly covalent because
   (a) Sodium is less reactive
   (b) Hydrogen is non-metal
   (c) Hydrogen chloride is a gas
   (d) Electronegativity difference in the case of Hydrogen and chlorine is less than 2.1.
2. For two ionic solids, CaO and Kl. Identify the wrong statement among the following
   (a) Lattice energy of CaO is much larger than that of Kl
   (b) KI is soluble in benzene
   (c) CaO has higher melting point
   (d) KI has lower melting point
3. The correct order of increasing C - O bond length of CO, $CO\ ^{-}$, CO_2 is
   (a) $CO\ ^{-}$ CO CO (b) CO $CO\ ^{-}$ CO
   (c) CO $CO\ ^{-}$ CO (d) CO CO $CO\ ^{-}$
4. Anti - bonding molecular orbital is formed by
   (a) Addition of wave functions of atomic orbitals
   (b) Subtraction of wave functions of atomic orbitals
   (c) Multiplication of wave functions of atomic orbitals
   (d) None of these
5. Among the following species, identify the isostructural pairs
   $NF_3, NO_3^-, BF_3, H_3O\ \ , HN_3$
   (a) $[NF_3, NO_3^-]$ and $[BF_3, H_3O\ \ ]$
   (b) $[NF\ , HN\ \ ]$ and $[NO^-, BF\ ]$
   (c) $[NF_3, H_3O\ \ ]$ and $[NO_3^-, BF_3]$
   (d) $[NF_3, H_3O\ \ ]$ and $[HN_3, BF_3]$
6. Which of the following is planar ?
   (a) XeO_4 (b) XeO_3F
   (c) XeO_2F_2 (d) XeF_4
7. The correct order of hybridization of the central atom in the following species NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is
   (a) dsp^2, dsp^3, sp^2 and sp^3 (b) sp^3, dsp^2, sp^3d, sp^2
   (c) dsp^2, sp^2, sp^3, dsp^3 (d) dsp^2, sp^3, sp^2, dsp^3
8. The common features among the species CN^-, CO and NO^+ are
   (a) bond order three and isoelectronic
   (b) bond order three and weak field ligands
   (c) bond order two and π - acceptors
   (d) isoelectronic and weak field ligands
9. Number of sigma bonds in P_4O_{10} is
   (a) 6 (b) 7
   (c) 17 (d) 16
10. Which one of the following arrangements of molecules is correct on the basis of their dipole moments?
    (a) $BF_3 > NF_3 > NH_3$ (b) $NF_3 > BF_3 > NH_3$
    (c) $NH_3 > BF_3 > NF_3$ (d) $NH_3 > NF_3 > BF_3$
11. Which of the following is the correct electron dot structure of N_2O molecule?
    (a) $:N \quad N \quad \ddot{O}:$ (b) $:N \quad N \quad \underset{\cdot\cdot}{\ddot{O}}:^{-}$
    (c) $\underset{\cdot\cdot}{\ddot{N}} \quad \ddot{N} \quad \ddot{O}:$ (d) $:N \quad N \quad \underset{\cdot\cdot}{\ddot{O}}:$
12. Consider the following statements. The common features of the molecules BF_3, CO & NO are that
    I. all are Lewis acids
    II. all are gaseous in nature
    III. all contain unpaired electrons
    IV. all do not conform to the octet rule
    Which of the above statements are correct ?
    (a) I and II (b) III and IV
    (c) I and III (d) II and IV
13. The nodal plane in the π -bond of ethene is located in
    (a) the molecular plane
    (b) a plane parallel to the molecular plane
    (c) A plane perpendicular to the molecular plane which bisects the carbon-carbon sigma bond at right angle
    (d) a plane perpendicular to the molecular plane which contains the carbon - carbon σ -bond
14. Which of the following statements is true ?
    (a) HF is less polar than HBr
    (b) Absolutely pure water does not contain any ions
    (c) Chemical bond formation takes place when forces of attraction overcome the forces of repulsion
    (d) In covalencey, transference of electrons takes place
15. In the anion $HCOO^-$ the two carbon - oxygen bonds are found to be of equal length. What is the reason for it ?
    (a) Electronic orbitals of carbon atom are hybridised
    (b) The C = O bond is weaker than the C –O bond
    (c) The anion $HCOO^-$ has two resonating structures
    (d) The anion is obtained by removal of a proton from the acid molecule
16. The pair of species having identical shapes for molecules of both species is
    (a) CF_4, SF_4 (b) XeF_2, CO_2
    (c) BF_3, PCl_3 (d) PF_5, IF_5
17. The solubilities of carbonates decrease down the magnesium group due to a decrease in
    (a) lattice energies of solids
    (b) hydration energies of cations
    (c) inter-ionic attraction
    (d) entropy of solution formation

18. In compounds of type ECl_3, where E = B, P, As or Bi, the angles Cl - E- Cl for different E are in the order.
(a) $B > P = As = Bi$ (b) $B > P > As > Bi$
(c) $B < P = As = Bi$ (d) $B < P < As < Bi$

19. Specify the coordination geometry around and hybridisation of N and B atoms in a 1 : 1 complex of BF_3 and NH_3
(a) N : tetrahedral, sp^3; B : tetrahedral, sp^3
(b) N : pyramidal, sp^3; B : pyramidal, sp^3
(c) N : pyramidal, sp^3; B : planar, sp^2
(d) N : pyramidal, sp^3; B : tetrahedral, sp^3

20. Which of the following are isoelectronic and isostructural?
$NO_3^-, CO_3^{2-}, ClO_3^-, SO_3$
(a) NO_3^-, CO_3^{2-} (b) SO_3, NO_3^-
(c) ClO_3^-, CO_3^{2-} (d) CO_3^{2-}, SO_3

21. Consider the chemical species NO_3^-, NO_2 and NO_2^- and point out the correct statement given below
(a) The hybrid state of N in NO_2 is sp^2
(b) The hybrid state of N in all the species is the same
(c) The shape of both NO_2 and NO_2^- is bent while NO_3^- is planar
(d) The hybrid state of N in NO_3^- and NO_2^- is the same

22. What is the true about – NF_5
(a) The molecule has trigonal bipyramidal geometry
(b) The oxidation state of N is 5
(c) N – F bonds are covalent Co-ordinate bonds
(d) The molecule does not exist

23. The molecules BF_3 and NF_3 are both covalent compounds, but BF_3 is non polar whereas NF_3 is polar. The reason for this is
(a) atomic size of Boron is larger than nitrogen
(b) Boron is metal while nitrogen is gas
(c) B – F bonds are non-polar while N – F bonds are polar
(d) BF_3 is planar but NF_3 is pyramidal

24. In a metallic crystal
(a) Both kernels as well electrons move rapidly
(b) The valence electrons remain within the field of influence of their kernels
(c) The valance electrons constitute sea of mobile electrons
(d) The valance electrons are localised between two kernels

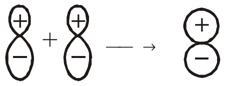
25. Which of the following accounts for the bond angle of 104° in water molecule
(a) sp^3 hybrid state of oxygen
(b) high electro negativity of H-atoms
(c) low ionisation energy of H-atoms
(d) lone pair-bond pair repulsions

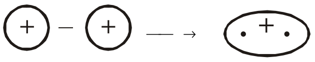
26. Anhydrous $AlCl_3$ is covalent but hydrated $AlCl_3.6H_2O$ is ionic because
(a) $AlCl_3$ dissolves in CS_2
(b) $AlCl_3$ has planar structure
(c) IE of Al is low
(d) Hydration energy of Al compensates the IE

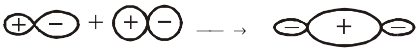
27. The molecule XY_2 contains two σ and two π bonds and one lone pair of electrons in valence shell of X. The arrangement of lone pair and bond pairs is
(a) linear
(b) trigonal planar
(c) square pyramidal
(d) unpredictable

28. A σ bonded molecule MX_3 is T-shaped. The number of non bonded pair of electrons is
(a) 0
(b) 2
(c) 1
(d) can be predicted only if atomic number is known

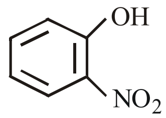
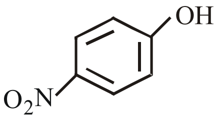
29. Which of the following overlap is correct ?

(a) 

(b) 

(c) 

(d) None of the above

30. The vapour pressure of  is higher than  due to
(a) Dipole moment
(b) Dipole- dipole interaction
(c) H – bonding
(d) Lattice structure

31. Of the molecules XeF_4, SF_4, SiF_4 one having tetrahedral structure
(a) Only SF_4 and XeF_4 (b) Only SiF_4
(c) Both SF_4 and SiF_4 (d) All the three

32. Considering greater polarisation in LiCl than in NaCl which of the following is wrong
(a) Fused LiCl would be less conducting than fused NaCl
(b) LiCl has lower melting point than NaCl
(c) LiCl dissolves more in organic solvents whereas NaCl does not
(d) LiCl would ionise in water more than NaCl

33. In which of the following set of molecules the order of boiling point is incorrect.

(a) $C_3H_8 \quad C_2H_6 \quad CH_4$ (b) $Xe > Ar > He$

(c) $HCl > HF > HBr$ (d) $H_2O \quad H_2Se \quad H_2S$

34. The stability of ionic crystals depends mainly on

(a) low heat of sublimation of cation formed

(b) high electron affinity of anion formed

(c) low I.E. of cation forming species.

(d) lattice energy of crystal

35. Silicon carbide is a

(a) covalent solid (b) ionic solid

(c) molecular solid (d) None of the above

36. If x-axis is the molecular axis of a diatomic molecule, then π molecular orbital are formed by overlap of

(a) s-atomic orbitals

(b) s and p_x atomic orbitals

(c) p_y and p_y-orbitals

(d) p_x and p_z-orbitals

37. The molecular size of ICl and Br_2 is approximately same, but boiling point of ICl is about 40°C higher than b.pt. of Br_2, because of

(a) I has larger size than Br

(b) I-Cl bond is stronger than Br-Br bond

(c) I E of Iodine < I E of Br

(d) ICl is polar while Br_2 is non polar

38. An element forms compounds of the formula ACl_3, A_2O_5 and Mg_3A_2 but does not form ACl_5, the A could be

(a) Al (b) P

(c) B (d) N

39. The magnitude of the lattice energy of a solid increases if

(a) charges on both the ions are small

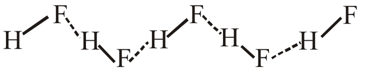
(b) the ions are large

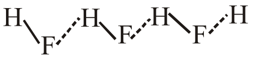
(c) the ions are small

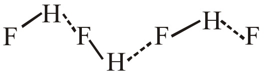
(d) the ions are of equal size

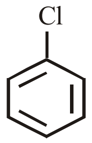
40. The correct representation of H-bond in solid HF

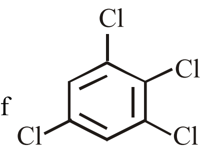
(a) H – F·····H – F·····H – F

(b)


(c)


(d)


41. The dipole moment of chlorobenzene  is 1.5 D.

The dipole moment of  is

(a) 2.86 D (b) 2.25 D

(c) 1.5 D (d) 0 D

42. The experimental value of the dipole moment of HCl is 1.03 D. The length of H – Cl bond is 1.275 Å. The percentage of ionic character on HCl

(a) 7 (b) 17

(c) 43 (d) 21

43. CaO and NaCl have the same crystal structure and approximately the same ionic radii. If U is the lattice energy of NaCl, the approximate lattice energy of CaO is

(a) U/2 (b) U

(c) 4C (d) 2U

44. Which of the following compounds has the highest lattice energy?

(a) MgO (b) LiCl

(c) NaCl (d) LiF

45. A diatomic molecule has a dipole moment of 1.2 D, if the bond distance is 1 Å, what percentage of electronic charge exists on each atom.

(a) 25 % of e (b) 29 % of e

(c) 19 % of e (d) 12 % of e

46. Which of the following statements is/are true

1. PH_5 and $BiCl_5$ donot exist

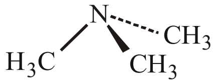
2. $p_\pi - d_\pi$ bond is present in SO_2

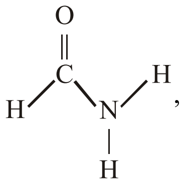
3. I_3 has bent geometry

4. SeF_4 and CH_4 have same shape

(a) 1, 2, 3 (b) 1, 3

(c) 1, 3, 4 (d) 1, 2, 4

47. Trimethylamine is a pyramidal molecule  and formamide is a planar molecule

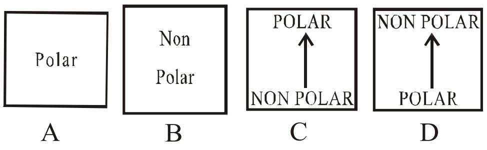


, The hybridisation of Nitrogen in both is

(a) sp^2, sp^2 (b) sp^3, sp^2

(c) sp^3, sp^3 (d) sp^2, sp

48. If climbing of water droplets is made to occur on a coated microscope slide, the slide would have to be coated in which of the following way



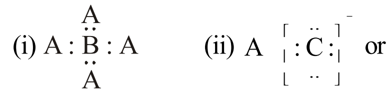
(a) A (b) B

(c) C (d) D

Hints & Solutions

EXERCISE 1

1. Bonding molecular orbital.
2. Because b.p. –b.p. repulsion is less in H_2S than in H_2O.
3. MgO
4. III, because like charges reside on adjacent atoms.
5. 1 – butyne has more dipole moment.
6. (i) Non-polar due to symmetric structure.
   (ii) Non-polar due to linear molecular structure.
   (iii) Polar due to non-symmetric molecular structure.
7. (a) A – group 1, B – group 14, C – group 17
   (b) A, C are expected to form ions A^+ and C^-
   (c) (i)

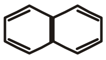


$$A : \overset{\overset{A}{\cdot\cdot}}{\underset{\underset{A}{\cdot\cdot}}{B}} : A \qquad \text{(ii) } A \left[: \ddot{\underset{\cdot\cdot}{C}} : \right]^- \text{ or } A^+Cl$$

11. $BeCl_2$ Since Be^{2+} ion is small in size.

19.	(b)	**20.**	(c)	**21.**	(b)
22.	(c)	**23.**	(c)	**24.**	(a)
25.	(c)	**26.**	(b)	**27.**	(d)
28.	(b)				

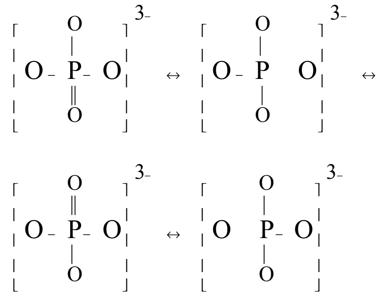
EXERCISE 2

1. **(c)** At bond distance the attractive forces overweigh the repulsive forces.
2. **(a)** In NaCl the bonding is ionic (electrovalent)
3. **(b)** Covalent (Fajan's rule see text)
4. **(d)** $\pi *2p_x^{\,2}\ \pi *2p_y^{\,1}$ antibonding molecular orbitals contain three electrons in O^-. Their energy being more and ionisation potential less.
5. **(a)** Polarizing power φ = charge/ radius. Thus φ charge.
6. **(d)** The larger the size of anion the more is its polarizability
7. **(b)** Covalent bonds are directional in nature
8. **(d)** BCl_3 is lewis acid and electron deficient. The octet around B is not complete
9. **(c)** Statement 1 is correct (see text)
10. **(d)**  number of π bonds is 5
11. **(b)** Bond order $\dfrac{N_b - N_a}{2} \quad \dfrac{8-2}{2} \quad 3$
12. **(c)** Bond order in NO is 2.5 (see text)
13. **(d)** Bond order in He_2 is zero (see text)
14. **(c)**

Species	N_2	O_2	N^-	O^-
Bond order	3	2	2.5	1.5

The O-O bond is O^- decreases

15. **(d)** $\sigma_b^2\, \sigma *_a^2\ \sigma_b^2\ \sigma_a^{*2}\ (\pi_b^2 = \pi_b^2)\sigma_b^1 (N_2 \quad 13\,\text{electrons})$
    it contains one unpaired electron hence paramagnetic
16. **(c)** NO is paramagnetic
17. **(c)**

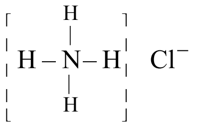


Bond order

$$\frac{\text{Number of bonds}}{\text{Number of Resonating structures}} \quad \frac{5}{4} \quad 1.25$$

Three unit negative charge is being shared by four O atoms.
Formal charge = –3/4

18. **(a)** O^- has Bond order 1.5 (see text)
19. **(c)**
20. **(c)** $\sigma_{1s}^2\, \sigma *_{1s}^2\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\ \sigma_{2p_z}^2 \begin{matrix} \pi_{2p_x}^2 & \pi *_{2p_x}^1 \\ \pi_{2p_y}^2 & \pi *_{2p_y}^1 \end{matrix}\ \sigma_{2p_z}^*$
    There are 7 pair of electrons
21. **(a)** Bond order in N_2 and O is 3 (calculate by energy level diagram)
22. **(b)** H^+
23. **(c)** $\sigma\ \ \sigma^*\ \ \sigma\ \ \sigma^*\ \ \sigma \begin{matrix} \pi & \pi^* \\ \pi & \pi^* \end{matrix}\ \sigma^*$
    4 pairs
24. **(b)** CO is diamagnetic while others are paramagnetic
25. **(c)** O^- (see text)
26. **(d)** In PH_6, P – H bond will have ionic character due to electron attracting tendency of P carrying +ve charge and least covalent.
27. **(c)**
28. **(d)** The electronegativity of S is least among others hence H -S bond is least polar in nature.
29. **(b)** Polarizing power of Zn^{2+} is more than others, hence $ZnCl_2$ is least ionic in nature.
30. **(a)** Electropositive character and size increases down the group, the ionic character increases.
31. **(a)** NH_4Cl contains both covalent and ionic bonds



$$\left[H - \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}} - H \right] Cl^-$$

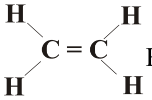
32. (b) Electronegativity difference is 4.0 - 1.20 = 2.8 percentage ionic character is 72.24% when the electronegativity difference is 1.7, the % ionic character is approx 51%.

33. (a) Ionic character follows the order HF > HCl > HBr > HI

34. (d)

35. (c) $H_3C-CH_2-CH=CH_2$. It has 11 σ bonds

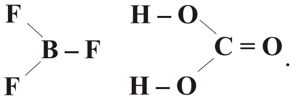
36. (c) Hybridisation in PF_5 is = ½ [5 + 5 + 0 –0] = 5 sp^3d, hence structure is trigonal bipyramidal.

37. (b)  Hybridisation of C is sp^2

38. (d) Hybridisation in $Si(CH_3)_4$ (½ [4 + 4 + 0 – 0] = 4) is sp^3 which is tetrahedral.

39. (d) Hybridisation in $SnCl_2$ (½ [4 + 2 + 0 - 0] =3) sp^3. It has V-shape.

40. (a) H_2CO_3 and BF_3 both have triangular planar structure



BF_3 is symmetrical

∴ $\mu = 0$ hence non polar, H_2CO_3 is not symmetrical hence polar in nature.

41. (b) SO_2 has sp^2 hybridisation.

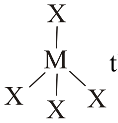
42. (c) AsF_5 is trigonal bipyramidal and sp^3d hybridised.

43. (c)

44. (c) Hybridisation of N = ½ [5 + 3 + 0 – 0] = 4 hence sp^3

45. (a) SF_6 is octahedral (see text)

46. (b) NO_2^+ = ½ [5 + O + O – 1] = 2 sp; NO_2^- = ½ [5 + 0 + 1 –0] = 3 sp^2; NH_4^+ = ½ [5 + 4 + 0 - 1] = 4 sp^3

47. (d)  three angle below M and three above M hence = 6

48. (c)

49. (b) NO_2^+ has sp hybridisation hence linear.

50. (c) O = C = C = C = O is sp hybridised

51. (d) In XeF_2 Total number of valence electrons of Xe = 8, two electrons shared with 2F atoms, 6 electrons left hence 3 lone pairs, in XeF_4 4 shared with 4 F atoms 4 left hence 2 lone pairs; in XeF_6 6 shared with 6 F atoms 2 left hence 1 lone pair.

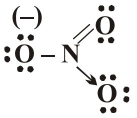
52. (b) In $CH_3\underline{C}H_2OH$ underlined C is forming 4 σ bonds, hence sp^3 hybridisation. In others it is sp^2 hybridised (due to 3 σ bonds).

53. (b) dsp^2 hybridisation involves $d_{x^2-y^2}$.

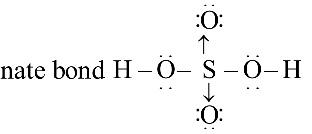
54. (b) Tetrahedral

55. (b) Hybridisation is sp^3 and shape pyramidal

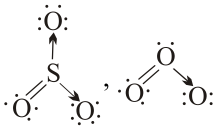
56. (b) Hybridisation in PO_4^{3-} = ½ [5 + 0 + 3 –0] = 4 sp^3. In π bonding only d orbital of P, p orbital of O can be involved. Since hybrid atomic orbitals do not form π bond.

57. (d)  it has 4 bond pairs and none lone pair.

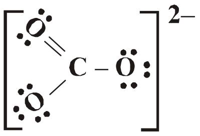
58. (b) $:\ddot{\underset{\cdot\cdot}{F}}-\ddot{\underset{\cdot\cdot}{O}}-\ddot{\underset{\cdot\cdot}{F}}:$ 2 bond pairs and 8 lone pairs

59. (d) All contain coordinate bond 

$$H-\ddot{\underset{\cdot\cdot}{O}}-\underset{\underset{:\ddot{O}:}{\downarrow}}{\overset{\overset{:\ddot{O}:}{\uparrow}}{S}}-\ddot{\underset{\cdot\cdot}{O}}-H$$,



60. (a) Coordinate bond

61. (c) CO_3^{2-} Its structure is 

62. (b) It is 4 See H - bonding.

63. (d) NH_3 forms intermolecular H - bonding.

64. (b) In H - bonding atoms involved are F, O and N.

65. (a) H -bonding interactions.

66. (c) It is due to H - bonding.

67. (d) In HCl No–H–bonding, H – F form zig zag; (cage like by H_2O, only NH_3 forms linear polymeric structures)

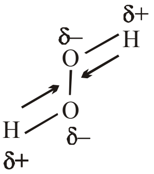
68. (a) H_2O (see H - bonding)

69. (b) C_2H_5OH soluble in water due to H-Bonding

70. (d) Metallic bond is electrostatic in nature.

71. (b) Non polar molecules have dispersive forces.

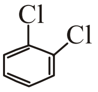
72. (d) The electronegativity difference is maximum between N & H hence NH_3 will have highest magnetic moment.

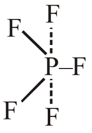
73. (d) H_2O_2 it is nonplanar 

The bonds are not in the plane of paper.

74. (b) $H_3C.C\equiv C.CH_3$ symmetrical and linear. Hence D.M. $(\mu) = 0$.

75. (c) In SiF_4 DM = zero due to symmetrical structure.

76. (b) Cis 1, 2 - dichloro benzene will have some D.M. 

77. (c) In PF_5 the hybridisation is sp^3d  axial. P – F bonds are longer than equatorial bonds.

78. (a) It is due to small size of Li compared to size of Na and K.

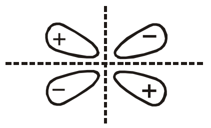
79. (c) Bond angles NH_3 (107.5°); BeF_2 (180°) H_2O (104.5°) and CH_4 (109°28')

80. (a) Bond angles

NH_3	PH_3	AsH_3	SbH_3
107.5°	92	91	90

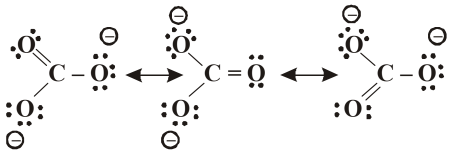
81. (d) $M_2^{+6}(SO_4)_3^{-6}$ Here metal atom is trivalent. Hence formula for phosphate will be MPO_4

82. (c) Since F form H-bond $[HF_2]^-$ exists. Therefore KHF_2 gives $K^+ + HF_2^-$

83. (c) 

It has two nodal planes. It is π^*2p_y

84. (b) Electronic configuration reveals it is monovalent (in fact Na) hence its oxide will be M_2O.

85. (b) 

86. (b) B.O. = ½ $[N_b - N_a]$ $Li_2 = \frac{4-2}{2} = 1; N_2 = 3; Be = 0, O_2 = 2.$

87. (d) In alcohol intermolecular H-bonding is possible whereas in ether it is not possible.

88. (c) Double helical structure of DNA is stabilised by H - bonding.

89. (a) Dipole moment follows the order $CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$

90. (a) $\underset{1}{CH_2} = \underset{2}{C}H - \underset{3}{C} \equiv \underset{4}{N}$

3σ bonds (sp^2 hybridisation); 2σ bonds (sp-hybridisation)

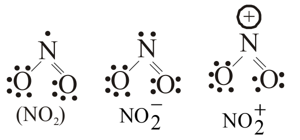
$C_1 = 3$ σ bonds, $C_2 = 3$ σ bonds,

$C_3 = 2$ σ bonds

EXERCISE 3

1. (c) Both BrO_3^- and XeO_3 have sp^3 hybridization but due to presence of one lp of electrons they have trigonal pyramidal geometry.

2. (b) From the structure of three species we can determine the number of lone pair electron(s) on central atom (i.e. N atom) and thus the bond angle.



We know that higher the number of lone pair electron(s) on central atom, greater is the lp – lp repulsion. Thus smaller is bond angle.

The correct order of bond angle is

$NO_2^- < NO_2 < \overset{+}{NO_2}$ i.e., option (b) is correct.

3. (d) Calculating the bond order of various species.

$O_2^- : KK\,\sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^1$

$$B.O. = \frac{1}{2}(N_b - N_a)$$

$$= \frac{8-5}{2} \text{ or } 1.5$$

NO =

$KK\,\sigma 2s^2, \sigma^* 2s^2, 62p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1$

$$B.O. = \frac{N_b - N_a}{2} = \frac{8-3}{2} \text{ or } 2.5$$

$= C_2^{2-} : KK\,\sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$

$$B.O. = \frac{N_b - N_a}{2} = \frac{8-2}{2} \text{ or } 3$$

$He_2^{2+} = \sigma 1s^2\, \sigma^* 1s^1$

$$B.O. = \frac{N_b - N_a}{2} = \frac{2-1}{2} \text{ or } 0.5$$

From these values we conclude that the correct order of increasing bond order is

$He_2^{2+} < O_2^- < NO < C_2^{2-}$

4. (d) Due to intermolecular hydrogen bonding in methanol, it exist as assosiated molecule.

5. (c) On determining hybridisation from H = 1/2 (V + M – C + A). The hybridisation of BF_3, NO_2^-, NH_2^- and H_2O are sp^2, sp^2, sp^3 and sp^3 respectively.

6. (a) Molecular orbital configuration of

$$N_2^{2-} = \sigma 1s^2\, \sigma^* 1s^2 \sigma 2s^2\, \sigma^* 2s^2 \text{ - } \begin{cases} \pi 2p_x^2 \\ \pi 2p_y^2 \end{cases} \sigma 2p_z^2 \begin{cases} \pi^* 2p_x^1 \\ \pi^* 2p_y^1 \end{cases}$$

Bond order = $\frac{10-6}{2}$ 2

$$N_2^- = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2 \sigma^* 2s^2 \begin{cases} \pi 2p_x^2 \\ \pi 2p_y^2 \end{cases} \sigma 2p_z^2 \begin{cases} \pi^* 2p_x^1 \\ \pi^* 2p_y^0 \end{cases}$$

Bond order = $\frac{10-5}{2}$ 2.5

$$N_2 = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2 \sigma^* 2s^2 \begin{cases} \pi 2p_x^2 \\ \pi 2p_y^2 \end{cases}, \sigma 2p_z^2$$

Bond order = $\frac{10-4}{2}$ 3

∴ The correct order is = N_2^{2-} N_2^- N_2

7. **(c)** For $SbCl_5^{2-}$, $H = \frac{5+5+2}{2} = 6$ means sp^3d^2 hybridization

I_3^-, SF_4, and PCl_5; all have sp^3d hybridization.

8. **(b)** In NO_3^-, nitrogen have sp^2 hybridisation, thus planar in shape. In H_3O^+, oxygen is in sp^3 hybridisation, thus tetrahedral geometry is expected but due to presence of one lp of electrons on central oxygen atom it is pyramidal in shape.

9. **(c)** NH_4^+ : sp^3 hybridisation

CH_4: sp^3 hybridisation

SF_4: sp^3d hybridisation

BF_4^- : sp^3 hybridisation

10. **(b)** Bond order of $Be_2 = 0$, hence Be_2 cannot exist.

11. **(b)** $\overset{sp^3}{H_3C} - \overset{sp}{C} \equiv \overset{sp}{C} - \overset{sp^3}{CH_3}$

Linear due to *sp* hybridized C atom.

12. **(a)** Hybridisation = $\frac{1}{2}$ [No. of valence electrons of central atom + No. of monovalent atoms attached to it + Negative charge if any – Positive charge if any]

NO_2^- $H = \frac{1}{2}[5+0+1-0] = 3 = sp^2$

NO_3^- $H = \frac{1}{2}[5+0+1-0] = 3 = sp^2$

NH_2^- $H = \frac{1}{2}[5+2+1+0] = 4 = sp^3$

NH_4^+, $H = \frac{1}{2}[5+4+0-1] = 4 = sp^3$

$SCN^- = sp$

i.e., NO_2^- and NO_3^- have same hybridisation.

13. **(a)** $O_2(16) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^1$$

B.O. = ½ ($N_b - N_a$) = ½ (10 – 6) = 2

O_2 (15) $= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^0$$

B.O. = ½ ($N_b - N_a$) = ½ (10 – 5) = 2.5

$O_2^-(17) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^1$$

B.O. = ½ ($N_b - N_a$) = ½ (10 – 7) = 1.5

$O_2^{2-}(18) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^2$$

B.O. = ½ ($N_b - N_a$) = ½ (10 – 8) = 1

Since, the bond length decreases as the bond order increases, hence, O_2^+ have least bond length.

14. **(c)** MOT configurations of O_2 and O_2^+ :

$O_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2$

$(\pi 2p^2_x = \pi 2p^2_y)\ (\pi^* 2p_x{}^1 = \pi^* 2p^0_y)$

Number of unpaired electrons = 1, so paramagnetic.

$O_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2$

$(\pi 2p^2_x = \pi 2p^2_y)\ (\pi^* 2p_x{}^1 = \pi^* 2p^1{}_y)$

Number of unpaired electrons = 2, so paramagnetic.

15. **(d)** BF_4^- hybridisation sp^3, tetrahedral structure.

NH_4 hybridisation sp^3, tetrahedral structure.

16. **(b)** $(O_2) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2P_y^1$$

Bond order $= \frac{N_b - N_a}{2} = \frac{10-6}{2} = \frac{4}{2} = 2$

O_2 ion $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1$$

Bond order $\frac{N_b - N_a}{2} = \frac{10-5}{2} = \frac{5}{2} = 2\frac{1}{2}$

$(O_2^-) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2P_z^2,$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^1$$

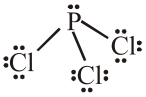
Bond order $= \frac{(N_b - N_a)}{2} = \frac{10-7}{2} = \frac{3}{2} = 1\frac{1}{2}$

O_2^{2-} $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^2$$

Bond order $\frac{N_b - N_a}{2} = \frac{10-8}{2} = \frac{2}{2} = 1$

17. **(d)** PCl_3



18. **(a)** Both O_2^{2-} and B_2 has bond order equal to 1.

$B_2(10) = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2$

$$\pi 2p^1{}_x = \pi 2p_y{}^1$$

Bond order $= \frac{N_b - N_a}{2}$

$$= \frac{6-4}{2} = \frac{2}{2} = 1$$

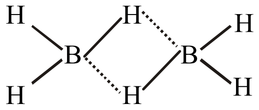
B_2 is known in the gas phase

$O_2^{2-} = (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2$

$(\pi 2p_x)^2 = (\pi 2p_y)^2 (\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$

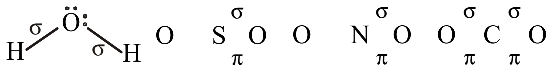
Bond order $= \frac{1}{2}$ 10 – 8 1

19. **(b)** $(BH_3)_2$ or (B_2H_6)



It contains two 3 centre - 2 electron bonds and present above and below the plane of molecules compounds which do not have sufficient number of electrons to form normal covalent bonds are called electron deficient molecules.

20. **(a)**



21. **(a)** Molecular orbital configuration of O_2^- is

O_2^- (17) = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2$,

$\sigma 2p_z{}^2, \pi 2p_x{}^2 = \pi 2p_y{}^2, \pi^* 2p_x{}^2 = \pi^* 2p_y{}^1$

22. **(b)** This type of attractive force operates between the polar molecules having permanent dipole and the molecules lacking permanent dipole.
HCl is polar (μ ¹ 0) and He is non polar (μ = 0), thus gives dipole-induced dipole interaction.

23. **(a)** In NH_3 and BF_4^- the hybridisation is sp^3 and the bond angle is almost 109° 28'

24. **(b)** Both NO_2 and O_3 have angular shape and hence will have net dipole moment.

25. **(b)** In H_2S, due to low electronegativity of sulphur the *l*.p. - *l*. p. repulsion is more than bp. - bp. repulsion and hence the bond angle is 92°.

26. **(a)** Both XeF_2 and CO_2 have a linear structure.

27. **(a)** The order of bond angles

$$\underset{120^\circ}{BF_3} > \underset{109^\circ 28'}{SiH_4} > \underset{107^\circ}{NH_3} > \underset{92.5^\circ}{H_2S}$$

28. **(b)** The lower the bond order the greater the bond length and vice-versa.

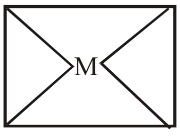
29. **(b)** In H_3BO_3 hybridisation of B is sp^2 and O is sp^3.

30. **(a)** XeF_4 (sp^3d^2 square planar),

$[Ni(CN)_4]^{2-}$ (dsp^2 square planar),

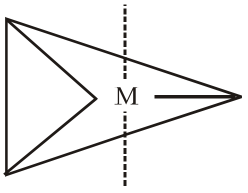
BF_4^- (sp^3 tetrahedral), SF_4 (sp^3d see saw shaped)

31. **(d)**



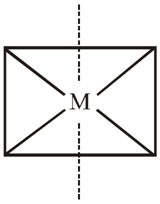
dsp^2 hybridisation

Number of 90° angle between bonds = 4



sp^3d or dsp^3 hybristion

Number of 90° angle between bonds = 6



sp^3d^2 hybridisation
Number of 90° angle
between bonds = 12

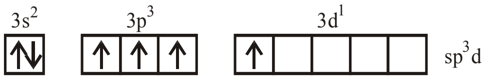
32. **(c)** H_2 is diamagnetic as it contains all paired electrons

$$\underset{\text{(diamagnetic)}}{H_2 = \sigma_b^2}\ ,\quad \underset{\text{(paramagnetic)}}{H_2^+ = \sigma_b^1},\quad \underset{\text{(paramagnetic)}}{H_2^- = \sigma_b^2},$$

$$\underset{\text{(paramagnetic)}}{\sigma_a^{*1}; He_2^+} \quad = \quad \underset{\text{(paramagnetic)}}{\sigma_b^2, \sigma_a^{*1}}$$

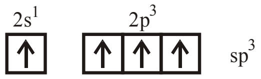
33. **(a)** The value of lattice energy depends on the charges present on the two ions and the distance between them.

34. (i) SF_4 – Configuration of excited S atom :



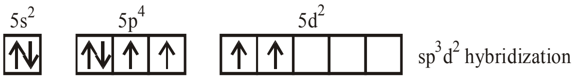
shape-square pyramidal, one lone pair

CF_4 – Configuration of excited C-atom :



shape-tetrahedral; no lone pair

XeF_6 – configuration of excited Xe atom :



shape-square planar, 2 lone pairs

35. **(c)** The distribution of electrons in MOs is as follows:

$N_2{}^+$(electrons 13) $\sigma^2\, \sigma^{*2}\, \sigma^2\, \sigma^{*2} \begin{smallmatrix}\pi^2\\ \pi^2\end{smallmatrix} \sigma^1 \begin{smallmatrix}\pi^*\\ \pi^*\end{smallmatrix} \sigma^*$

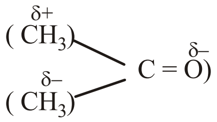
O_2 (electrons 16) $\sigma^2\, \sigma^{*2}\, \sigma^2\, \sigma^{*2}\, \sigma^2 \begin{smallmatrix}\pi^2\\ \pi^2\end{smallmatrix} \begin{smallmatrix}\pi^{*1}\\ \pi^{*1}\end{smallmatrix} \sigma^*$

$O_2{}^{2-}$ (electrons 18) $\sigma^2\, \sigma^{*2}\, \sigma^2\, \sigma^{*2}\, \sigma^2 \begin{smallmatrix}\pi^2\\ \pi^2\end{smallmatrix} \begin{smallmatrix}\pi^*\\ \pi^*\end{smallmatrix} \sigma^*$

B_2 (electrons 10) $\sigma^2\, \sigma^{*2}\, \sigma^2\, \sigma^{*2} \begin{smallmatrix}\pi^1\\ \pi^1\end{smallmatrix} \sigma\ \pi^*\ \sigma^*$

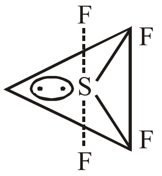
Only $O_2{}^{2-}$ does not contain any unpaired electron.

36. **(d)** Acetonitrile $(CH_3 - \overset{\delta+}{C} \equiv \overset{\delta-}{N})$ and acetone



both are polar molecules, hence dipole-dipole interaction exist between them. Between KCl and water ion-dipole interaction is found and in benzene-ethanol and benzene-carbon tetra chloride disperion force is present

37. **(d)** In SF_4 the hybridisation is sp^3d and the shape of molecule is



38. **(b)** Diamagnetic species have no unpaired electrons

$O_2^{2-} \Rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$
$\{\pi 2p_x^2 = \pi 2p_y^2, \{\pi^* 2p_x^2 = \pi^* 2p_y^2$

Whereas paramagnetic species has one or more unpaired electrons as in

$O_2 \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \{\pi 2p_x^2 = \pi 2p_y^2,$

$\{\pi^* 2p_x^1 \quad \pi^* 2p_y^1$ 2 unpaired electrons

$O_2^+ \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$\pi 2p_x^2 = \pi 2p_y^2 \; \pi^* 2p_x^1 = \pi^* 2p_y^0$ 1 unpaired electron

$NO \rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$\pi 2p_x^2 = \pi 2p_y^2, \; \pi^* 2p_y^1 = \pi^* 2p_z^0 = 1$ unpaired electron

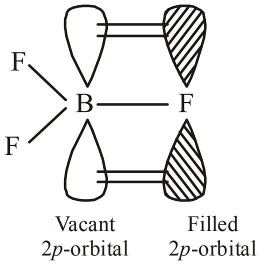
39. **(d)** Smaller the size and higher the charge more will be the polarising power of cation. Since the order of the size of cation is $K^+ > Ca^{++} > Mg^{++} > Be^{++}$. So the correct order of polarising power is
$K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

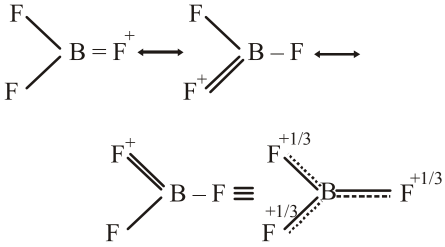
40. **(c)** (i) N_2 : bond order = 3, diamagnetic
N_2^- : bond order = 2.5, paramagnetic
(ii) C_2 : bond order = 2, diamagnetic
C_2^+ : bond order = 1.5, paramagnetic
(iii) NO : bond order = 2.5, paramagnetic
NO^+ : bond order = 3, diamagnetic
(iv) O_2 : bond order = 2, paramagnetic
O_2^+ : bond order = 2.5, paramagnetic

41. **(c)** Greater the difference between electro-negativity of bonded atoms, stronger will be the bond. Since F is most electronegative hence F – H ...... F is the strongest bond.

42. **(a)** For any species to have same bond order we can expect them to have same number of electrons. Calculating the number of electrons in various species.
$O_2^- (8+8+1=17)$; $CN^- (6+7+1=14)$
$NO^+ (7+8-1=14)$; $CN^+ (6+7-1=12)$
We find CN^- and NO^+ both have 14 electrons and bond order 3.

43. **(b)** The delocalised $p\pi - p\pi$ bonding between filled *p*-orbital of F and vacant *p*-orbital of B leads to shortening of B–F bond length which results in higher bond dissociation energy of the B–F bond.





44. **(d)** Calcium carbide exists as Ca^{2+} and C_2^{2-}. According to the molecular orbital model, C_2^{2-} should have molecular orbital configuration :

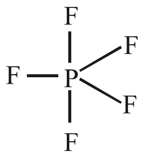
$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$

$\{\pi 2p_x^2 = \pi 2p_y^2\}, \sigma 2p_z^2$

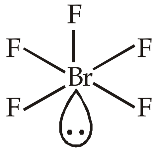
Thus M.O. configuration suggests that it contains one σ & 2π bonds.

45. **(c)** All the members form volatile halides of the type AX_3. All halides are pyramidal in shape. The bond angle decreases on moving down the group due to decrease in bond pair-bond pair repulsion.

46. **(c)** PF_5 trigonal bipyramidal



BrF_5 square pyramidal (distorted due to presence of one lp of electrons on central atom)



47. **(a) & (b)** The molecular orbital structures of C_2 and N_2 are

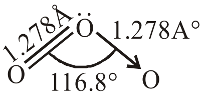
$$N_2 = \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2$$

$$C_2 = \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2 \pi 2py^2 \pi 2P_z^2$$

Both N_2 and C_2 have paired electrons, hence they are diamagnetic.

48. All options are correct,

(a) ONCl 8 7 17 32e⁻ } not isoelectronic
ONO⁻ 8 7 8 1 24e⁻

(b) 

The central atom is sp^2 hybridized with one lone pair.

(c) It is a pale blue gas. At – 249.7°, it forms violet black crystals.

(d) It is diamagnetic in nature due to absence of unpaired electrons.

49. **(c)** $H_2^{2+} = \sigma 1s^0\, \sigma^*1s^0$

Bond order for $H_2^{2+} = \frac{1}{2}(0-0)\quad 0$

$He_2 = \sigma 1s^2 \sigma^* 1s^2$

Bond order for $He_2 = \frac{1}{2}(2-2)\quad 0$

so both H_2^{2+} and He_2 does not exist.

50. **(b)** $Li_2 = \sigma 1s^2\, \sigma^*1s^2\, \sigma 2s^2$

$\therefore$ Bond order $= \frac{1}{2}(4-2) = 1$

$Li_2^+ = \sigma 1s^2\, \sigma^*1s^2\, \sigma 2s^1$

B.O. $= \frac{1}{2}(3-2) = 0.5$

$Li_2^- = \sigma 1s^2\, \sigma^*1s^2 \sigma 2s^2 \sigma^*2s^1$

B.O. $= \frac{1}{2}(4-3) = 0.5$

The bond order of Li_2^+ and Li_2^- is same but Li_2^+ is more stable than Li_2^- because Li_2^+ is smaller in size and has 2 electrons in antibonding orbitals whereas Li_2^- has 3 electrons in antibonding orbitals. Hence Li_2^+ is more stable than Li_2^-.

51. **(d)** (i) In Na_2O_2, we have O_2^{2-} ion. Number of valence electrons of the two oxygen in O_2^{2-} ion $= 8 \times 2 + 2$ $=18$ which are present as follows

$\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_z^2, \{\pi 2p_x^2 = \pi 2p_y^2,$

$\{\pi^*2p_x^2 = \pi^*2p_y^2$

$\therefore$ Number of unpaired electrons = 0, hence, O_2^{2-} is diamagnetic.

(ii) No. of valence electrons of all atoms in $O_3 = 6 \times 3 = 18$.
Thus, it also, does not have any unpaired electron, hence it is diamagnetic.

(iii) No. of valence electrons of all atoms in N_2O $= 2 \times 5 + 6 = 16$. Hence, here also all electrons are paired. So it is diamagnetic.

(iv) In KO_2, we have O_2^-. No. of valence electrons of all atoms in $O_2^- = 2 \times 8 + 1 = 17$,

$$\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_z^2$$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi^*2p_x^2 = \pi^*2p_y^1$$

Thus it has one unpaired electron, hence it is paramagnetic.

52. **(a)** Molecular electronic configuration of

$CO: \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \{\pi 2p_x{}^2 = \pi 2p_y{}^2, \sigma 2p_z{}^2$

Therefore, bond order $\frac{N_b - N_a}{2}\quad \frac{10-4}{2}\quad 3$

$NO\ : \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_z{}^2, \{\pi 2p_x{}^2 = \pi 2p_y{}^2$

Bond order $\frac{10-4}{2}\quad 3$

$CN^- = \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2,$

$\{\pi 2p_x{}^2 = \pi 2p_y{}^2, \sigma 2p_z{}^2$

Bond order $\frac{10-4}{2}\quad 3$

$N_2 : \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \{\pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$

Bond order $\frac{10-4}{2}\quad 3$

$NO^- : \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_z^2,$

$\{\pi 2p_x^2 = \pi 2p_y^2,\ \{\pi^*2p_x^1 = \pi^*2p_y^1$

Bond order $\frac{10-6}{2}\quad 2$

$\therefore$ NO^- has different bond order from that in CO.

53. **(a)** Molecular orbital configuration of $B_2(10)$ as per the condition given in question will be

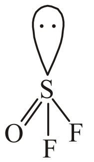
$\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \pi 2p_x^2$

Bond order of $B_2 = \frac{6-4}{2}\quad 1$.

B_2 will be diamagnetic.

54. **(d)** $OSF_2 :\ H = \frac{6+2}{2} = 4$.

It has 1 lone pair.



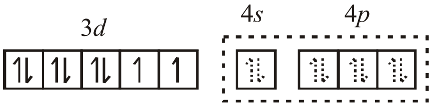
(Shape is trigonal pyramidal)

The shapes of SO_3, BrF_3 and SiO_3^{2-} are triangular planar respectively.

55. **(b)** $Ni^{+2} + 4Cl^- \longrightarrow \underset{sp^3}{[NiCl_4]^{2-}}$

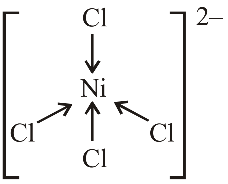
$[NiCl_4]^{2-}$. = $3d^8$ configuration with nickel in + 2 oxidation state, Cl^- being weak field ligand does not compel for pairing of electrons.
So,

$[NiCl_4]^{2-}$



sp^3 hybridisation

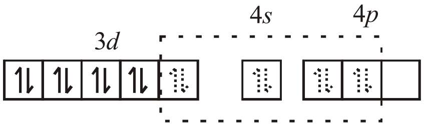
Hence, complex has tetrahedral geometry



$Ni^{+2} + 4CN^- \longrightarrow [Ni(CN)_4]^{2-}$

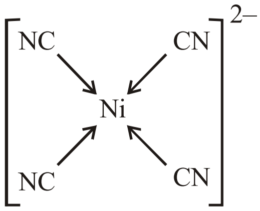
$[Ni(CN)_4]^{2-}$ = $3d^8$ configuration with nickel in + 2 oxidation state, CN^- being strong field ligand compels for pairing of electrons.
So,

$[NiCN_4]^{-2}$



dsp^2 hybridisation

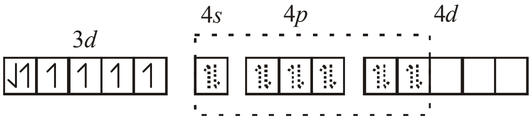
Hence, complex has square planar geometry.



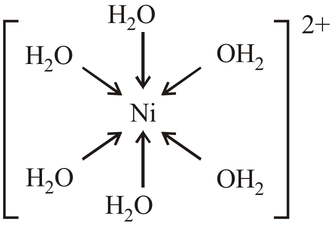
$Ni^{+2} + 6H_2O \longrightarrow [Ni(H_2O)_6]^{2+}$

$[Ni(H_2O)_6]^{2+}$ = $3d^8$ configuration with nickel in + 2 oxidation state. As with $3d^8$ configuration two d-orbitals are not available for d^2sp^3 hybridisation. So, hybridisation of Ni (II) is sp^3d^2 and Ni (II) with six co-ordination will have octahedral geometry.

$[Ni(H_2O)_6]^{2+}$



sp^3d^2 hybridisation



56. **(b)** Allene (C_3H_4) is $\overset{sp^2}{H_2C}\ \ \overset{sp}{C}\ \ \overset{sp^2}{CH_2}$

EXERCISE 4

1. **(b)** Hydrogen is non metal and non metal atoms form covalent bond

2. **(b)** KI is insoluble in benzene being ionic compound (Like dissolves like)

3. **(d)** The Bond order of C- O in CO, CO_2 and CO_3^{2-} is 3, 2 and 1.33.

Hence bond length follows the order CO < CO_2 < CO_3^{2-}

4. **(b)**

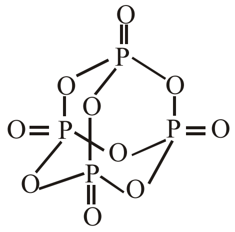
5. **(c)** Hybridisation in NF_3 and H_3O^+ is sp^3 and they have pyramidal shape. Hybridisation in NO_3^- and BF_3 is sp^2 and they have triangular planar shape.

6. **(d)** In XeO_4 hybridisation is ½[8 + 0 + 0 –] = 4 sp^3 tetrahedral; XeO_3F = ½[8 + 1 + 0 –0] = Q + R = 5 sp^3d trigonal bipyramidal; XeO_2F_2 = ½ [8 + 2 + 0–0] = 5 sp^3d trigonal bipyramidal one equatorial position occupied by lone pair of electrons; XeF_4 = ½ [8 + 4 + 0 – 0]=6 sp^3d^2 octatradral two axial position occupied by lone pair of electrons.

7. **(b)** Hybridisation in NH_3 = sp^3, $[PtCl_4]^{2-}$ dsp^2 (inner complex); PCl_5 = sp^3d and BCl_3 is sp^2.

8. **(a)** Bond order in CN^-, CO and NO^+ is three and they are isoelectronic.

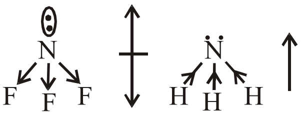
9. **(d)** Structure of P_4O_{10} is



Number of σ bonds in P_4O_{10} is 16

10. (d) In NF_3 D.M. due to lone pair and F act in opposite direction and cancel each other while in NH_3 it acts in one direction only Hence D.M. of NH_3 is more than NF_3.

11. (b)



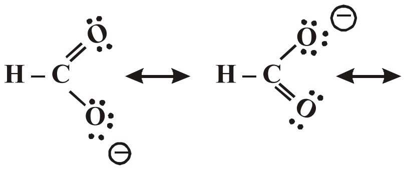
$:N\equiv\overset{+}{N}-\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{O}}:$ octet of each atom is complete.

12. (d) All gaseous and do not conform to octet rule

13. (a) The molecular plane does not contain π electron density. Hence nodal plane in the π bond is in the molecular plane.

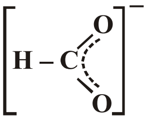
14. (c)

15. (c)



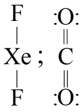
or Resonance

hybrid



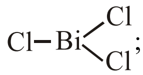
due to resonance C – O bond length is the same.

16. (c) XeF_2 and CO_2 have linear structure



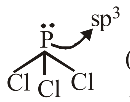
17. (b) $\text{Solubility} \propto \frac{1}{\text{lattice energy}}$. Lattice energy opposes solubility and $\text{Solubility} \propto \text{heat of hydration}$. Heat of hydration favours solubility. For second groups ions heat of hydration is $Be^{++} > Mg^{++} > Ca^{++} > Sr^{++} > Ba^{++}$ hence solubility decreases down the group.

18. (b) $BiCl_3$:



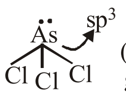
; sp^2 - Hybridisation (Trigonal geometry); Bond angle = 120°

In PCl_3



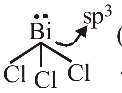
(Pyramidal geometry)

In $AsCl_3$–



(Pyramidal geometry)

In $BiCl_3$–



(Pyramidal geometry)

Bond angle = below 109° 28' and decreases from PCl_3 to $BiCl_3$

In these, order of bond angle : $BCl_3 > PCl_3 > AsCl_3 > BiCl_3$

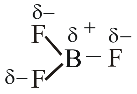
19. (a) $H_3N \to BF_3$ where both N, B are attaining tetrahedral geomerty.

20. (a) NO_3^- and CO_3^{2-} both have same number of electrons (equal to 32) and central atom in each being sp^2 hybridised, are isostructural too.

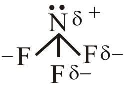
21. (d) The hybrid state of N in NO_3^- and NO_2^- is the same and it is sp^2 while in NO_2^+ it is sp

22. (d) Since the N does not contain d orbitals, the formation of NF_5 is not possible

23. (d) The shape of BF_3 is trigonal planar



and $\mu = 0$ hence it is non polar. The shape of NF_3 is pyramidal



and $\mu \neq 0$ hence it is polar.

24. (c) In metallic crystals the Kernels constitute the lattice and electrons are mobile and form sea of electrons.

25. (d) Bond angles are affected by repulsions which are $lp - lp > lp - bp > bp - bp$.

26. (d) The hydrated Aluminium chloride trivalent complex ion $[Al.(H_2O)_6]^3$, formation of which is exothermic process. The energy released is sufficient to cause the ionisation of Al.

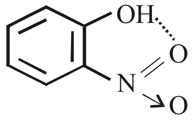
27. (b) Since XY_2 forms 2σ, 2π bonds and has 1 lone pair of electrons. It must have the structure $Y=\ddot{X}=Y$. Hence Y is divalent. The hybridisation of X is $sp^2\left(\frac{1}{2}(6+0+0-0)=3\right)$. So XY_2 is trigonal planar

(like SO_2).

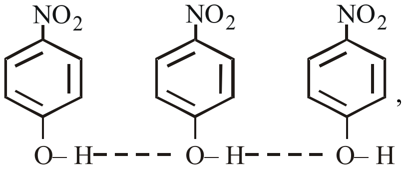
28. (b) For T-shape geometry the molecule must have 3 bonded pair and 2 lone pair of electrons.

29. (a) See text

30. (c) Ortho-nitrophenol has intramolecular H-bonding



and para-nitrophenol has intermolecular H-bonding.



Hence former is more volatile than latter.

31. (b) SF_4 (sp^3d) has see saw shape, $XeF_4(sp^3d^2)$ square planar and $SiF_4(sp^3)$ is tetrahedral.

32. (d) LiCl is covalent in nature due to small size of Li^+ ion, hence LiCl will ionise less than NaCl.

33. (c) Due H -bonding in H – F its boiling point is more than HCl.

34. (d) Although all the factors are correct but out of these lattice energy is the most important one. (See Born-Haber cycle).

35. (a) Silicon carbide is covalent solid.

36. (c) A π bond is formed by orbitals having same symmetry about the internuclear axis.

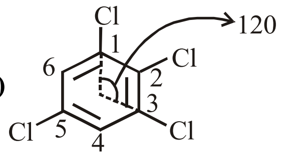
37. (d) The more the polar nature of molecule the more is the boiling point.

38. (d) Nitrogen can form NCl_3, N_2O_5 and Mg_3N_2 but not NCl_5 due to non availability of d atomic orbitals.

39. (c) The smaller the size, the more the charge, the more is the lattice energy.

40. (b)

41. (c)



Dipole moments of 2Cl and 5Cl are vectorically cancelled.

It is due 1 Cl and 3 Cl $\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_{21}\cos\theta$

$= (1.5)^2 + (1.5)^2 + 2 \times 1.5 \times 1.5 \cos 120$

$\therefore \quad \mu = 1.5\,D$

42. (b) $\mu_{cal} = e \times l = (4.802 \times 10^{-10}\,esu)\ (1.275 \times 10^{-8}\,cm)$

Percentage ionic character $= \frac{\mu_{obs}}{\mu_{cal}} \times 100 = \frac{1.03}{6.12} = 100 = 17\%$

43. (c) Lattice energy $= \frac{\text{Product of charges}}{\text{interionic distance}}$

In NaCl the product of charges = 1 × 1; In CaO product of charges = 2 × 2 = 4 while the inter ionic distance is almost same in both. Thus lattice energy of CaO is almost four times the lattice energy of NaCl.

44. (a) MgO has highest lattice energy, since 2 × 2 = 4 is maximum in MgO.

45. (a) $\mu = e \times d$

$$\therefore\ e = \frac{\mu}{d} = \frac{1.2\ D}{1.0\ A} = \frac{1.2 \times 10^{-18}\ esu\ cm}{1.0 \times 10^{-8}\ cm}$$

$= 1.2 \times 10^{-10}$ esu

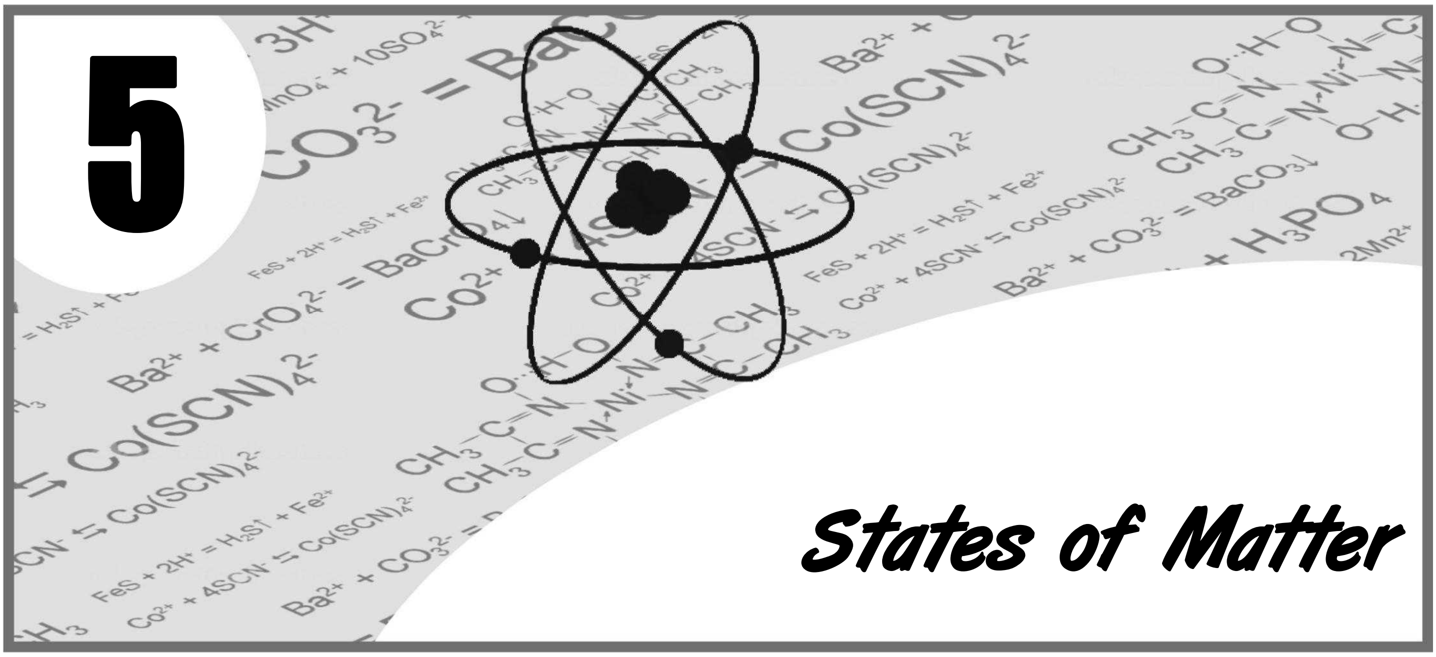
Percentage of electronic charge

$$= \frac{1.2 \times 10^{-10}\ esu}{4.8 \times 10^{-10}\ esu} \times 100 = 25\ \%$$

46. (a) All the statements are correct (see text).

47. (b) In amine the nitrogen is sp^3 hybridised and in amide the nitrogen is sp^2 hybridised.

48. (c) Since water is polar in nature and like dissolves like, the coating must be nonpolar to polar manner.



5

States of Matter

STATES OF MATTER :

The three important states of the matter are (i) **Solid state** (ii) **Liquid state** (iii) **Gaseous state**, which can exist together at a particular temperature and pressure e.g. water has three states in equilibrium at 4.58 mm and 0.0098°C.

PLASMA STATE :

It is the gaseous mixture of electrons and positive ions existing at extremely high temperatures (in the interior of stars) or internal electrical fields in discharge tubes.

SINGLE SUPER ATOM STATE :

At extermely low temperature, all atoms lose their identity and get condensed into a single entity behaving like a single super atom.

SOME CHARACTERISTICS OF THE THREE COMMON FORMS OF MATTER ARE :

	Property	*Gaseous state*	*Liquid State*	*Solid state*
1	**General**	It has definite mass but no definite shape and volume	It has definite mass and volume but no definite shape	It has definite mass, volume and shape.
2.	**Forces**	Almost negligible	Weaker than those in solids	Strongest
3.	**Density**	Low	Lower than solids	High
4.	**Motion**	Molecules have large rotatory, vibratory and translatory motions	Low values of motions	No translatory or rotatory motion. Possess vibratory motion
5.	**Packing**	No proper packing	Less closely packed	Molecules closely packed
6.	**Energy**	Least	Higher than solids	Molecules possess maximum energy
7.	**Thermal Expansion**	High	Higher than solid	Least
8.	**Compression**	High	Slightly higher than solid	Least compressibility
9.	**Intermixing**	Spontaneous	Spontaneous but slow	Least-intermixing
10.	**Pressure**	Exert pressure on the walls of container	Negligible	Negligible

MEASURABLE PROPERTIES OF GASES :

Four measurable properties are.

(i) Mass : It is expressed in grams or kg. 1 kg=10^3 g moles of gas $= \frac{\text{Mass in grams}}{\text{Molar mass}} = \frac{m}{M}$

(ii) Volume : It is equal to the volume of the container and is expressed in terms of litres (L), millilitres (ml), cubic centimeters (cm^3), cubic meters (m^3) or cubic decimeters (dm^3).

$$1\ell = 1000\,\text{ml} = 1000\,\text{cm}^3 = 1\,\text{dm}^3$$

$$1\,\text{m}^3 = 10^3\,\text{dm}^3 = 10^6\,\text{cm}^3 = 10^6\,\text{ml} = 10^3\,l$$

(iii) Pressure : It is equal to force per unit area and expressed in the units such as atmosphere, millimetres (mm), centimetres (cm), torr, bar etc. SI unit of pressure is pascal (Pa) or kilopascal (kPa)

$$1\,\text{atm} = 76\,\text{cm of Hg} = 760\,\text{mm of Hg} = 760\text{ torr}$$

$$1\,\text{atm} = 101.325\text{ kPa} = 101325\,\text{Pa} = 101.325\,\text{Nm}^{-2}$$

$$= 1.01325\text{ bar} = 14.7\,\text{lb}\,\text{m}^{-2}\text{ (psi)}$$

$1\,\text{bar} = 10^5$Pa. Pressure is measured with manometer

(iv) Temperature : It is measured in celcius scale (°C)or in Kelvin scale (K). SI unit of temperature is Kelvin (K) or absolute degree T (K) = $t\,°\text{C} + 273$

GAS LAWS :

Boyle's Law - The volume of a given mass of a gas is inversely proportional to its pressure at constant temperature.

$$V \propto \frac{1}{P} \quad or \quad VP = k\text{, a constant}$$

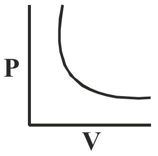
Value of k depends on mass, temperature and nature of gas.

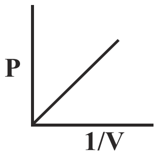
When mass and temperature are the same we have $P_1V_1 = P_2V_2$

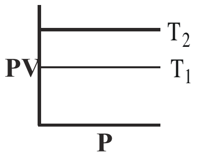
ISOTHERMS :

Graphs of V vs P or PV vs P at constant temperature are known as Isotherms.

GRAPHICAL REPERSENTATION OF BOYLES LAW :







CHARLE'S LAW :

The volume of the given mass of a gas increases or decreases by $\frac{1}{273.15}$ of its volume at 0°C for each degree rise or fall of temperature at constant pressure.

$$V_t = V_0\left(1+\frac{t}{273.15}\right) \text{ at constant. P and n}$$

or

The volume of a given mass of a gas is directly proportional to the absolute temperature at constant pressure.

$$V \propto T \text{ at constant P and n or } \frac{V}{T} = \text{const. or } \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

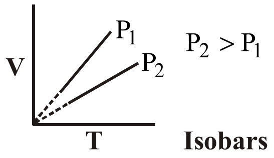
ABSOLUTE ZERO :

If in the above equation we put the value of t as –273.15 ºC the volume of the gas will be zero. It means gas will not exist, which is not possible. In fact all gases get liquified before this temperature is reached. This hypothetical or imaginary temperature at which the gases occupy zero volume is called **absolute zero.**

ISOBAR :

A graph of V vs T at constant pressure is known as Isobar.

GRAPHICAL REPRESENTATION OF CHARLE'S LAW:



GAY LUSSAC'S LAW : (AMANTON'S LAW) :

The pressure of a given mass, of gas increases or decreases by $\frac{1}{273.15}$ of its pressure at 0°C for each degree rise or fall of temperature at constant volume.

$$P_t = P_0\left(1+\frac{t}{273.15}\right) \text{at constant V and n}$$

or

The pressure of a given mass of a gas at constant volume is directly proportional to absolute temperature

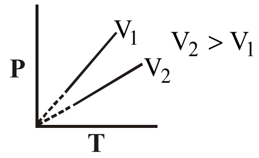
$$P \propto T \text{ or } P = kT \text{ or } \frac{P}{T} = k \text{ at constnat V and n}$$

$$\text{or } \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

ISOCHORES :

A graph of P vs T at constant volume is known as Isochore

GRAPHICAL REPRESENTATION OF GAY LUSSAC'S LAW :



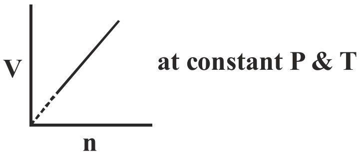
AVOGADRO'S LAW :

The volume of a gas is directly proportional to number of molecules or moles at constant temperature and pressure.

$$V \propto n \text{ at constant T and P}$$

$$\text{or } \frac{V}{n} = K \quad \text{or} \quad \frac{V_1}{n_1} = \frac{V_2}{n_2} \quad \text{at constant T and P}$$

GRAPHICAL REPRESENTATION OF AVOGADRO'S LAW :



IDEAL GAS EQUATION :

$$V \propto \frac{1}{P}, \text{ T and n constant (Boyle's law)}$$

$$V \propto T, \text{ P and n constant (Charle's law)}$$

$$V \propto n, \text{ P and T constant (Avogadro's law)}$$

$$\Rightarrow V \propto \frac{nT}{P} \text{ or } PV \propto nT \text{ or } PV = nRT.$$

This is known as ideal gas equation. R is known as universal gas constant.

IDEAL GAS :

The gas which obeys the equation $PV = nRT$ at every temperature and pressure range strictly.

REAL OR NON-IDEAL GASES :

Since none of the gases present in universe strictly obey the equation $PV = nRT$, hence they are known as real or non ideal gases. Real gases behave ideally at low P and high T.

DENSITY OF A GAS :

We have $PV = nRT$, $PV = \frac{w}{M}RT$;

$$\left(\text{Moles(n)} = \frac{\text{weight (w)}}{\text{Molecular weight (M)}}\right)$$

Further, $d = \frac{w}{V} = \frac{PM}{RT}$

The above equation shows that density of a gas depends on P and T.

UNIT OF DENSITY OF GAS :

It is usually expressed in gm/ litre

VAPOUR DENSITY (V.D.) :

It is the ratio under similar conditions of P and T

$$\text{V.D.} = \frac{\text{Density of gas}}{\text{Density of } H_2 \text{which is } 0.00009}$$

$$= \frac{\text{Mass of 1litre of gas}}{\text{Mass of 1litre of } H_2} = \frac{\text{Mass of V litre of gas}}{\text{Mass of V litre of } H_2}$$

$$= \frac{\text{Mass of N molecules of gas}}{\text{Mass of N molecules of } H_2}$$

$$= \frac{\text{Mass of 1 molecule of gas}}{\text{Mass of 1 molecule of } H_2}$$

$$= \frac{\text{Mass of 1 molecule of gas}}{2 \times \text{mass of 1 atom of H}}$$

$$= \frac{1}{2} \text{molecular mass of gas}$$

UNIT OF VAPOUR DENSITY :

It is a ratio and has no unit.

NATURE OF GAS CONSTANT, (R) :

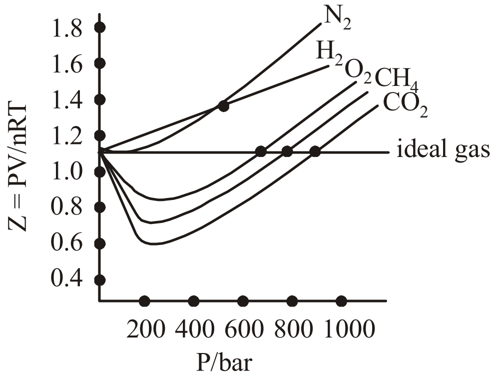
$$R = \frac{PV}{nT} = \frac{(\text{Force/Area}) \times \text{Volume}}{\text{Moles} \times \text{Degree/K}}$$

$$= \frac{[\text{Force}/(\text{Length})^2]}{\text{Moles} \times \text{Degree/K}} \times (\text{length})^3$$

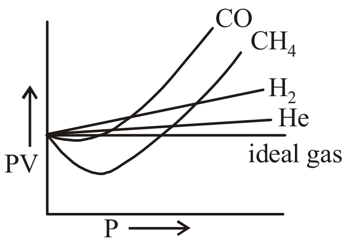
$$= \frac{\text{Force} \times \text{length}}{\text{Moles} \times \text{degree}} = \frac{\text{work}}{\text{Moles} \times \text{degree}}$$

= *Work done per degree per mole*

Deviation from ideal behaviour in terms of compressibility factor Z



Deviation from ideal behaviour in terms of PV-P curve



NUMERICAL VALUE OF R :

As the work can be expressed in different systems of units, R will have different values.

(i) In litre - atmosphere :

At NTP, P = 1atm, V=22.4 litre and T= 273.15K

$$R = \frac{1 \times 22.4}{273.15} = 0.0821 \text{litre atm } K^{-1} \text{ mol}^{-1}$$

(ii) In cgs system :

P = 1 atm = 1×76×13.6×980 dyne cm^{-2}; V = 22400 cm^3; T = 273.15 K

$$R = \frac{1 \times 76 \times 13.6 \times 980 \times 22400}{273.15}$$

$$= 8.314 \times 10^7 \text{ ergs } K^{-1} \text{mol}^{-1}$$

$$= 1.987 \text{ or } 2.0 \text{ Cal } K^{-1} \text{mol}^{-1}$$

Since 1 Cal = 4.184×10^7 ergs

(iii) In mks or SI units :

Unit of R is JouleK^{-1} mol^{-1}

10^7 ergs = 1 Joule or R = 8.314 Joule K^{-1} mol^{-1}

NTP OR STP AND SATP

Normal or standard temperature & pressure means 0°C or 273.15 K and 1 atm pressure.

Normal boiling : At 1 atm pressure the boiling temperature is called **Normal boiling point.**

Standard boiling point : At 1 bar pressure the boiling temperature is called **standard boiling point.**

Normal boiling point of water is 100 °C (373.13 K)

Standard boiling point of water is 99.6 °C (372.6K)

Standard temperature and pressure (STP)

273.15 K(0 °C) temperature

1 bar (10^5 pascal) pressure

Molar volume at STP = 22.71098 L mol^{-1}

Normal temperature and pressure

273.15 K(0 °C) temperature

1 atom (1.01325 pascal) pressure

Molar volume at NTP = 22.413996 L mol^{-1}

Standard ambient temperature and pressure (SATP)

298.15 K (25 °C) temperature

1 bar (10^5 pascal) pressure

Molar volume at SATP = 22.784 L mol^{-1}

BOLTZMANN CONSTANT (k) :

It is the gas constant per molecule thus $k = \frac{R}{N_0}$; Where R=gas constant., N_0= Avogadro number.

Value of $k = 8.314 \text{ JK}^{-1}\text{mol}^{-1}/6.02 \times 10^{23} \text{ mol}^{-1}$

$$= 1.38 \times 10^{-23} \text{J} \text{K}^{-1}$$

DALTON'S LAW OF PARTIAL PRESSURE :

At constant temperature the total pressure, exerted by a mixture of non reacting gases, is the sum of partial pressure of each gas

$$P = p_1 + p_2 + p_3 + ...$$

Partial pressure p of a gas = mole fraction of the gas × total pressure.

For a gas A, $p_A = x_A \times P$

If n_1, n_2 and n_3 are moles of non reacting gases filled in a vessel of volume V at temperature T.

The total pressure P is given by $PV = (n_1 + n_2 + n_3)RT$

This is the equation of state of a gaseous mixture.

RELATIONSHIP BETWEEN TOTAL PRESSURE AND INDIVIDUAL PRESSURE :

On mixing of gases at constant temperature. If a gas A at pressure p_1 and volume V_1 is mixed with gas B at pressure p_2 and volume V_2 at same temperature, then

$$\text{Total pressure, } P = \frac{p_1V_1 + p_2V_2}{V_1 + V_2}$$

AQUEOUS TENSION :

It is the pressure exerted by water vapour at a particular temperature. It depends upon temperature.

PRESSURE OF A DRY GAS :

When a gas is collected over water, its observed pressure is equal to the sum of the pressure of dry gas and the pressure of water vapour (aqueous tension), then

Pressure of dry gas = pressure of moist gas − aqueous tension.

DIFFUSION :

The tendency of every gaseous substance to distribute itself uniformly throughout the available space is known as diffusion. It also takes place through a porous vessel.

EFFUSION :

The movement of a gas through a small hole when it is subjected to pressure is known as effusion.

GRAHAM'S LAW OF DIFFUSION (OR EFFUSION) :

At constant temperature and pressure, the rate of diffusion or effusion of a gas is inversly proportional to the square root of its density.

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{d}}$$

If r_1 and r_2 are rates of diffusion of two gases and d_1 and d_2 their respective densities then,

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{V.D_2}{V.D_1}} = \sqrt{\frac{M_2}{M_1}}$$

$$\text{Rate of diffusion} = \frac{\text{Volume diffused or effused}}{\text{time taken}}$$

$$= \frac{\text{Moles diffused or effused}}{\text{time taken}}$$

$$\frac{r_1}{r_2} = \frac{V_1/t_1}{V_2/t_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

If volume diffused is same $\frac{r_1}{r_2} = \frac{T_2}{T_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$

If time of diffusion is same $\frac{r_1}{r_2} = \frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$

Effect of pressure on the rate of diffusion.

Rate of diffusion ∝ pressure, therefore, $\frac{r_1}{r_2} = \frac{p_1}{p_2} \times \sqrt{\frac{M_2}{M_1}}$

APPLICATIONS OF GRAHAM'S LAW OF DIFFUSION:

(i) Determination of densities and molecular masses of unknown gases.

(ii) Separating the gases having different densities.

(iii) Separation of Isotopes

ATMOLYSIS :

The phenomenon of separation of a mixture of gases due to difference in their rates of diffusion is called atmolysis.

KINETIC THEORY OF GASES :

Postulates of kinetic theory of gases.

(i) A gas consists of large number of tiny particles called molecules.

(ii) Volume occupied by gas molecules, is negligible as compared to the total volume of gas.

(iii) There is continuous rapid random motion of gas molecules. The molecules collide with each other and against walls of container.

(iv) The molecules are perfect elastic bodies and there is no loss of kinetic energy during collisions.

(v) There are no attractive forces between the molecules of gas.

(vi) The pressure exerted by a gas is due to bombardment of gas molecules against the walls of the container.

(vii) The different molecules possess different velocities and hence different energies. The average K.E. is directly proportional to absolute temperature.

KINETIC GAS EQUATION :

Based upon the postulates of Kinetic theory of gases, the kinetic gas equation is

$$PV = \frac{1}{3} mNU^2$$

where m = mass of a gas molecule, N= number of molecules, U= Root mean square velocity.

KINETIC ENERGY OF GAS :

It can be obtained from kinetic gas equation

$$\text{KE of one molecule} = \frac{1}{2}mv^2$$

$$PV = \frac{1}{3}mNU^2 = \frac{2}{3}\cdot\frac{1}{2}mNU^2 = \frac{2}{3}KE = RT$$

$$(N = n \text{ and } m \times n = M)$$

$$\therefore\ KE = \frac{3}{2}RT \text{ for 1 mole of a gas}$$

(i) KE of n moles of gas = 3/2 nRT

(ii) At absolute zero, KE is zero

MAXWELL'S GENERALISATION :

Kinetic Energy of translation of ideal gas is directly proportional to absolute temperature of gas or its pressure and is independent of the nature of gas.

THERMAL MOTION :

$$KE \propto U^2 \text{ or } U^2 \propto T \qquad \therefore\ U \propto \sqrt{T}$$

The molecular velocity of a gas is proportional to square root of the absolute temperature. The molecular motion is called thermal motion of molecules.

CALCULATION OF MOLECULAR VELOCITIES OF GASES :

(i) Calculation of velocity when temperature alone is given :

From Kinetic gas equation,

$$PV = \frac{1}{3}MU^2,\ U^2 = \frac{3PV}{M} = \frac{3RT}{M}$$

$$\therefore\ U = \sqrt{\frac{3RT}{M}}; \qquad R = 8.314 \times 10^7 \text{ ergs } K^{-1} \text{ mol}^{-1}$$

$$U = \sqrt{\frac{3 \times 8.314 \times 10^7 \times T}{M}} = 1.58 \times 10^4 \sqrt{\frac{T}{M}} \text{ cm/sec}$$

(ii) Calculation of velocity at NTP

It is given by the formula, $U = \sqrt{\frac{3PV}{M}}$

$$U = \sqrt{\frac{3 \times 76 \times 13.6 \times 981 \times 22400}{M}}$$

AT NTP, $P = 76 \times 13.6 \times 981$ dynes cm$^{-2,}$ $V = 22400$ ml (molar volume).

(iii) Calculation of velocity when pressure and density are given.

It is given by the following formula,

$$U = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{D}} \qquad (\text{since}, D = \frac{M}{V})$$

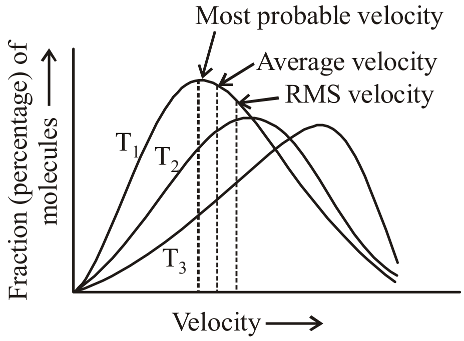
(iv) Calulation of velocity when pressure and temperature are given but are not the same as NTP

$U = \sqrt{\frac{3PV}{M}}$; In such case molecular volume (22400ml) is converted into the volume under given conditions of T and P using relation, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

MAXWELL'S DISTRIBUTION OF VELOCITIES :

The molecules present in a given sample of gas move with different velocites in all possible directions. Velocities and directions of molecules keep on changing due to intermolecular collisions. Hence it is impossible to find out the individual velocity of each molecule. It is however possible to predict fraction ($\Delta N / N$) of the total number of molecules having specific velocities at a particular temperature. As shown by the curve,

The gases show ideal behavior at low presence/large volume. Since the volume of molecules can be neglected and at high temperature since intermolecular forces decrease.



Fraction of molecules having very small or very high velocities is very low. No molecule has zero velocity. Fraction of molecules possessing a particular velocity at a particular temperature is constant. The different velocities possessed by gas molecules are:

(i) **Most probable velocity (α) :** It is the velocity possessed by maximum fraction of gas molecules at a particular temperature

Mathematically, $\alpha = \sqrt{\frac{2RT}{M}}$

(ii) **Average velocity ($\bar{v}$) :** This is the average of the different velocities of all the molecules.

$$\bar{v} = \frac{n_1c_1 + n_2c_2 + n_3c_3 + \ldots\ldots}{n_1 + n_2 + n_3 + \ldots\ldots}$$

where c_1, c_2, c_3 etc. are individual velocities of n_1, n_2, n_3 molecules.

Mathematically, $\bar{v} = \sqrt{\frac{8RT}{\pi M}}$

(iii) Root mean square velocity (U) : It is the square root of the mean of the square of the different velocites of the molecules

$$U = \sqrt{\frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + ...}{n_1 + n_2 + n_3 + ...}};$$

$$\text{Mathematically, } U = \sqrt{\frac{3RT}{M}}$$

RELATIONSHIP BETWEEN DIFFERENT TYPES OF VELOCITIES :

$$\alpha : \bar{v} : U \equiv \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$= 1.414 : 1.595 : 1.732 = 1 : 1.128 : 1.224$$

Calculation of root mean square velocity (U_{rms}) : As already discussed, the U_{rms} can be calculated by any of the following relations:

$$U_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{D}}$$

RATIO OF U_{RMS} FOR TWO DIFFERENT GASES AT THE SAME TEMPERATURE

$$\frac{U_1}{U_2} = \sqrt{\frac{M_2}{M_1}}$$

RATIO OF U_{RMS} FOR THE SAME GAS AT DIFFERENT TEMPERATURE

$$\frac{U_1}{U_2} = \sqrt{\frac{T_1}{T_2}}$$

EFFECT OF TEMPERATURE ON DISTRIBUTION OF MOLECULAR VELOCITIES:

Most proabable velocity increases with the rise in temperature but fraction of molecules possessing such velocity decreases.

Deviation from ideal behaviour of gas :

At high pressure and low temperature the gases deviate considerably from the ideal behaviour. Deviation can be expressed in terms of compressibility factor (Z), expressed as

$$Z = \frac{PV}{nRT}$$

In case of ideal gas, $PV = nRT,\ Z = 1$

In case of real gas, $PV \neq nRT,\ Z \neq 1$

NEGATIVE DEIVATION:

In such case, $Z < 1$, gas is more compressible.

POSITIVE DEVIATION :

In such case, $Z > 1$, gas is less compressible.

FACTORS AFFECTING THE DEVIATION :

The factors affecting the deviation are:

(i) **Nature of the gas :** In general, the most easily liquefiable and highly soluble gases show larger deviation.

(ii) **Pressure :** The deviation is more at high pressure. CO_2 and N_2 show negative deviation at low pressure and positive deviation at high pressure.

(iii) Temperature : The deviation is more at low temperature. H_2 and He always show positive deviations at 0°C

BOYLE'S TEMPERATURE:

Temperature at which a real gas exhibits ideal behaviour for considerable range of pressure is called Boyle's temperature. Mathematically,

$$T_b = \frac{a}{bR},$$ where a and b are Vander Waal's constants

(i) Boyle temperature is different for different gases

(ii) Below Boyle's temperature a gas shows negative deviation.

(iii) Above Boyle's temperature a gas shows positive deviation

CAUSE OF DEVIATION FROM THE IDEAL BEHAVIOUR :

It is due to two faulty assumptions of Kinetic theory of gases particularly not valid at high pressure and low temperature.

(i) **Volume** occupied by the gas molecules is negligible as compared to the total volume of gas.

(ii) There are no **attractive forces** between the gas molecules.

VAN DER WAAL'S EQUATION :

After volume & pressure correction, van derWaals obtained the following equation for n moles of a gas

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT, \text{ For one mole } \left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Excluded volume or co-volume, (b) :

The constant b in van der Waal's equation is known as **excluded** volume or **co-volume**. It is nearly four times the actual volume occupied by the gas molecules.

Excluded or co-volume (b) = 4 × actual volume of gas molecules.

MAGNITUDE OF ATTRACTIVE FORCES BETWEEN GAS MOLECULES (a) :

It is given by van der Waals constant 'a'. Different gases have different value for 'a'.

(i) The greater the value of 'a', the greater the strength of van der Waals forces.

(ii) The greater the value of 'a', the greater is the ease with which a gas can be liquefied.

UNITS FOR VAN DER WAAL'S CONSTANT:

Pressure correction,

$$p = \frac{n^2a}{V^2} \qquad \therefore\ a = \frac{pV^2}{n^2} = \text{atm litre}^2\ \text{mole}^{-2}$$

$$\text{Volume correction, } V = nb \qquad \therefore\ b = \frac{V}{n} = \text{litre mole}^{-1}$$

vAN dER WAAL'S CONSTANTS FOR SOME COMMON GASES :

Gas	a $(\text{lit}^2 \text{atm mol}^{-2})$	b.(lit mol^{-1})
NH_3	4.17	0.0371
CO_2	3.59	0.0427
CO	1.49	0.0399
Cl_2	6.49	0.0562
H_2	0.024	0.0266
HCl	3.67	0.0408
NO	1.34	0.0279
O_2	1.36	0.0318
SO_2	6.71	0.0564
He	0.034	0.0237
Water	5.46	0.0305

DISCUSSION OF VAN DER WAAL'S EQUATION :

van der Waal's equation for one mole of gas

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

(i) At low pressure and ordinary temperature : V is very large and b can be neglected then

$$\left(P+\frac{a}{V^2}\right)V=RT$$

or $PV=RT-\frac{a}{V}$ or $\frac{PV}{RT}=\left(1-\frac{a}{RTV}\right)$;

Therefore Z is less than 1.

Hence at low pressure the gases show **negative deviation**.

(ii) At high pressure and ordinary temperature : At high pressure, volume V will be quite small. The quantity $\frac{a}{V^2}$ become negligible but 'b' cannot be ignored.

$P(V-b)=RT$

or $\frac{PV}{RT}=1+\frac{Pb}{RT}$; Therefore Z is more than 1.

At high pressure the gases show positive deviation

Note : At some intermediate range of pressure and ordinary temperature the gas shows the ideal behaviour.

(iii) At low pressure and high temperature: The effect of $\frac{a}{V^2}$ and b is negligible. We have

$PV=RT$ or $\frac{PV}{RT}=1$;

Therefore Z = 1. Hence gas shows ideal behaviour.

EXCEPTIONAL BEHAVIOUR OF HYDROGEN AND HELIUM :

Due to their small size, the attractive forces between the molecules are too small, $\frac{a}{V^2}$ is negligible, then

$$\frac{PV}{RT}=1+\frac{Pb}{RT};Z>1$$

Hence they always show positive deviation.

LIMITATION OF VAN DER WAAL'S EQUATION :

There is specific range of temperature and pressure, to apply the equation. It deviates at too high pressure and too low temperature.

OTHER EQUATIONS OF STATES :

(i) Dieterici equation : $P(V-b)=RT\,e^{\frac{-a}{RTV}}$

(ii) Berthelot's equation : $\left(P+\frac{a}{TV^2}\right)(V-b)=RT$

(iii) Clausius equation : $\left(P+\frac{a}{T(V+c)^2}\right)(V-b)=RT$

Where c is a new constant

(iv) Kammerling onne's equation (virial equation):

$PV=A+BP+CP^2+DP^3$

(a) The coefficients A,B,C,D, etc are known as first, second, third, fourth virial coefficients

(b) At low pressure only A (which is equal to RT) is important, the others cancel out.

(c) A is always positive and increases with rise of temperature.

(d) At Boyle temperature B=0

(e) Relation between B and van der Waals constant is

$$B=b-\frac{a}{RT}$$

CRITICAL PHENOMENON AND LIQUEFACTION OF GASES :

Increase of pressure and decrease of temperature tend to cause liquefaction of gases. The effect of temperature is, however more important.

CRITICAL TEMPERATURE (T_c) :

It may be defined as the temperature above which no gas can be liquefied howsoever high the pressure may be, critical temperature of CO_2 is 31.1°C.

Critical temperature (T_c) of some gases,

He	5.2	CO_2	304.1	CH_4	190.2
H_2	33.2	N_2O	309.6	HCl	324.5
N_2	126.0	NH_3	405.5	H_2S	373.5
CO	134.4	Cl_2	417.1	Ar	150.7
O_2	154.3	SO_2	430.3		

CRITICAL PRESSURE (P_c) :

At critical temperature the pressure needed to liquefy a gas is known as critical pressure.

CRITICAL VOLUME (V_c) :

The volume occupied by one mole of a gas at critical temperature and critical pressure is known as critical volume.

RELATIONSHIP BETWEEN CRITICAL CONSTANTS AND VAN DER WAAL'S CONSTANT:

$$V_c = 3b, T_c = \frac{8a}{27Rb}, P_c = \frac{a}{27b^2}$$

Relationship between boiling point and critical temperature:

Boiling point $= \frac{2}{3}$ critical temperature.

Compressibility for 1 mole of gas at critical state:

$$z = \frac{P_c V_c}{RT_c} = \frac{3}{8} = 0.375, \text{ almost constant.}$$

JOULE THOMSON EFFECT :

When a gas under high pressure is allowed to expand adiabatically into a region of extremly low pressure, it suffers change of temperature. The phenomenon is kown as Joule -Thomson effect.

CONDITION FOR JOULE-THOMSON EFFECT (INVERSION TEMPERATURE):

In Joule -Thomson effect, cooling is observed only if the gas is present below certain temperature known as inversion temperature, T_i. It is characteristic of each gas and related to van der Waal's constant a and b as, $T_i = \frac{2a}{Rb}$

At exact inversion temperature there is no Joule-Thomson effect. Above inversion temperature, there is heating during Joule-Thomson effect. Below inversion temperature there is cooling during Joule-Thomson effect.

Inversion temperature for hydrogen = –80°C and for He = –240°C. Joule-Thomson effect is zero in an ideal gas and enthalpy remains constant. When an ideal gas expands in vacuum, it does no work i.e. W=0 ; $\Delta E = 0$ (Adiabatic condition). ***Hence internal energy of a given quantity of an ideal gas at constant temperature is independent of its volume.***

$\left(\frac{\partial E}{\partial V}\right)_T = 0$ (for an ideal gas) ; This quantity is called ***internal pressure*** and is positive for real gases.

Thermodynamically an ideal gas may be defined by following the equations.

(i) PV = constant, at constant temperature.

(ii) $\left(\frac{\partial E}{\partial V}\right)_T = 0$

JOULE-THOMSON COEFFICIENT ($\mu_{J.T.}$) :

The temperature change produced per atmosphere drop in pressure under constant enthalpy conditions on passing a gas through the porous plug is called Joule-Thomson coefficient

The quantity $\left(\frac{\partial T}{\partial P}\right)_H$ is called Joule -Thomson coefficient.

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)$$

(i) Joule Thomson Coefficient $\left(\frac{\partial T}{\partial P}\right)_H$ is positive for real gases, (cooling)

Or Joule Thomson Coefficient will be positive when $\frac{2a}{RT} > b$

(ii) When Joule Thomson Coefficient $\left(\frac{\partial T}{\partial P}\right)_H$ is negative, (heating)

Or Joule Thomson Coefficient will be negative when $\frac{2a}{RT} < b$

(iii) When Joule Thomson Coefficient $\left(\frac{\partial T}{\partial P}\right)_H$ is zero, (no heating or cooling)

Or Joule Thomson Coefficient will be zero when $\frac{2a}{RT} = b$

Since a, b and R are constants, the sign of Joule-Thomson Coefficient will depend only upon the temperature at which the gas is being allowed to expand. The temperature at which the Joule-Thomson Cofficient changes sign is known as the **inversion temperature.**

$$\frac{2a}{RT_i} = b \quad \therefore T_i = \frac{2a}{Rb}$$

LAW OF CORRESPONDING STATES :

When the values of pressure, volume and temperature are expressed as fractions of the corresponding critical values we have. $\frac{P}{P_c} = \pi, \frac{V}{V_c} = \phi, \frac{T}{T_c} = \theta$

where π, ϕ and θ are termed, the reduced pressure, the reduced volume and the reduced temperature respectively. If we replace P,V and T by πP_c, ϕV_c and θT_c in van der Waal's equation and put the values of P_c, V_c and T_c terms of a, b and R we get,

$$(\pi + \frac{3}{\phi^2})(3\phi - 1) = 8\theta$$

If the two substances have the same reduced temperature and the same reduced pressure, they will have the same reduced volume. **The statement is known as the law of corresponding states.**

HEAT CAPACITY OF SYSTEM :

For gases it can be at constant volume or at constant pressure.

(i) Heat capacity at constant volume (C_V) is defined as the increase in internal energy of a gas per degree rise of temperature.

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2} R$$

(ii) Heat capacity at constant pressure (C_p) is defined as increase in enthalpy of a gas per degree rise of temperature.

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P = \frac{5}{2} R$$

For one mole of gas, the heat capacities at constant volume and constant pressure are denoted by C_v and C_p and are termed as molar heat capacities.

RELATION BETWEEN C_p AND C_v :

$C_p - C_v = R$

R = 1.987 cal or 8.314 Joule

R= $P\Delta V$ = Work done by one mole of an ideal gas in expansion at constant pressure when heated through 1°C.

MOLAR HEAT CAPACITIES FOR POLYATOMIC GASES:

The values $C_V = \frac{3}{2}R$ and $C_p = \frac{5}{2}R$ are for monoatomic gases like He, Ar etc. where the energy supplied increases translational kinetic energy only. In polyatomic gases heat supplied is utilised to increase vibrational and rotational energy also. Thus we have

$$C_V = \frac{3}{2}R + x \quad \text{and} \quad C_p = \frac{5}{2}R + x$$

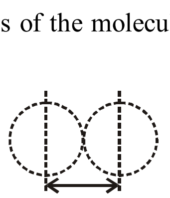
For monoatomic gas, x = 0, $\gamma = \frac{C_p}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.66$

for diatomic gases, x = R, $\gamma = \frac{C_p}{C_V} = \frac{\frac{5}{2}R + R}{\frac{3}{2}R + R} = \frac{7}{5} = 1.46$

for triatomic gases, $x = \frac{3}{2}R$, $\gamma = \frac{C_p}{C_V} = \frac{\frac{5}{2}R + \frac{3}{2}R}{\frac{3}{2}R + \frac{3}{2}R} = \frac{8}{6} = 1.33$

COLLISION PROPERTIES :

(i) **Molecular diameter or collision diameter :** The distance between the centers of the molecules at the point of their closest approach.



(ii) **Collision frequency (Z) :** The number of collisions experienced by molecules per cc of a gas per second is known as collision frequency of gas, $Z = \frac{1}{\sqrt{2}}\sigma^2 \bar{v} N^2$

$\bar{v}$ = average velocity

N = number of molecules per cm^3

σ = collision diameter

At constant pressure, $Z \propto T^{\frac{2}{3}}$

At constant temperature, $Z \propto p^2$

(iii) **Collision number (Z_1) :** Number of collisions undergone by a molecule with other molecules per second present in 1cm^3.

Z_1 = Collision number = $\sqrt{2}\pi\sigma^2 \bar{v} N$

σ = diameter of molecules, $\bar{v}$ = Average velocity, N = Number of molecules per unit volume of the gas

(iv) **Mean free path (*l*) :** The average distance travelled by the molecule between two successive collisions

$$l = \frac{1}{\sqrt{2}\pi\sigma^2 N}$$

At constant pressure, $l \propto T$

At constant temperature, $l \propto \frac{1}{P}$

VOLUME COEFFICIENT :

It is defined as the ratio of the increase in volume of the gas at constant pressure per degree rise of temperature to its volume at 0°C

$$\alpha_V = \frac{v_t - v_0}{v_0 \times t}$$

V_0 =Volume of a given mass of a gas at 0°C

V_t = Volume of a given mass of a gas at t°C

$V_t = V_0(1 + \alpha_V t)$

The value of α_v is found be 1/273 for all gases (charle's law)

Therefore, $V_t = V_0(1 + \frac{t}{273})$

PRESSURE COEFFICIENT (α_p) :

It is defined as the ratio of the increase in pressure of the gas at constant volume per degree rise of temperature to its pressure at 0°C

$$\alpha_p = \frac{P_t - P_0}{P_0 \times t}$$

P_0 =Pressure of given mass of gas at 0°C

P_t =Pressure of given mass of gas at t°C

$P_t = P_0(1 + \alpha_p t)$

The value found by Ragnault & Gay Lussac was in the vicinity of $1/273$ for all gases and hence $P_t = P_0\left(1 + \frac{t}{273}\right)$

AMAGAT LAW OF PARTIAL VOLUME :

The total volume of a mixture of non reacting gases at constant temperature and pressure is equal to the sum of the individual partial volumes of the constituents

$$V_{(total)}=V_1+V_2+V_3+.....+V_n=\sum V_i$$

LOSCHMIDT NUMBER :

It is the number of molecules present in 1cc of a gas or vapour at STP. Its value is 2.617×10^{19} per cc.

AVERAGE MOLECULAR WEIGHT OF A GASEOUS MIXTURE :

$$M_{mix}=\frac{\sum n_iM_i}{\sum n_i}$$

n_i= number of moles
M_i= molecular weight of each component

BAROMETIC FORMULA :

The decrease in the atmospheric pressure with increase in altitude given by the following expression is called barometic formula.

$$\ln\left(\frac{P}{P_0}\right)=\frac{\overline{M}gh}{RT}$$

P_0=Pressure at the sea level
P = Pressure at height h
$\overline{M}$ = Average molecular mass of air, $29\times10^{-3}\,\text{kgmol}^{-1}$
g = acceleration due to gravity, 9.8 ms^{-2}
R = gas constant (8.314 $JK^{-1}\,mol^{-1}$)
T= Temperature in kelvin

ESCAPE VELOCITY :

Velocity required by an object to escape from the gravitational field of a body. It is given by $V_e=\sqrt{2gr}$

AVERAGE KINETIC ENERGY :

It is KE of a single molecule, and $\overline{KE}=\frac{3}{2}kT=\frac{3}{2}.\frac{R}{N_o}T$, where k=

Boltzmann constant $\left(k=\frac{R}{N_o}=\frac{\text{Gas Constant}}{\text{Avogadro Number}}\right)$

Total KE =N (average KE), N $(\overline{KE})$ = $\frac{3}{2}$nRT

LIQUEFACTION OF GASES : LIQUEFACTION OF GAS CAN BE ACHIEVED BY

1. **Increasing pressure :** It increases attraction among molecules.
2. **Decreasing temperature :** It decrease Kinetic energy of molecules. The temperature of gas must be lower than its critical temperature, T_C.

Liquefaction is further based on the following principles

(a) **Cooling by freezing mixture :** eg NaCl & ice (-22°C), $CaCl_2$ & ice(-55°C), KOH & ice (-65°C)

(b) **Cooling by adiabatic expansion (Claude's Method) :** The gas in this process suffers a loss in temperature.

$$\Delta E=q+w \quad \text{if} \quad q=0 \text{ then } \Delta E=w \quad \text{or } -\Delta E=-w$$

Work is done by the gas at the cost of internal energy and temeprature is lowered.

(c) **Cooling by Joule-Thomson effect (Linde's method) :** Expansion of a gas through a small jet under adiabatic conditions results in cooling and liquefaction of gas

LIQUID STATE :

- Liquid state of the matter is the intermediate state between the gaseous and the solid state.
- In liquids the molecules of the matter are held together by strong intermolecular forces in comparison to those in gases.
- On the basis of kinetic molecular model, the liquid state is described as follow:
  - (i) A liquid is composed of small molecules.
  - (ii) The molecules of the liquid are held closer by some kind of intermolecular forces.
  - (iii) The intermolecular forces are not very strong and thus the molecules are always in constant random motion.
  - (iv) The average kinetic energy of molecules of a liquid is directly proportional to their absolute temperature.
- **Properties of the liquid :**

  Most of the physical properties of liquids are controlled by the strength of intermolecular attractive forces existing between molecules of a liquid. These intermolecular forces arranged in order of their increasing strength are

  London forces/induced diplole<dipole attraction< Hydrogen bonding.

  (1) **Shape**: Liquids have no definite shape of thier own. It acquires the shape of the container in which it is put.
  (2) **Volume:** Liquids have a definite volume.
  (3) **Density:** The densities of liquids are nearly 1000 times more than the densities of the gases under identical conditions.
  (4) **Compressibility:** Liquids are very less compressible compared to gases.
  (5) **Diffusion:** Liquids diffuse like gases but the process of diffusion (also known as intermixing) is much slower.
  (6) **Evaporation: The process of conversion of a liquid into its vapours (i.e.) gaseous state) at room temperature is known as evaporation.**

VAPOUR PRESSURE :

At equilibrium state the pressure exerted by vapour phase is called vapour pressure at a specific temperature.

- The magnitude of vapour pressure depends upon the following two factors.
  - (i) The liquids having weak intermolecular attraction have greater tendency of escaping from the liquid surface in comparison to liquids having stronger forces of intermolecular attraction. For example, the vapour pressure of ether and acetone is more than that of water or acetic acid at any specific temperature.
  - (ii) The vapour pressure of a liquid increases with the increase in temperature.
- The vapour pressures of a given liquid at two different temperatures may be compared using Clausius Clapeyron equation

$$\log\frac{P_2}{P_1}=\frac{\Delta H}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

  where P_1 and P_2 are the vapour pressures at temperature T_1 and T_2 Δ H is the heat of vapourisation and R is molar gas constant.
- The temperature at which the vapour pressure of liquid becomes equal to atmospheric pressure (or the external pressure) is termed as the boiling point of liquid. For example at 1 atmospheric pressure acetone boils at 56°C. benzene at 80°C, ethyl alcohol at 78.4°C and water at 100°C.
- The temperature at which the solid state and the liquid form of a substance are in equilibrium at one atmospheric pressure is known as freezing point

SURFACE TENSION :

- The surface tension is defined as the force per cm acting perpendicular to the tangential line on the surface of the liquid which tend to compress the surface area.
  The units of surface tension are force per unit length i.e. dynes cm^{-1} or Nm^{-1} (in SI units)
- Stronger the forces of intermolecular attraction (cohesive forces) greater is the surface tension.
- The surface tension decreases with rise in temperature or surface tension in inversely proportional to temperature.
  Surface tension $\propto$ 1/Temperature
  Measurement of surface tension of a liquid by the drop number method is the most convenient method.

VISCOSITY:

- Viscosity may be defined as the force of friction between two layers of a liquid moving past one another with different velocities.
- The viscosities of liquids are compared in terms of coefficient of viscosity which is defined as the force per unit area needed to maintain a unit difference in velocities between two consecutive parallel layers which are one cm. apart.
- The units of viscosity are poise (*P*) where $1P = g\ cm^{-1}\ sec^{-1}$. In SI units of viscosity $1P = 0.1\ N\ sec\ m^{-2}$.
- The liquid having stronger forces of attraction has a higher viscosity.
- With the rise in temperature, viscosity of a liquid decreases because the intermolecular attractive force between consecutive layers decrease as temperature increases.

Miscellaneous Solved Examples

1. The density of a gas at 30°C and 1.3 atmosphere pressure is 0.027 g/cc. Calculate the molecular weight of the gas.

Sol. $M=\frac{RTd}{P}$; R = 0.0821 atm lit K^{-1} mol^{-1};

$d = .027\,g/cc = 27\,g/l;$

$T = 273+30 = 303\,K;\ P = 1.3\ atm$

$$M=\frac{27\times .0821\times 303}{1.3}=516.66\,g/mol$$

2. Density of ammonia is 0.77 g/l. Calculate its vapour density.

Sol. $V.D.=\frac{\text{Density of gas}}{\text{Density of } H_2\ 0.09\,g/l}=\frac{0.77}{0.09}=8.55$

3. A gas cylinder containing cooking gas can withstand a pressure of 14.9 atmosphere. The pressure gauge of cylinder indicates 12 atmosphere at 27°C. Due to sudden fire in the building the temperature starts rising. At what temeprature, cylinder will explode.

Sol. $\frac{P_1}{T_1}=\frac{P_2}{T_2}\Rightarrow\ \frac{14.9}{T_1}=\frac{12}{300}\ \Rightarrow T_1=372.5\,K$

4. The total pressure exerted by a mixture of gases containing 0.4g H_2, 2.2g of CO_2, 1.4 g N_2 and 3.2g SO_2 is 2.5 atmosphere . What are the partial pressures of each gas under the same conditions?

Sol. Partial pressure of a gas = mole fraction × total pressure

$$\text{Total moles} = \frac{0.4}{2}+\frac{2.2}{44}+\frac{1.4}{28}+\frac{3.2}{64}=0.35$$

$$pH_2 = \frac{0.2}{0.35}\times 2.5 \;=\; 1.428\,\text{atm};$$

$$pCO_2 = \frac{0.05}{0.35}\times 2.5 = 0.357\,\text{atm}$$

$$pN_2 = \frac{0.05}{0.35}\times 2.5 = 0.357\,\text{atm};$$

$$pSO_2 = \frac{0.05}{0.35}\times 2.5 = 0.357\,\text{atm}$$

5. Calculate the total pressure in a 10 litre cylinder which contains 0.4 g He, 1.6g O_2 and 1.4 g of N_2 at 27°C. Also calculate the partial pressure of the He gas in the cylinder. Assume ideal behaviour of gases, R = 0.0821 atm lit K^{-1} mol^{-1}.

Sol. $PV=(n_1+n_2+n_3)RT$

$$P\times 10=\left(\frac{0.4}{4}+\frac{1.6}{32}+\frac{1.4}{28}\right)\times 0.821\times 300\;;\;P=0.4926\,\text{atm}$$

Total moles = 0.2

$$p_{He} = \frac{0.1}{0.2}\times 0.4926 \quad 0.2463\,\text{atm}$$

6. For the reaction $N_2O_5\,(g) \rightleftharpoons 2\,NO_2 + 0.5\,O_2$ .Calculate the mole fraction of $N_2O_5(g)$ decomposed at constant volume and temperature, if initial pressure is 600 mm Hg and pressure at any time is 960 mm Hg. Assume ideal gas behaviour.

Sol. At constant V and T, Pressure is directly proportional to number of moles.

$$N_2O_5\,(g) \rightleftharpoons 2NO_2 + 0.5O_2$$

Initial Moles	1	0	0
At time t moles	$1-x$	2x	0.5x
Total moles		=1+1.5x	

$$\text{Pressure of } (1+1.5x)\text{ moles} \;=\; 960\,\text{mm}$$

$$\text{Pressure of 1mole} = \frac{960}{(1+1.5x)} = 600$$

Mole fraction decomposed, x = 0.4

7. The pressure exerted by 12 g of an ideal gas at temperature t°C in a vessel of volume V litres is one atmosphere. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10%. Calculate t and V (molecular weight of gas = 120).

Sol. PV = nRT

$$\text{First equation} \qquad 1\times V = \frac{12}{120}\times .0821(t+273)$$

$$\text{Second equation} \quad 1.1\times V = \frac{12}{120}\times .0821(t+273+10)$$

$$\text{Dividing} \qquad \frac{1}{1.1}=\frac{t+273}{t+283} \quad \text{or } t=-173°C$$

$$=273-173^{\circ}C=100\,K$$

$$\Rightarrow V=\frac{12}{120}\times 0.0821(100)=0.821\text{ litre}$$

8. Calculate the molecular mass of a gas if its specific heat at constant pressure is 0.125 and at constant volume is 0.075

Sol. $\gamma \quad \frac{C_p}{C_v} \quad \frac{0.125}{0.075} \quad 5/3 \quad 1.66$ hence gas is monoatomic

Molar heat at constant volume $C_v \quad 3/2\,R \quad 3/2\times 2 \quad 3$ cal.

Also, specific heat × molar mass $\quad C_v$

$$0.075\times M = 3 \qquad \therefore M \quad \frac{3}{0.075} \quad 40\,g/mol$$

9. An open vessel at 27°C is heated until $3/5$ th of the air in it has been expelled. Assuming that the volume of the vessel remains constant find,

(a) Temperature at which vessel is heated

(b) The air escaped out of it if vessel is heated to 900 K

(c) The temperature at which the half of air escapes out

Sol. An open vessel has constant V and P.

$$\therefore n_1T_1 = n_2T_2$$

$$\text{(a)} \quad 1\times 300 = 2/5\,T_2$$

$$\therefore T_2 = 750K = 477^{\circ}C\;\left(3/5\text{ expelled}, 2/5\text{ left}\right)$$

$$\text{(b)} \quad 1\times 300 = n_2\times 900 \;\therefore n_2 = 1/3 \quad (1/3\text{ left}, 2/3\text{ expelled})$$

$$\text{(c)} \quad 1\times 300 = \frac{1}{2}\times T$$

$$=600K = 327^{\circ}C\;\left(\frac{1}{2}\text{ left}, 1/2\text{ expelled}\right)$$

10. A balloon of diameter 20m weights 100 kg. Calculate its pay load if it is filled with helium at 1.0 atm and 27°C. Density of air = 1.2 kg/m^3, R= 0.0821 dm^3 atm $K^{-1}mol^{-1}$.

Sol. Volume of balloon $= 4/3\,\pi r^3 = \frac{4}{3}\times\frac{22}{7}(10)^3 \quad 4190.47m^3$

Mass of the air displaced = $4190.47\times 1.2 \quad 5028.56\,kg$

$$\text{Moles of helium in the balloon} \quad \frac{1\times 4190.47\times 10^3}{0.082\times 300} \quad 170344$$

Mass of helium $= 4\times 170344\text{ g}\ \ 681.376\text{ kg}$

Mass of filled balloon $\ 681.376\ \ 100\ \ 781.376\text{ kg}$

Pay load = Mass of air displaced − Mass of filled balloon

$= 5028.56 - 781.376\ \ 4247.184\text{ kg}$

11. An evacuated glass vessel weighs 50.0g when empty, 148.0g when filled with a liquid of density 0.98g/ml and 50.5g when filled with an ideal gas at 760 mm Hg and 300K. Determine the molecular weight of gas.

Sol. Weight of liquid $= 148 - 50\ \ 98\text{g}$

Volume of liquid $\frac{98}{0.98}$ 100 ml volume of vessel

weight of gas $= 50.5 - 50.0\ \ 0.5\text{g}$

Gas equation $PV = \frac{w}{M}\times RT$ or $\frac{760}{760}\times\frac{100}{1000}$

$$= \frac{0.5}{M}\times .0821\times 300$$

or M 123

12. 20 dm³ SO_2 diffuse through a porous partition in 60 seconds What volume of O_2 will diffuse under similar conditions in 30 seconds.

Sol. $\frac{V/30}{20/60}\ \ \sqrt{\frac{64}{32}}$ or V 14.1dm^3

13. At 27°C hydrogen is leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure as that of hydrogen leaked through the same hole for 20 minutes. After the effusion of the gases the mixture exerts a pressure of 6 atm. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 litre, what is the molecular mass of the unknown gas?

Sol. The partial pressure of hydrogen and unknown gas (ug) can be obtained as

$$p_{H_2} = \frac{0.7}{3}\times 0.0821\times 300$$

$$p_{ug} = \frac{n}{3}\times 0.0821\times 300 \quad n\ \ \text{number of moles}$$

$$p_{H_2}\ \ p_{ug}\ \ 6\ \ \frac{1}{3}\times 0.0821\times 300(0.7\ \ n)$$

or n = 0.0308 mole

Applying law of diffusion, $\frac{0.7/20}{0.308/20}\ \ \sqrt{\frac{m}{2}}$,

or m 10.33

14. One mole of nitrogen gas at 0.8 atm takes 38 seconds to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm. takes 57 seconds to diffuse through the same hole. Calculate the molecular formula of the compound.

Sol. $\frac{r_1}{r_2}\ \ \frac{P_1}{P_2}\times\sqrt{\frac{M_2}{M_1}}$ or $\frac{n_1}{n_2}\times\frac{t_2}{t_1}\ \ \frac{P_1}{P_2}\times\sqrt{\frac{M_2}{M_1}}$

$$\frac{1}{38}\times\frac{57}{1}\ \ \frac{0.8}{1.6}\sqrt{\frac{M_2}{28}}$$

$M_2\ \ 252$

The compound is XeF_6 $131\ \ 19\times 6\ \ 245$

Where atomic weight of Xe is 131 and atomic weight of F is 19. If two Xe atoms were there, weight would have exceeded 252 which is not possible.

15. A 4:1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to hole in the vessel, the gas mixture leaks out what is the composition of the mixture effusing out initially? (IIT 1994).

Sol. Molar ratio of He and CH_4 is 4:1

Partial pressure ratio of He and CH_4 16 : 4

(∵Total Pressure = 20bar)

$$\frac{r_1}{r_2}\ \ \frac{p_1}{p_2}\sqrt{\frac{M_2}{M_1}};\ \text{or}\ \frac{r_{He}}{r_{CH4}}\ \ \frac{16}{4}\times\sqrt{\frac{16}{4}}\ \ 8:1$$

Composition of the mixture effusing initially for He and CH_4 is 8:1.

16. A container of capacity 2 litre contains 10^{24} gas molecules each weighing 10^{-22}g. The root mean square velocity is 1.5×10^5 cms^{-1} Calculate (i) Total pressure (ii) Total kinetic energy (iii) Temperature of the gas

Sol. (i) Kinetic gas equation is $PV\ \ \frac{1}{3}mNU^2$

$$P = \frac{1}{3}\times\frac{10^{-22}\times 10^{24}\times(1.5\times 10^5)^2}{2\times 10^3} = 3.75\times 10^8\ \text{dynes}/\text{cm}^2$$

(ii) Total Kinetic energy $N\times\left(\frac{1}{2}mU^2\right)$

$$\frac{10^{24}\times 10^{-22}}{2}(1.5\times 10^5)^2\ \ 1.125\times 10^{12}\ \text{ergs}$$

(iii) The number of moles $\frac{1\times 10^{24}}{6.02\times 10^{23}}$ 1.66 moles

KE ${}^3\!/_2$nRT

$$\therefore T\ \ \frac{2KE}{3nR}\ \ \frac{2\times 1.125\times 10^{12}}{3\times 1.66\times 8.314\times 10^7}\ \ 5434.3\text{K}$$

17. Calculate translational KE of 2 moles of a gas at 27°C

Sol. $KE = \frac{3}{2}nRT = \frac{3}{2}\times 2\times 8.314\times 10^7\times 300\ \text{ergs}$

7482.5×10^7 ergs 7482.5 Joules

18. Calculate the average and total kinetic energy of 0.5 mole of an ideal gas at 0°C

Sol. Average KE per molecule of the gas $= \frac{3}{2}.\frac{R}{N_0}T$

$$= {}^{3}\!/_{2} \times \frac{8.314\times10^{7}}{6.023\times10^{23}} \times 273 = 5.65\times10^{-14}\text{ ergs}$$

Total Kinetic energy of 0.5 moles of a gas

$$= 5.65\times10^{-21}\text{ Joules} = {}^{3}\!/_{2}nRT = {}^{3}\!/_{2}\times0.5\times8.314\times10^{7}\times373$$

$$= 1.702\times10^{10}\text{ ergs} = 1.702\text{kJ}$$

19. The composition of the equilbrium mixture, $Cl_2 \rightleftharpoons 2Cl$, which is attained at 200° C, is determined by measuring the rate of effusion through a pin hole. It is observed that at 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast as krypton effuses under the same condition. Calculate the fraction of the chlorine molecules dissociated into atmosphere. (Atomic wt. of krypton 84)

Sol. $\frac{r_{mix}}{r_{Kr}} = \sqrt{\frac{M_{kr}}{M_{mix}}}$ or $1.16 = \sqrt{\frac{84}{M}} \Rightarrow M_{mix} = 62.425$

Dissociation: $\quad Cl_2 \rightleftharpoons 2Cl$

$\qquad 1-\alpha \qquad 2\alpha$

Total number of moles $= 1+\alpha$

$$\frac{\text{Normal M.wt}}{\text{Experimental M.wt}} = 1+\alpha\ ;\ \frac{71}{62.425} = 1+\alpha$$

$\alpha = 0.137 = 13.7\%$

20. The average speed at T_1 K and the most probable speed at T_2 K of CO_2 gas is 9×10^4 cm sec^{-1}. Calculate the value of T_1 and T_2.

Sol. Average speed at $T_1K = \sqrt{\frac{8RT_1}{\pi M}}$

Most probable speed at $T_2K = \sqrt{\frac{2RT_2}{M}}$

According to Question, $\sqrt{\frac{8RT_1}{\pi M}} = \sqrt{\frac{2RT_2}{M}} = 9\times10^{4}$

$$\therefore \sqrt{\frac{8\times8.314\times10^{7}\times T_1}{3.14\times44}} = \sqrt{\frac{2\times8.314\times10^{7}\times T_2}{44}} = 9\times10^{4}$$

On calculating, we get $T_2 = 2143.37\text{K}$ and $T_1 = 1684.0\text{K}$

21. A glass bulb of 1 litre capacity contains 2×10^{21} molecules of N_2 exerting pressure 7.57×10^{3} Nm^{-2}. Calculate the RMS speed and temperature of gas molecules. If the ratio of U_{mp} to U_{rms} is 0.82 calculate the V_{mp} for these molecules at this temperature.

Sol. Given $P = 7.57\times10^{3}\text{ Nm}^{-2}$

$V = 1\text{ litre} = 10^{-3}\text{m}^{3},\ R = 8.3145\text{ J K}^{-1}\text{ mol}^{-1}$

$$n = \frac{2\times10^{21}}{6.023\times10^{23}\text{mol}}$$

$$\therefore \quad T = \frac{PV}{nR} = \frac{7.57\times10^{3}\times10^{-3}}{2\times10^{21}\times8.314}\times6.023\times10^{23}$$

$T = 274.2\text{K}$

$$U_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\times8.314\times274.2}{28\times10^{-3}}}\quad(\text{M.W.in Kg})$$

$$= 494.22\text{ms}^{-1}$$

$$\frac{U_{mp}}{U_{rms}} = 0.82\ ;U_{mp} = 494.22\times0.82 = 405.26\text{ms}^{-1}$$

22. A gaseous mixture of helium and oxygen is found to a density of 0.518 g dm^{-3} at 25°C and 720 torr. What is the percent by mass of helium in the mixture?

Sol. $M_{av} = \frac{dRT}{P} = \frac{0.518\times0.0821\times298}{720/760} = 13.36\text{g mol}^{-1}$

Let x be the mole fraction of helium in the mixture,

then $M_{av} = xM_{He} + (1-x)\ M_{O_2}$

$13.36 = x\times4 + (1-x)32 \quad \therefore\ x = 0.666$

$$\text{Mass percent of helium} = \frac{0.666\times4}{(0.666\times4+0.334\times32)}\times100$$

$= 19.95$

23. Using Van der Waal's equation calculate the constant ‘a’ when the moles of a gas confined in a 4 *l* flask exerts a pressure of 11.0 atm at a temperature of 30 K. The value of ‘b’ is 0.05 lit mol^{-1}.

Sol. $\left(P+\frac{n^2a}{V^2}\right)(V-nb) = nRT$

$$\left(11+\frac{2^2a}{4^2}\right)(4-2\times0.05) = 2\times0.0821\times300$$

$a = 6.46\text{ atm lit}^2\text{ mol}^{-2}$

24. (a) Calculate the pressure exerted by 5 mol of CO_2 in one litre vessel at 47°C using van der Waal's equation. Also report the pressure of gas if it behaves ideally in nature. Given that a = 3.592 atm ltr^2 mol^{-2}. b = 0.042 litre mol^{-1}

(b) If volume occupied by CO_2 molecules is negligible, then calculate the pressure exerted by one mol of CO_2 gas at 273K.

Sol. (a) $\left(P+\frac{n^2a}{V^2}\right)(V-nb) = nRT$

$$\left(P+\frac{5^2\times3.592}{1}\right)(1-5\times0.0427) = 5\times.0821\times320$$

$P = 77.218\text{ atm}$

when the gas behaves ideally then $PV = nRT$

$P\times1 = 5\times.0821\times320. \Rightarrow P = 131.36\text{ atm}$

(b) For 1 mole $\left[P+\frac{a}{V^2}\right][V-b]=RT$

If b is negligible $P=\frac{RT}{V}-\frac{a}{V^2}=\frac{.0821\times 273}{22.4}-\frac{3.592}{(22.4)^2}$

P =0.9922 atm

25. The compression factor's (compressibility factor) for 1 mol of a van der Waal's gas at 0°C and 100 atmospheric pressure is found to be 0.5. Assuming that the volume of gas molecules is negligible, calculate the van der Waals constant 'a'.

Sol. $Z=\frac{PV}{nRT},\quad 0.5=\frac{100\times V}{1\times .0821\times 273}\quad \therefore V=0.112\,\text{litre.}$

van der Waal's equation when 'b' is negligible

$$\left[P+\frac{a}{V^2}\right]V=RT \text{ or } \left[100+\frac{a}{(0.112)^2}\right]=0.0821\times 273$$

$a = 1.253\,\text{atm litre}^2\,\text{mol}^{-2}$

26. Using van der Waal's equation calculate the constant 'a' when two moles of a gas is confined in a four litre flask exerts a pressure of 11.0 atm at a temperature of 300 K. The value of 'b' is 0.5 litre mol^{-1}.

Sol. van der Waals equation for n moles

$$\left[P+\frac{n^2a}{v^2}\right](V-nb)=nRT$$

Given T = 300 K, V = 4 litre, P = 11.0 atm, n = 2

We have

$$\left[11+\frac{2^2a}{4^2}\right][4.2\times 0.05]=2\times 0.0821\times 300$$

$a=6.46\,\text{atm litre}^2\text{mol}^{-2}$

27. At room temperature ammonia gas at 1 atm pressure and hydrogen chloride at p atmospheric pressure are allowed to diffuse through identical pin holes from opposite ends of a glass tube of 1 meter length and uniform cross section. Ammonium is first formed at a distance of 60 cm from the through which HCl gas is sent in what is the value of p?

Sol. $\frac{r_{NH_3}}{r_{HCl}}=\sqrt{\frac{M_{HCl}}{M_{NH_3}}}\times\frac{P_{NH_3}}{P_{HCl}}=\frac{40}{60}$

or $\sqrt{\frac{36.5}{17}}\times\frac{1}{P_{HCl}}=\frac{40}{60}$

$P_{HCl}=2.198$ atm

28. It is found that at 1470 K the mixture ($Cl_2 \rightleftharpoons 2Cl$) diffuses 1.16 times as fast as Krypton (83.8) diffuses under identical conditions. Find the degree of dissociation at equilibrium.

Sol. $Cl_2 \rightleftharpoons 2Cl$

$1-x \qquad 2x$

Where x is degree of dissociation.

The molecular weight of mixture of Cl_2 and Cl at equilibrium is given by

$$M_{mix}=\frac{(1-x)\times 71+2x\times 35.5}{(1-x)+2x}=\frac{71}{1+x}$$

$$\frac{R_{mix}}{R_{Kr}}=\sqrt{\frac{M_{Kr}}{M_{mix}}}=\sqrt{\frac{83.5}{71/(1+x)}}=1.16$$

$\therefore\ x=0.14$

29. What is the molar volume of N_2 at 500 K and 600 atm according to (a) ideal gas law (b) virial equation. The virial coefficient. B of N_2(g) at 500 K = 0.0169 lit mol^{-1}. How do you interpret the result.

Sol. For 1 mole of ideal gas PV = 1RT

$$V=\frac{0.0821\times 500}{600}=6.84\times 10^{-2}\,\text{lit mol}^{-1}$$

(b) using virial equation, neglecting high powers

$$Z=\frac{PV}{RT}=1+\frac{B}{V}=1+\frac{BP}{RT}$$

$$Z=1+\frac{0.0169\times 600}{0.082\times 500}=1.247$$

For 1 mol of a real gas

$$Z=\frac{PV}{RT};\ V=\frac{ZRT}{P}=\frac{1.247\times 0.0821\times 500}{600}$$

$=8.53\times 10^{-2}\,\text{lit mol}^{-1}$

The molar volume of the real gas is greater because of finite volume of the gas molecules.

30. An evacuated glass vessel weighs 50 g when empty 148 g when filled with a liquid of density 0.98 g/ml and 50.5 g when filled with ideal gas at 760 mm Hg at 300 K. Determine the molecular wt of the gas.

Sol. Weight of liquid = 148 – 50 = 98 g

Volume of liquid $=\frac{w}{d}=\frac{98}{0.98}=100$ ml

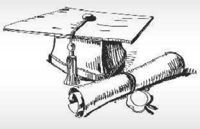
wt of gas = 50.5 – 50 = 0.5g

$$PV=\frac{W}{M}RT$$

or $\frac{760\times 100}{760\times 1000}=\frac{0.5}{m}\times 0.821\times 300$

or m = 123.15

Exercise-1 | NCERT Based Questions



Very Short/Short Answer Questions

1. When do real gases behave as ideal gas?

2. The size of weather balloon becomes larger and larger as it ascends up into higher altitudes. Why?

3. What do you mean by Boyle temperature ? Give its expression and its relation with inversion temperature.

4. Liquid is transferred from a large beaker to a small beaker, what will be the effect on its vapour pressure ?

5. Explain, why the bubbles of a gas in a boiling liquid generally increase in volume as they approach the upper surface ?

6. What is the effect of temperature on the vapour pressure of a liquid ?

7. Two different gases 'A' and 'B' are filled in separate containers of equal capacity under the same conditions of temperature and pressure. On increasing the pressure slightly the gas 'A' liquefies but gas B does not liquify even on applying high pressure until it is cooled. Explain this phenomenon.

8. A gas occupying a volume of 100 litres is at 20°C under a pressure of 2 bar. What temperature will it have when it is placed in an evacuated chamber of volume 175 litres ? The pressure of the gas in the chamber is one-third of its initial pressure.

9. The values of the van der Waal's constants for a gas are a = 4.10 dm^6 bar mol^{-2} and b = 0.035 dm^3 mol^{-1}. Calculate the values of the critical temperature and critical pressure for the gas.

10. Compressibility factor, Z, of a gas is given as $Z \quad \frac{pV}{nRT}$

(i) What is the value of Z for an ideal gas ?

(ii) For real gas what will be the effect on value of Z above Boyle's temperature ?

11. For real gases the relation between p, V and T is given by van der Waals equation :

$$\left(p+\frac{an^2}{V^2}\right)V-nb \quad nRT$$

where 'a' and 'b' are van der Waals constants, 'nb' is approximately equal to the total volume of the molecules of a gas.

'a' is the measure of magnitude of intermolecular attraction.

(i) Arrange the following gases in the increasing order of 'b'. Give reason. O_2, CO_2, H_2, He

(ii) Arrange the following gases in the decreasing order of magnitude of 'a'. Give reason.

CH_4, O_2, H_2

12. A bacterial culture isolated from sewage produced 41.3 ml of methane, CH_4 at 31ºC and 753 mm Hg. What is the volume of this methane at STP?

Long Answer Questions

13. (i) A quantity of hydrogen is confined in a chamber of constant volume. When the chamber is immersed in a bath of melting ice, the pressure of the gas is 1000atm.

(a) What is the Celsius temperature when the pressure manometer indicates an absolute pressure of 400 atm?

(b) What pressure will be indicated when the chamber is brought to 100 ºC?

(ii) A steel tank containing air at 15 atm pressure at 15° C is provided with a safety valve that will yield at a pressure of 30 atm. To what minimum temperature must the air be heated to blow the safety valve?

14. (i) One mole of the CO_2 occupies 1.5 L at 25ºC. Calculate the pressure exerted by the gas using:

(a) an ideal gas equation

(b) van der Waal's equation if:

a = 3.012 atm mol^{-2} and b = 0.04 L mol^{-1}.

(ii) The critical temperature and pressure for NO gas are 177 K and 64.5 atm. respectively. Calculate the van der Waal's constants 'a' and 'b'.

15. (i) A spherical balloon of 21 cm diameter is to be filled with hydrogen at STP from a cylinder containing the gas at 20 atm at 27ºC. If the cylinder can hold 2.82 L of water, calculate the number of balloons that can be filled up.

(ii) Two van der Waals gases A and B have volumes 0.112 and 0.111 L mol^{-1} respectively. Calculate the compressibility factors for one mole of each at 273 K and 200 atm and hence state which gas is more compressible.

Multiple Choice Questions

16. Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of dipoles possess 'partial charges'. The partial charge is

(a) more than unit electronic charge

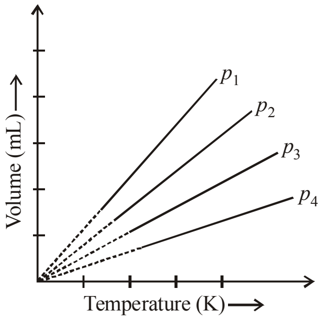
(b) equal to unit electronic charge

(c) less than unit electronic charge

(d) double the unit electronic charge

17. A plot of volume (V) versus temperature (T) for a gas at constant pressure is a straight line passing through the origin. The plots at different values of pressure are shown in figure. Which of the following order pressure is correct for this gas ?

(a) $p_1 > p_2 > p_3 > p_4$
(b) $p_1 = p_2 = p_3 = p_4$
(c) $p_1 < p_2 < p_3 < p_4$
(d) $p_1 < p_2 = p_3 < p_4$



18. The pressure of a 1 : 4 mixture of dihydrogen and dioxygen enclosed in a vessel is one atmosphere. What would be the partial pressure of dioxygen ?
(a) 0.8×10^5 atm (b) $0.008\ \text{Nm}^{-2}$
(c) $8 \times 10^4\ \text{Nm}^{-2}$ (d) 0.25 atm

19. The ratio of Boyle's temperature and critical temperature for a gas is :
(a) $\frac{8}{27}$ (b) $\frac{27}{8}$ (c) $\frac{1}{2}$ (d) $\frac{2}{1}$

20. Gases possess characteristic critical temperature which depends upon the magnitude of intermolecular forces between the particles. Following are the critical temperature of some gases.

Gases	H_2	He	O_2	N_2
Critical temperature in Kelvin	33.2	5.3	154.3	126

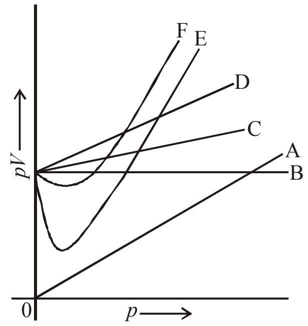
From the above data what would be the order of liquefaction of these gases ?
Start writing the order from the gas liquefying first
(a) H_2, He, O_2, N_2 (b) He, O_2, H_2, N_2
(c) N_2, O_2, He, H_2 (d) O_2, N_2, H_2, He

21. Atmospheric pressures recorded in different cities are as follows :

Cities	***p* in N/m^2**
Shimla	1.01×10^5
Bangalore	1.2×10^5
Delhi	1.02×10^5
Mumbai	1.21×10^5

Consider the above data and mark the place at which liquid will boil first.
(a) Shimla (b) Bangalore
(c) Delhi (d) Mumbai

22. Which curve in figure represents the curve of ideal gas ?
(a) B only
(b) C and D only
(c) E and F only
(d) A and B only



23. Increase in kinetic energy can overcome intermolecular forces of attraction. How will the viscosity of liquid be affected by the increase in temperature ?
(a) Increase (b) No effect (c) Decrease
(d) No regular pattern will be followed

Exercise-2 | CONCEPTUAL MCQs

1. Which one of the following statements is wrong for gases?
(a) Gases do not have a definite shape and volume
(b) Volume of the gas is equal to the volume of the container confining the gas
(c) Confined gas exerts uniform pressure on the walls of its container in all directions
(d) Mass of the gas cannot be determined by weighting a container in which it is enclosed.

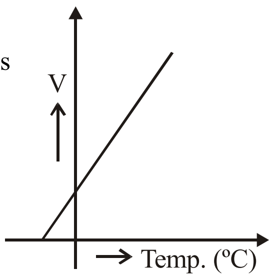
2. Non reacting gases have a tendency to mix with each other. This property is known as
(a) diffusion (b) fusion
(c) mixing (d) None of these

3. Which of the following mixtures of gases does not obey Dalton's law of partial pressure ?
(a) O_2 and CO_2 (b) N_2 and O_2
(c) Cl_2 and O_2 (d) NH_3 and HCl

4. Densities of two gases are in the ratio 1:2 and their temperatures are in the ratio 2:1 then the ratio of their respective pressures is
(a) 1:1 (b) 1:2
(c) 2:1 (d) 4:1

5. Gas equation PV = nRT is obeyed by
(a) only isothermal process
(b) only adiabatic process
(c) both (a) and (b)
(d) None of these

6. The following graph illustrates
(a) Dalton's law
(b) Charle's law
(c) Boyle's law
(d) Gay-Lussac's law

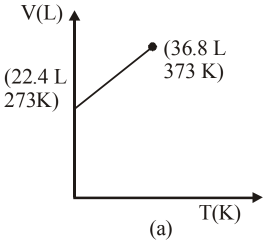


7. 4.4 g of a gas at STP occupies a volume of 2.24 L, the gas can be

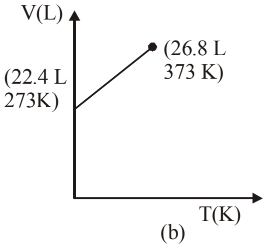
(a) O_2 (b) CO

(b) NO_2 (d) CO_2

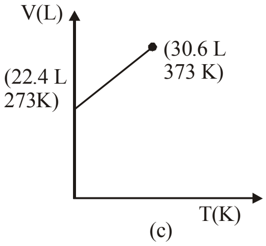
8. Which of the following volume (V) - temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure ?



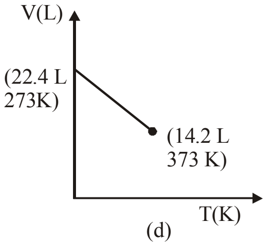
(a)



(b)



(c)



(d)

9. If the four tubes of a car are filled to the same pressure with N_2, O_2, H_2 and Ne separately, then which one will be filled first ?

(a) N_2 (b) O_2

(c) H_2 (d) Ne

10. When the product of pressure and volume is plotted against pressure for a given amount of the gas, the line obtained is

(a) parallel to X-axis

(b) parallel to Y-axis

(c) linear with positive slope

(d) linear with negative slope

11. Air at sea level is dense. This is a practical application of

(a) Boyle's law (b) Charle's law

(c) Kelvin's law (d) Brown's law

12. Use of hot air balloons in sports and meteorological observations is an application of

(a) Boyle's law (b) Charle's law

(b) Kelvin's law (d) Gay-Lussac's law

13. "Equal volumes of all gases at the same temperature and pressure contain equal number of particles." This statement is a direct consequece of

(a) Perfect gas law (b) Avogadro's law

(c) Charle's law (d) Boyle's law

14. If 300 ml of a gas at 27^0 C is cooled to 7^0 C at constant pressure, its final volume will be

(a) 135 ml (b) 540 ml

(c) 350 ml (d) 280 ml

15. For an ideal gas, correct relation is-

(a) $\left[\frac{\delta E}{\delta V}\right]_T = 0$ (b) $\left[\frac{\delta E}{\delta T}\right]_P = 0$

(c) $\left[\frac{\delta E}{\delta T}\right]_V = 0$ (d) All of these

16. The value of R in SI units is :

(a) 8.315×10^7 erg K^{-1} mol^{-1}

(b) $8.315 JK^{-1}$ mol^{-1}

(c) 0.0815 litre atm K^{-1} mol^{-1}

(d) 2 cal K^{-1} mol^{-1}

17. The compressibility factor for H_2 and He is usually :

(a) >1 (b) =1

(c) <1 (d) Either of these

18. The densities of two gasses are in the ratio of 1: 16. The ratio of their rates of diffusion is

(a) 16:1 (b) 4:1

(c) 1:4 (d) 1:16

19. At what temperature, the rate of effusion of N_2 would be 1.625 times than that of SO_2 at 50^o C ?

(a) 110 K (b) 173 K

(c) 373 K (d) 273 K

20. The rate of diffusion of methane at a given temperature is twice that of X. The molecular weight of X is

(a) 64.0 (b) 32.0

(c) 40.0 (d) 80.0

21. X ml of H_2 gas effuse through a hole in a container in 5 seconds. The time taken for the effusion of the same volme of the gas specified below under identical conditions is

(a) 10 seconds : He (b) 20 seconds : O_2

(c) 25 seconds : CO (d) 55 seconds : CO_2

22. The rate of diffusion of a gas having molecular weight just double of nitrogen gas is 56 ml s^{-1}. The rate of diffusion of nitrogen will be

(a) 79.19 ml s^{-1} (b) 112.0 ml s^{-1}

(c) 56.0 ml s^{-1} (d) 90.0 ml s^{-1}

23. Which pair of the gaseous species diffuse through a small jet with the same rate of diffusion at same P and T

(a) NO, CO (b) NO, CO_2

(c) NH_3, PH_3 (d) NO, C_2H_6

24. The rate of diffusion of SO_2, CO_2, PCl_3 and SO_3 are in the following order

(a) $PCl_3 > SO_3 > SO_2 > CO_2$

(b) $CO_2 > SO_2 > PCl_3 > SO_3$

(c) $SO_2 > SO_3 > PCl_3 > CO_2$

(d) $CO_2 > SO_2 > SO_3 > PCl_3$

25. Which of the following expression correctly represents the relationship between the average molar kinetic energy $\overline{KE}$ of CO and N_2 molecules at the same temperature

(a) $\overline{KE}_{CO} = \overline{KE}_{N_2}$

(b) $\overline{KE}_{CO} > \overline{KE}_{N_2}$

(c) $\overline{KE}_{CO} < \overline{KE}_{N_2}$

(d) Can not be predicted unless the volumes of the gases are not given

26. Kinetic theory of gases presumes that the collisions between the molecules to be perfectly elastic because

(a) the gas molecules are tiny particles and not rigid in nature

(b) the temperature remains constant irrespective of collision

(c) collision will not split the molecules

(d) the molecules are large particleand rigid in nature

27. The average kinetic energy of an ideal gas per molecule in SI unit at 25° C will be

(a) 6.17×10^{-21} kJ (b) 6.17×10^{-21} J

(c) 6.17×10^{-20} J (d) 7.16×10^{-20} J

28. Boyle's law, according to kinetic equation can be expressed as

(a) $PV = KT$ (b) $PV = RT$

(c) $PV = \frac{3}{2}kT$ (d) $PV = \frac{2}{3}kT$

29. The ratio between the root mean square velocity of H_2 at 50 K and that of O_2 at 800 K is

(a) 4 (b) 2

(c) 1 (d) 1/4

30. The r.m.s velocity of hydrogen is $\sqrt{7}$ times the r.m.s velocity of nitrogen. If T is the temperature of the gas , than

(a) $T(H_2) = T(N_2)$ (b) $T(H_2) > T(N_2)$

(c) $T(H_2) < T(N_2)$ (d) $T(H_2) = \sqrt{7}T(N_2)$

31. The r.m.s velocity of CO_2 at temperature T (in kelvin) is $x\,cm\,s^{-1}$. At what temperature (in kelvin) the r.m.s. velocity of nitrous oxide would be $4x\ cms^{-1}$?

(a) 16 T (b) 2 T

(c) 4 T (d) 32 T

32. Which of the following has maximum root mean square velocity at the same temperature?

(a) SO_2 (b) CO_2

(c) O_2 (d) H_2

33. Density ratio of O_2 and H_2 is 16:1. The ratio of their r.m.s. velocities will be

(a) 4 : 1 (b) 1 : 16

(c) 1 : 4 (d) 16 : 1

34. At what temperature the RMS velocity of SO_2 be same as that of O_2 at 303 K ?

(a) 273 K (b) 606 K

(c) 303 K (d) 403 K

35. The temperature of an ideal gas is reduced from 927^{0}C to 27^{0}C. the r.m.s. velocity of the molecules becomes.

(a) double the inital value

(b) half of the initial value

(c) four times the initial value

(d) ten times the initial value

36. If the average velocity of N_2 molecues is 0.3 m/s at 27°C, then the velocity of 0.6 m/s will take place at

(a) 273 K (b) 927 K

(c) 1000 K (d) 1200 K

37. Gas deviates from ideal gas nature because molecules

(a) are colouress

(b) attaract each other

(c) contain covalent bond

(d) show Brownian movement.

38. The compressibility factor for an ideal gas is

(a) 1.5 (b) 1.0

(c) 2.0 (d) ∞

39. A gas will approach ideal behaviour at

(a) low temperature and low pressure

(b) low temperature and high pressure

(c) high temperature and low pressure

(d) high temperature and high pressure

40. The compressibility of a gas is less than unity at STP. Therefore

(a) $V_m > 22.4$ litres (b) $V_m < 22.4$ litres

(c) $V_m = 22.4$ litres (d) $V_m = 44.8$ litres

41. An ideal gas will have maximum density when

(a) P = 0.5 atm, T = 600 K (b) P = 2 atm, T = 150 K

(c) P = 1 atm, T = 300 K (d) P = 1 atm, T = 500 K

42. 120 g of an ideal gas of molecular weight 40 g mol^{-1} are confined to a volume of 20 L at 400 K. Using R=0.0821 L atm K^{-1} mol^{-1}, the pressure of the gas is

(a) 4.90 atm (b) 4.92 atm

(c) 5.02 atm (d) 4.96 atm

43. The volume of 0.0168 mol of O_2 obtained by decomposition of $KClO_3$ and collected by displacement of water is 428 ml at a pressure of 754 mm Hg at 25^0 C. The pressure of water vapour at 25^0 C is

(a) 18 mm Hg (b) 20 mm Hg

(c) 22 mm Hg (d) 24 mm Hg.

44. Pressure of a mixture of 4 g of O_2 and 2 g of H_2 confined in a bulb of 1 litre at 0^0 C is

(a) 25.215 atm (b) 31.205 atm

(c) 45.215 atm (d) 15.210 atm

45. Same mass of CH_4 and H_2 is taken in container, The partial pressure caused by H_2 is

(a) $\frac{8}{9}$
(b) $\frac{1}{9}$
(c) $\frac{1}{2}$
(d) 1

46. There are 6.02×10^{22} molecules each of N_2, O_2 and H_2 which are mixed together at 760 mm and 273 K. The mass of the mixture in grams is

(a) 6.02
(b) 4.12
(c) 3.09
(d) 6.2

47. The density of air is 0.00130 g/ml. The vapour density of air will be

(a) 0.00065
(b) 0.65
(c) 14.4816
(c) 14.56

48. An ideal gas is one which obeys the gas laws under

(a) a few selected experimental conditions
(b) all experimental conditions
(c) low pressure alone
(d) high temperature alone

49. The temperature at which real gases obey the ideal gas laws over a wide range of pressure is called

(a) Critical temperature
(b) Boyle's Temperature
(c) Inversion temperature
(d) Reduced temperature

50. Which of the following exhibits the weakest inter- molecular forces

(a) NH_3
(b) HCl
(c) He
(d) H_2O

51. The van der Waal's equation reduces itself to the ideal gas equation at

(a) high pressure and low temperature
(b) low pressure and low temperature
(c) low pressure and high temperature
(d) high pressure alone

52. An ideal gas obeying kinetic theory of gases can be liquefied if:

(a) its temperature is more than critical temperature T_C
(b) its pressure is more than critical pressure P_C
(c) its pressure is more than P_C at a temperature less than T_C
(d) it cannot be liquefied at any value of P and T

53. The ratio of Boyle's temperature and critical temperature for a gas is :

(a) $\frac{8}{27}$
(b) $\frac{27}{8}$
(c) $\frac{1}{2}$
(d) $\frac{2}{1}$

54. The value of van der waals constant 'a' for gases O_2, N_2, NH_3 and CH_4 are 1.360, 1.390, 4.170 and 2.253 liter ^{2} atm mol^{-2} respectively. The gas which can most easily be liquefied is :

(a) O_2
(b) N_2
(c) NH_3
(d) CH_4

55. Joule- Thomson coefficient $\left(\frac{\delta T}{\delta P}\right)_H$ for an ideal gas is

(a) zero
(b) positive
(c) negative
(d) None of these

56. The inversion temperature (T_i) for a gas is given by

(a) a / Rb
(b) 2a / Rb
(c) $\frac{Rb}{a}$
(d) $\frac{2Rb}{a}$

57. The Joule-Thomson coefficient for a gas is zero at

(a) Inversion temperature
(b) Critical temperature
(c) Absolute temperature
(d) Below 0°C

58. Longest mean free path under similar conditions of P and T stands for.

(a) N_2
(b) O_2
(c) H_2
(d) Cl_2

59. The mean free path (λ) of a gas sample is given by

(a) $\lambda = \sqrt{2\pi\sigma^2 N}$
(b) $\lambda = \frac{1}{\sqrt{2}.\pi\sigma^2 N}$
(c) $\lambda = \sqrt{2\pi u\sigma^2 N}$
(d) None of these

60. Which of the following statements is false

(a) Avogadro Number = 6.02×10^{21}
(b) The relationship between average velocity $(\overline{v})$ and root mean square velocity (u) is $(\overline{v})$ =.9213u
(c) The mean kinetic energy of an ideal gas is independent of the pressure of the gas
(d) The root mean square velocity of the gas can be calculated by the formula $(3RT/M)^{1/2}$

61. At higher altitude the boiling point of water lowers because

(a) atmospheric pressure is low
(b) temperature is low
(c) atmospheric pressure is high
(d) None of these

62. Which of the following liquid will exhibit highest vapour pressure?

(a) $C_2H_5OH(l)$
(b) $NH_3\,(l)$
(c) $HF\,(l)$
(d) $H_2O(l)$

63. A manifestation of surface tension is :
(a) rise of liquid in a capillary tube
(b) spherical shape of liquid drops
(c) upward movement of water in soils
(d) All the above

64. Generally , liquid drops assume spherical shape because:
(a) a sphere has maximum surface area
(b) a sphere has minimum surface area
(c) sphere is symmetrical in shape
(d) none of these

65. On heating a liquid, its surface tension
(a) increases (b) decreases
(c) remains same (d) is reduced to zero

66. Water drops stick to a glass surface due to:
(a) cohesion (b) adhesion
(c) flocculation (d) None of these

67. The internal resistance to flow in liquid is called
(a) Fluidity (b) Specific resistance
(c) Viscosity (d) Surface tension.

68. With rise in temperature, viscosity of a liquid
(a) increase
(b) decrease
(c) remains constant
(d) may increase or decrease.

69. With the increasing molecular weight of a liquid, the viscosity
(a) decreases (b) increases
(c) remain constant (d) All are wrong

Exercise-3 | PAST COMPETITION MCQs

1. A weather ballon filled with hydrogen at 1 atm and 27°C has volume equal to 12000 litres. On ascending it reaches a place where the temperature is –23°C and pressure is 0.5 atm. The volume of the balloon is **[CBSE-PMT 1991]**
(a) 24000 litres (b) 20000 litres
(c) 10000 litres (d) 12000 litres

2. If a gas expands at constant temperature, it indicates that : **[CBSE-PMT 2008]**
(a) kinetic energy of molecules decreases
(b) pressure of the gas increases
(c) kinetic energy of molecules remains the same
(d) number of the molecules of gas increases

3. The pressure exerted by 6.0g of methane gas in a 0.03 m^3 vessel at 129°C is (Atomic masses : C = 12.01, H = 1.01 and R = 8.314 kpa dm^3K^{-1} mol^{-1}) **[CBSE-PMT 2010]**
(a) 31684 Pa (b) 215216 Pa
(c) 13409 Pa (d) 41777 Pa

4. By what factor does the average velocity of a gaseous molecule increase when the temperature (in Kelvin) is doubled ? **[CBSE-PMT 2011]**
(a) 2.0 (b) 2.8 (c) 4.0 (d) 1.4

5. Two gases A and B having the same volume diffuse through a porous partition in 20 and 10 seconds respectively. The molecular mass of A is 49 u. Molecular mass of B will be : **[CBSE-PMT 2011]**
(a) 50.00 u (b) 12.25 u (c) 6.50 u (d) 25.00 u

6. A gaseous mixture was prepared by taking equal mole of CO and N_2. If the total pressure of the mixture was found 1 atmosphere, the partial pressure of the nitrogen (N_2) in the mixture is : **[CBSE-PMT 2011]**
(a) 0.5 atm (b) 0.8 atm (c) 0.9 atm (d) 1 atm

7. A bubble of air is underwater at temperature 15°C and the pressure 1.5 bar. If the bubble rises to the surface where the temperature is 25°C and the pressure is 1.0 bar, what will happen to the volume of the bubble ? **[CBSE-PMT 2011M]**
(a) Volume will become greater by a factor of 1.6.
(b) Volume will become greater by a factor of 1.1.
(c) Volume will become smaller by a factor of 0.70.
(d) Volume will become greater by a factor of 2.5.

8. 50 mL of each gas A and of gas B takes 150 and 200 seconds respectively for effusing through a pin hole under the similar condition. If molecular mass of gas B is 36, the molecular mass of gas A will be : **[CBSE-PMT 2012]**
(a) 96 (b) 128 (c) 20.25 (d) 64

9. A certain gas takes three times as long to effuse out as helium. Its molecular mass will be : **[CBSE-PMT 2012]**
(a) 27 u (b) 36 u (c) 64 u (d) 9 u

10. Maximum deviation from ideal gas is expected from :
(a) $N_2(g)$ (b) $CH_4(g)$ **[NEET 2013]**
(c) NH_3 (g) (d) $H_2(g)$

11. For an ideal gas, number of moles per litre in terms of its presure P, gas constant R and temperature T is **[AIEEE 2002]**
(a) PT/R (b) PRT
(c) P/RT (d) RT/P

12. Value of gas constant *R* is **[AIEEE 2002]**
(a) 0.082 litre atm (b) 0.987 cal mol^{-1} K^{-1}
(c) 8.3 J mol^{-1} K^{-1} (d) 83 erg mol^{-1} K^{-1}.

13. Kinetic theory of gases proves **[AIEEE 2002]**
(a) only Boyle's law
(b) only Charles' law
(c) only Avogadro's law
(d) All of these.

14. The heat required to raise the temperature of body by 1 K is called **[AIEEE 2002]**

(a) specific heat (b) thermal capacity

(c) water equivalent (d) none of these.

15. What volume of hydrogen gas, at 273 K and 1 atm pressure will be consumed in obtaining 21.6 g of elemental boron (atomic mass = 10.8) from the reduction of boron trichloride by hydrogen ? **[AIEEE 2003]**

(a) 67.2 L (b) 44.8 L

(c) 22.4 L (d) 89.6 L

16. According to the kinetic theory of gases, in an ideal gas, between two successive collisions a gas molecule travels

(a) in a wavy path **[AIEEE 2003]**

(b) in a straight line path

(c) with an accelerated velocity

(d) in a circular path

17. As the temperature is raised from 20ºC to 40ºC, the average kinetic energy of neon atoms changes by a factor of which of the following ? **[AIEEE 2004]**

(a) $^{313}\!/_{293}$ (b) $\sqrt{(313/293)}$

(c) $^{1}\!/_{2}$ (d) 2

18. In van der Waals equation of state of the gas law, the constant ‘b’ is a measure of **[AIEEE 2004]**

(a) volume occupied by the molecules

(b) intermolecular attraction

(c) intermolecular repulsions

(d) intermolecular collisions per unit volume

19. Which one of the following statements is NOT true about the effect of an increase in temperature on the distribution of molecular speeds in a gas? **[AIEEE 2005]**

(a) The area under the distribution curve remains the same as under the lower temperature

(b) The distribution becomes broader

(c) The fraction of the molecules with the most probable speed increases

(d) The most probable speed increases

20. The volume of a colloidal particle, V_C as compared to the volume of a solute particle in a true solution V_S, could be **[AIEEE 2005]**

(a) $\frac{V_C}{V_S} \simeq 10^3$ (b) $\frac{V_C}{V_S} \simeq 10^{-3}$

(c) $\frac{V_C}{V_S} \simeq 10^{23}$ (d) $\frac{V_C}{V_S} \simeq 1$

21. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is **[AIEEE 2007]**

(a) 1/2 (b) 2/3

(c) $\frac{1}{3} \times \frac{273}{298}$ (d) 1/3.

22. If 10^{-4} dm^3 of water is introduced into a 1.0 dm^3 flask at 300 K, how many moles of water are in the vapour phase when equilibrium is established ? **[AIEEE 2010]**

(Given : Vapour pressure of H_2O at 300 K is 3170 Pa; $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$)

(a) 5.56×10^{-3} mol (b) 1.53×10^{-2} mol

(c) 4.46×10^{-2} mol (d) 1.27×10^{-3} mol

23. When r, P and M represent rate of diffusion, pressure and molecular mass, respectively, then the ratio of the rates of diffusion (r_A / r_B) of two gases A and B, is given as : **[AIEEE 2011 RS]**

(a) $(P_A / P_B)(M_B / M_A)^{1/2}$ (b) $(P_A / P_B)^{1/2}(M_B / M_A)$

(c) $(P_A / P_B)(M_A / M_B)^{1/2}$ (d) $(P_A / P_B)^{1/2}(M_A / M_B)$

24. The molecular velocity of any gas is **[AIEEE 2011 RS]**

(a) inversely proportional to absolute temperature.

(b) directly proportional to square of temperature.

(c) directly proportional to square root of temperature.

(d) inversely proportional to the square root of temperature.

25. The compressibility factor for a real gas at high pressure is : **[AIEEE 2012]**

(a) $1 + \frac{RT}{pb}$ (b) 1 (c) $1 + \frac{pb}{RT}$ (d) $1 - \frac{pb}{RT}$

26. For gaseous state, if most probable speed is denoted by C*, average speed by $\overline{C}$ and mean square speed by C, then for a large number of molecules the ratios of these speeds are :

(a) $C^* : \overline{C} : C = 1.225 : 1.128 : 1$ **[JEE Main 2013]**

(b) $C^* : \overline{C} : C = 1.128 : 1.225 : 1$

(c) $C^* : \overline{C} : C = 1 : 1.128 : 1.225$

(d) $C^* : \overline{C} : C = 1 : 1.225 : 1.128$

27. At constant volume and temperature conditions, the rate of diffusion D_A and D_B of gases A and B having densities ρ_A and ρ_B are related by the expression. **[IIT-JEE 1993]**

(a) $D_A = \left[D_B \frac{\rho_A}{\rho_B}\right]^{1/2}$ (b) $D_A = \left[D_B \frac{\rho_B}{\rho_A}\right]^{1/2}$

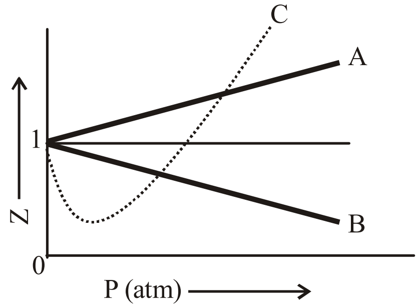
(c) $D_A = D_B \left(\frac{\rho_A}{\rho_B}\right)^{1/2}$ (d) $D_A = D_B \left(\frac{\rho_B}{\rho_A}\right)^{1/2}$

28. The compression factor (compressibility factor) for 1 mole of a van der Waal’s gas at 0°C and 100 atm pressure if found to be 0.5. Assuming that the volume of gas molecules is negligible, calculate the van der Waal’s constant 'a'. **[IIT-JEE 2001]**

(a) $0.253\ L^2 mol^{-2} atm$ (b) $0.53\ L^2 mol^{-2} atm$

(c) $1.853\ L^2 mol^{-2} atm$ (d) $1.253\ L^2 mol^{-2} atm$

29. The given graph represents the variation of Z (compressibility factor $= \frac{PV}{nRT}$) versus P, for three real gases A, B and C. Identify the only incorrect statement **[IIT-JEE 2006]**

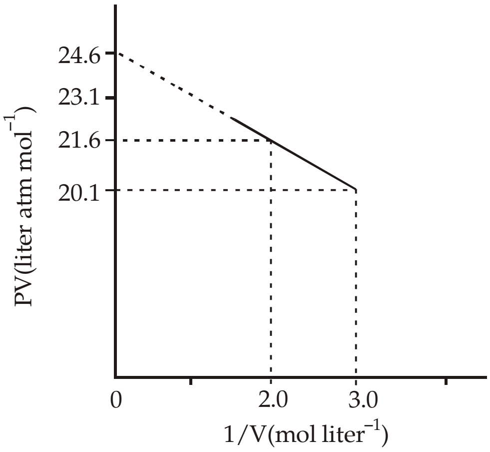


(a) For the gas A, a = 0 and its dependence on P is linear at all pressure.
(b) For the gas B, b = 0 and its dependence on P is linear at all pressure
(c) For the gas C, which is typical real gas for which neither a nor b = 0. By knowing the minima and the point of intersection, with Z = 1, a and b can be calculated
(d) At high pressure, the slope is positive for all real gases

30. The term that corrects for the attractive forces present in a real gas in the van der Waals equation is **[IIT-JEE 2009]**

(a) nb (b) $\frac{an^2}{V^2}$ (c) $-\frac{an^2}{V^2}$ (d) $-nb$

31. For one mole of a van der Waals gas when $b = 0$ and T = 300 K, the PV vs, 1/V plot is shown below. The value of the van der Waals constant a (atm. liter^2 mol^{-2}) is : **[IIT-JEE 2012]**



(a) 1.0 (b) 4.5 (c) 1.5 (d) 3.0

Exercise-4 | Applied MCQs

1. N_2O_4 is 20 % dissociated at 27°C and 760 torr. The density of the equilibrium mixture is
(a) 3.1 g/l (b) 6.2 g/l
(c) 12.4g/l (d) 18.6 g/l

2. Helium atom is two times heavier than a hydrogen molecule at. 298K. The average KE of helium is
(a) 2 times of H_2 molecule
(b) same as that of H_2 molecule
(c) 4 times that of hydrogen molecule
(d) $\frac{1}{2}$ that of H_2 molecule

3. The units of 'a' in van der Waals equation of state is
(a) atm. litre mol^{-1} (b) atm. litre^2 mol^{-2}
(c) atm litre^2 mol^2 (d) atm. litre mol^{-2}

4. A container contains certain gas of mass 'm' of high pressure. Some of the gas has been allowed to escape from the container and after some time the pressure of the gas becomes half and its absolute temperature 2/3 rd. The amount of the gas escaped is
(a) 2/3 m (b) 1/2 m
(c) 1/4 m (d) 1/6 m

5. The partial pressure of hydrogen in a flask containing 2.016 g of H_2 and 96.0 g of O_2 is
(a) 1/8 of the total pressure (b) 1/6 of the total pressure
(c) 1/4 of the total pressure (d) 2/3 of the total pressure

6. At 27°C a gas was compressed to half of its volume. To what temperature it must be now heated so that it occupies just its original volume. The pressure remains constant
(a) 54°C (b) 327°C
(c) 600°C (d) 327 °C.

7. Equal volumes of the gases which do not react together are confined in separate vessels. The pressure is 200 mm and 400 mm of Hg respectively. If the two gases are mixed together what will be the pressure of the resulting mixture (temperature remaining constant)
(a) 400mm (b) $\sqrt{400}$ mm
(c) 300mm (d) 200mm

8. A flask containing air (open to the atmosphere) is heated from 300 K to 500 K. The percentage of the air escaped into the atmosphere is
(a) 16.6 (b) 40
(c) 60 (d) 20

9. A sample of O_2 gas is collected over water at 23°C at a barometer pressure of water at 751 mm Hg (Vapour pressure of water at 23°C is 21 mm Hg). The partial pressure of O_2 gas in the sample collected is

(a) 21 mm Hg (b) 751 mm Hg
(c) 0.96 atm. (d) 1.02 atm.

10. Which of the following is a false statement ?

(a) Gases having same molecular masses diffuse at the same rate
(b) 0.5 litre of nitrogen and 1 litre of helium will have the same number of the atoms at the same temperature and pressure
(c) The value of molar gas constant does not vary with the nature of the gas
(d) None is false

11. The density of SO_2 at STP is 2.06 kg m^{-3}. Its density at 819°C and 2 atmosphere is

(a) 2.86 kg m^{-3} (b) 1.43 kg m^{-3}
(c) 0.715 kg m^{-3} (d) 4.2686 kg m^{-3}

12. When helium is allowed to expand into vacuum, heating effect is observed. Its reason is that

(a) helium is an ideal gas
(b) helium is an inert gas
(c) inversion temperature of helium is low
(d) the boiling point of helium is the lowest amongst the element.

13. What would be the vapour density of a gas 260 cm^3 of which at 290 K and 100.40 KPa pressure weights 0.160g

(a) $17.9\ gL^{-1}$ (b) $14.2\ gL^{-1}$
(c) $7.4\ g\ cm^{-3}$ (d) None of these

14. Reducing the pressure from 1.0 atm to 0.5 atm would change the number of molecules in one mole of ammonia to

(a) 25% of its initial value
(b) 50% of its initial value
(c) 75% of its initial value
(d) None of the above

15. The ratio of diffusion of nitrogen at 25°C would be .... times that of carbon dioxide at 75°C

(a) 0.90 (b) 1.16
(c) 1.41 (d) 1.76

16. The average kinetic energy of 28 g CO at, 300 K is E kcal. The average kinetic energy of 2 g H_2 at the same temperature would be..... kcal.

(a) E (b) 14E
(c) 1/14E (c) 28E

17. The critical temperature of water is higher than that of O_2 because the H_2O molecule has

(a) fewer electrons than O_2
(b) two covalent bonds
(c) V-shape
(d) dipole moment.

18. A bubble of the gas released at the bottom of a lake increases to eight times the original volume when it reaches at the surface. Assuming that the atmospheric pressure is equivalent to pressure exerted by a column of water 10 m high, what is the depth of the lake

(a) 80m (b) 90m
(c) 10m (d) 70m

19. SO_2 and He are kept in a container at partial pressure P_1 and P_2. A thin perforation is made in the wall of the container and it is observed that gases effuse at the same rate. The ratio of P_1 and P_2 will be

(a) 4 : 1 (b) 1 : 4
(c) 1 : 16 (d) 16 : 1

20. Helium has the van der Waals constant $b = 24\ ml\ mol^{-1}$. The molecular diameter of helium will be

(a) 267 pm
(b) 133.5 pm
(c) 26.7 pm
(d) Data not sufficient for calculation the diameter.

21. At 100°C and 1 atm, if the density of liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3}, then the volume occupied by water molecules in 1 litre of steam at that temperature is

(a) 6 cm^3 (b) 60 cm^3
(c) 0.6 cm^3 (d) 0.06 cm^3

22. Which of the following graphs is not a straight line for an ideal gas?

(a) $n \to T$ (b) $T \to p$
(c) $n \to \frac{1}{T}$ (d) $n \to \frac{1}{p}$

23. A volume V of a gas at temperature T_1 and a pressure p is enclosed in a sphere. It is connected to another sphere of volume V/2 by a tube and stopcock. The second sphere is initially evacuated and the stopock is closed. If the stopcock is opened the temperature of the gas in the second sphere becomes T_2. The first sphere is maintained at a temperature T_1. What is the final pressure p_1 within the apparatus ?

(a) $\frac{2pT_2}{2T_2 + T_1}$ (b) $\frac{2pT_2}{T_2 + 2T_1}$
(c) $\frac{pT_2}{2T_2 + T_1}$ (d) $\frac{2pT_2}{T_1 + T_2}$

24. The molecular velocities of two gases at the same temperature are u_1 and u_2 and their masses are m_1 and m_2 respectively. Which of the following expressions are correct ?

(a) $\frac{m_1}{u_1^2} = \frac{m_2}{u_2^2}$ (b) $m_1u_1 = m_2u_2$
(c) $\frac{m_1}{u_1} = \frac{m_2}{u_2}$ (d) $m_1u_1^2 = m_2u_2^2$

25. At low pressure, the van der Waal's equation is reduced to

(a) $Z=\frac{pV_m}{RT}=1-\frac{aP}{RT}$ (b) $Z=\frac{pV_m}{RT}=1+\frac{b}{RT}p$

(c) $pV_m=RT$ (d) $Z=\frac{pV_m}{RT}=1-\frac{a}{RT}$

26. The van der Waal's equation for n = 1 mol may be expressed as $V^3-\left(b+\frac{RT}{p}\right)V^2+\frac{aV}{p}-\frac{ab}{p}=0$

Where V is the molar volume of the gas. Which of the following is correct?

(a) For a temperature less than T_c, V has three real roots

(b) For a temperature more than T_c, V has one real and two imaginary roots

(c) For a temperature equal to T_c all three roots of V are real and identical

(d) All of these

27. According to kinetic theory of gases, for a diatomic molecule

(a) the pressure exerted by the gas is proportional to the mean velocity of the molecule.

(b) the root mean square velocity of the molecule is inversely proportional to the temperature.

(c) the pressure exerted by the gas is proportional to the rms velocity of the molecule.

(d) the mean translational kinetic energy of the molecule is proportional to the absolute temperature.

28. A perfect gas is found to obey the relation $PV^{3/2}$ = constant. If the gas is compressed to half of its volume at temperature T adiabatically, the final temperature of the gas will be

(a) $2T\sqrt{2}$ (b) 4T

(c) $T\sqrt{2}$ (d) 2T

29. A vessel containing gas at pressure 60 cm of Hg was connected to an arm A of open end manometer. The atmospheric pressure was recorded as 74 cm of Hg. If mercury in arm A stands at 84.5 cm height, the mercury in arm B will stand at

(a) 24.5 cm (b) 70.5 cm

(c) 88 cm (d) 74 cm

30. Three gases A, B, C have volumes V_1, V_2, V_3 at pressure P and temperature T are mixed keeping the temperature and pressure constant. The final volume of the gaseous mixture will be

(a) $V_1+V_2+V_3$ (b) $\frac{V_1+V_2+V_3}{3}$

(c) $\frac{V_1+V_2+V_3}{P}$ (d) $V_1\times V_2\times V_3$

31. A spherical balloon of 21 cm diameter is to be filled with H_2 at NTP from a cylinder containing the gas at 20 atm at 27°C. The cylinder can hold 2.82 L of water at NTP. The number of balloons that can be filled up is

(a) 15 (b) 10

(c) 20 (d) 25

32. The mass of N_2 in a 15 L gaseous mixture at 20°C and 740 mm pressure of the composition of the mixture by volume is $H_2=10\%$, $O_2=20\%$ and $N_2=70\%$

(a) 11.91 g (b) 16.2 g

(c) 21.91 g (d) 28.00 g

33. What will be the mole fraction of N_2 in a mixture of N_2 and O_2 if partial pressure of O_2 is 63 cm and total pressure of the mixture is 90 cm

(a) 3.0 (b) 0.3

(c) 0.7 (d) 0.5

34. The bottles of NH_3 and HBr gases are connected through a tube of 1 metre length. The distance of white solid formed in the tube from the end of NH_3

(a) 68.56 cm from NH_3 bottle

(b) 68.56 cm from HBr bottle

(c) At the centre of the tube

(d) None is correct.

35. At a temperature TK the pressure of 4 g of argon in a bulb is p. The bulb is put in a bath having temperature higher by 50 K than the first one. 0.8 g of argon has to be removed to maintain original pressure. The temperature T is equal to

(a) 510 K (b) 200 K

(c) 73 K (d) 100 K

36. Let the most probable velocity of hydrogen molecules at a temperature of t° C be V_0. When the temperature is raised to (2t + 273)°C the new rms velocity is (suppose all the molecules dissociate into atoms at latter temperature)

(a) $2\sqrt{3}V_0$ (b) $\sqrt{6}V_0$

(c) $\sqrt{3\left(2+\frac{273}{t}\right)}V_0$ (d) $\sqrt{\frac{2}{3}}V_0$

37. A vessel is filled with a mixture of O_2 and N_2. At what ratio of partial pressures will be the mass of gases be identical

(a) $p_{(O_2)}=8.75\,p_{(N_2)}$

(b) $p_{(O_2)}=0.78\,p_{(N_2)}$

(c) $p_{(O_2)}=0.875\,p_{(N_2)}$

(d) $p_{(O_2)}=11.4\,p_{(N_2)}$

38. A compound exists in the gaseous state both as monomer A and dimer A_2. The M. wt. of monomer is 48. In an experiment 96 g of the compound was confined in vessel of 33.6 L and heated to 273° C. Calculate the pressure developed, if the compound exists as a dimer to the extent of 50% by weight under the conditions

(a) 0.9 atm (b) 4.0 atm

(c) 2.0 atm (d) 1.0 atm

39. A mixture of 1 mol of H_2 and 1 mole of Cl_2 with little charcoal in a 10 L evacuated flask was irriadiated with light until the reaction was completed. Subsequently 5L of water was introduced into the flask and the flask was cooled to 27°C. The pressure exerted by the system is approximately equal to

(a) $\frac{2\times0.0821\times300}{5}$ atm

(b) ≈ 26 mm Hg

(c) $\frac{2\times0.0821}{10}$ atm

(d) $\frac{4\times0.0821\times300}{5}$ atm

40. The relative humidity of air is 80% at 27°C. If the aqueous tension at the same temperature is 27 mm Hg. The partial pressure of water vapour in the air will be

(a) 21.60 mm Hg (b) 27 mm Hg

(c) 25 mm Hg (d) 23 mm Hg

41. A closed vessel contains He and Ozone at pressure of P atm. The ratio of He and oxygen atoms is 1 : 1. If He is removed from the vessel, the pressure of the system will reduce to

(a) 0.25 P (b) 0.5 P

(c) 0.75 P (d) 0.33 P

42. The factor that has the largest effect on vapour pressure of a liquid is

(a) liquid surface area

(b) molecular dipole moment

(c) presence of H-bonding

(d) molecular mass of liquid

43. The molecular mass of a compound does not effected by

(a) vapour pressure of a liquid

(b) vapour density

(c) vapour pressure of solid

(d) molar volume of vapour

44. Which of the following liquids has the highest viscosity?

(a) Benzene (b) Carbon disulphide

(c) Acetone (d) Ethanol

Hints & Solutions

EXERCISE 1

1. At high temperature and low pressure.

3. $T_b = \frac{a}{bR}$, $T_i = 2T_b$

4. No effect, because vapour pressure is an intensive property.

5. The pressure on them decreases and hence volume increases.

6. Vapour pressure is directly proportional to the temperature.

7. Gas 'A' is at or below its critical temperature and gas 'B' is at a temperature higher than critical temperature.

8. $T_2 = -102.1°C$

9. $T_c = 422.76\,K$

$P_c = 123.96$ bar

10. (i) Z = 1 for ideal gas

(ii) For a real gas Z > 1 above Boyle's temperature.

12. $V_2 = 36.7$ ml.

13. (i) (a) $T_2 = -164°\,C$

(b) $P_2 = 1.37 \times 10^3$ atm

(ii) $T_2 = 303°C$

14. (i)

(a) P = 16.29 atm.

(b) P = 15.137 atm.

(ii) $a = 1.34\ L^2$ atm. mol^{-2}

$b = 0.02813\ L\ mol^{-1}$

15. (i) Number of balloons filled = 10.

(ii) $\therefore\ Z_A = 1.00062$

and $Z_B = 0.9917$

$Z_A > Z_B$, therefore B is more compressible.

16. **(c)** **17.** **(c)** **18.** **(c)** **19.** **(b)**

20. **(d)** **21.** **(a)** **22.** **(a)** **23.** **(c)**

EXERCISE 2

1. (d) Mass of the gas can be determined by weighing the (container + gas) – container alone.

2. (a) Intermixing of gases in known as diffusion.

3. (d) Dalton's law of partial pressure is applicable to non reacting gases. Here NH_3 and HCl react to form NH_4Cl.

4. (a) $P \propto d$ and T, $\frac{P_1}{P_2} = \frac{d_1 T_1}{d_2 T_2} = \frac{1}{2} \times \frac{2}{1} \Rightarrow P_1 : P_2 = 1:1$

5. (c) PV = nRT is for and ideal gas following isothermal or adiabatic process.

6. (b) Charle's law $V \propto T$ at constant P.

7. (d) 44g at STP occupies volume 22.4 litre which is molecular mass of CO_2. Molecular mass occupies 22.4 litre at STP.

8. (c) $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ at const. pressure

$\Rightarrow \frac{22.4}{273} = \frac{V_2}{373}$, $V_2 = 30.6$ litre

9. (c) Lesser the density more is the volume and H_2 has lowest density. ($d = \frac{MP}{RT}$ at constant P, R and T, $d \propto M$)

10. (a) Plot of PV vs P at constant T is parallel to X axis.

11. (a) $d \propto p$, Boyle's law, $\left(d = \frac{MP}{RT}\right)$. At sea level pressure is more, hence density of air is more.

12. (b) Hot air is lighter due to less density (Charle's law) $\left(d = \frac{MP}{RT}\right)$

13. (b) When P, V and T are same no. of particles will also be same (Avogadro law)

14. (d) At constant pressure

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow \frac{300}{300} = \frac{V_2}{280} \text{ or } V_2 = 280 \text{ ml}$$

15. (a) $\left(\frac{\partial E}{\partial V}\right)_T = 0$ For ideal gas and positive for real gas.

16. (b) In SI unit value of R= 8.314 J K^{-1} mol^{-1} (see text)

17. (a) Since for H_2 and He, PV > nRT and $Z = \frac{PV}{nRT}$. Hence Z is more than 1

18. (b) $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{16}{1}} = 4:1$

19. (c) $r \propto U$ and $U = \sqrt{\dfrac{3RT}{M}}$

$\therefore \quad \dfrac{r_1}{r_2} = \sqrt{\dfrac{T_1 M_2}{T_2 M_1}}$ or $\dfrac{r_{N_2}}{r_{SO_2}} = \sqrt{\dfrac{T_1 \times 64}{323 \times 28}} = 1.625$ or

$T_2 = 373K$

20. (a) $\dfrac{2}{1} = \sqrt{\dfrac{M_x}{16}} \quad \therefore M_x = 64$

21. (b) For effusion of same volume,

$\dfrac{t_1}{t_2} = \sqrt{\dfrac{M_1}{M_2}} \Rightarrow \dfrac{t_1}{\sqrt{M_1}} = \dfrac{t_2}{\sqrt{M_2}}$

This is clearly seen from the options that the ratio of $\dfrac{t}{\sqrt{M}}$ is same for H_2 and O_2. $\left(\dfrac{5}{\sqrt{2}} = \dfrac{20}{\sqrt{32}} = \dfrac{5}{\sqrt{2}} \right)$

22. (a) $\dfrac{r_x}{r_{N_2}} = \sqrt{\dfrac{M_{N_2}}{M_x}} \Rightarrow \sqrt{\dfrac{28}{56}} = \dfrac{56}{r_{N_2}} = \sqrt{\dfrac{1}{2}}$ or $r_{N_2} = 79.19 \text{ mls}^{-1}$

23. (d) NO and C_2H_6 both have same molecular weight. Hence their rate of diffusion will be same.

24. (d) Rate $\propto \sqrt{\dfrac{1}{M}}$. The smaller the value of M the more is the rate of diffusion

25. (a) At the same temperature KE is the same, as KE $\propto$ T.

26. (a) The gas molecules are tiny particles and not rigid in nature rather they are perfect elastic bodies

27. (b) $\overline{KE} = \dfrac{3}{2}kT = \dfrac{3}{2} \times \dfrac{8.313}{6.023 \times 10^{23}} \times 298 = 6.17 \times 10^{-21} J$.

(Average Kinetic energy $\overline{KE} = \dfrac{3}{2}kT = \dfrac{3}{2}\dfrac{R}{N}T$)

28. (d) $PV = \dfrac{1}{3}mnU^2 = \dfrac{1}{3} \times mU^2 = \dfrac{2}{3}\ KE = \dfrac{2}{3}KT$.

The product PV will have constant value at constant temperature. This is Boyle's law

29. (c) $\dfrac{U_1}{U_2} = \sqrt{\dfrac{T_1 M_2}{T_2 M_1}} = \sqrt{\dfrac{50 \times 32}{800 \times 2}} = 1$

30. (c) $\dfrac{U_{H_2}}{U_{N_2}} = \sqrt{\dfrac{T_{H_2} \times 28}{T_{N_2} \times 2}} = \sqrt{7} \Rightarrow \dfrac{T_{H_2}}{T_{N_2}} = \dfrac{1}{2} \Rightarrow T_{N_2} = 2T_{H_2}$

$\therefore T_{N_2} > T_{H_2}$

31. (a) $\dfrac{U_{CO_2}}{U_{N_2O}} = \sqrt{\dfrac{T_{CO_2} \times M_{N_2O}}{M_{CO_2} \times T_{N_2O}}}$

$\Rightarrow \dfrac{x}{4x} = \sqrt{\dfrac{T_{CO_2}}{44} \times \dfrac{44}{T_{N_2O}}} \Rightarrow T_{N_2O} = 16T_{CO_2}$

32. (d) $U \propto \sqrt{\dfrac{1}{M}}$ hence hydrogen (molecular weight being the lowest) has the maximum root mean square velocity.

33. (c) $\dfrac{U_1}{U_2} = \sqrt{\dfrac{d_2}{d_1}} = \sqrt{\dfrac{1}{16}} = 1:4$

34. (b) Apply $\dfrac{U_1}{U_2} = \sqrt{\dfrac{T_1 M_2}{T_2 M_1}}$

35. (b) $U = \sqrt{\dfrac{3RT}{M}} \Rightarrow \dfrac{U_1}{U_2} = \sqrt{\dfrac{T_1}{T_2}} = \sqrt{\dfrac{1200}{300}} = 2; \ \therefore U_2 = \dfrac{1}{2}U_1$

36. (d)

37. (b) Due to intermolecular interactions appreciable at high P and low T, the ideal gas deviates from ideal behaviour.

38. (b) Ideal gas strictly follows PV= nRT, $\quad Z = \dfrac{PV}{nRT} = 1$

39. (c) Ideal behaviour at low P and high temperature. The larger the volume the lesser are the interactions, higher the temperature the more is KE the lesser are interactions between the molecules.

40. (b) $Z = \dfrac{PV}{nRT} < 1 \Rightarrow nRT > PV$

or $\ 1 \times 0.0821 \times 273 > 1 \times V \ $ or $\ V < 22.4$

41. (b) Higher P lower T greater the density. $\left(d = \dfrac{MP}{RT} \right)$

42. (b) $PV = RT, \ PV = \dfrac{w}{M}RT, \ 20P = \dfrac{120}{40} \times .0821 \times 400$

or P = 4.92 atm

43. (d) Volume of 0.0168 moles at STP

$= 0.0168 \times 22400 = 376.3 ml.$

$\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$ or $\dfrac{760 \times 376.3}{273} = \dfrac{P_2 \times 428}{298}$ or $P_2 = 730mm$

Pressure of water = 754 – 730=24 mm

44. (a) Total moles

$$=\frac{4}{32}+\frac{2}{2}=1.125;\ PV=nRT\ \Rightarrow\ P=1.125\ \times .0821\times 273$$

$P=25.215$ atm

45. (a) Let the mass be x, then moles of CH_4 and H_2 are $\frac{x}{16}$ & $\frac{x}{2}$;

Total moles = $\frac{9x}{16}$

$$pH_2=\text{mole}\ \ \text{Fraction}\times P=\frac{x/2}{9x/16}.P=\frac{8}{9}P$$

46. (d) 6.02×10^{23} molecules : $28\ g N_2=32\ g O_2=2\ g H_2$

6.02×10^{22} molecules : $2.8\ g N_2=3.2\ g O_2=0.2\ g H_2$

Total mass = $2.8+3.2+0.2=6.2$

47. (d) VD of air = mass of 11200cc of air = 11200 × density of air = 11200 × .00130 = 14.56

48. (b) An ideal gas obeys the gas laws under all experimental conditions.

49. (b) Boyle's temperature by definition. At this temperature the real gases obey ideal gas laws over wide range of P.

50. (c) He possess van der waals forces of attraction, which are weak in nature.

51. (c) At low pressure and high temperature terms a and b are negligible hence PV= nRT

52. (d) Ideal gas cannot be liquefied at any value of P and T since there are no intermolecular interactions between molecules

53. (b) Boyle's temperature,

$$T_b=\frac{a}{Rb}\ \text{and critical temperature, } T_c=\frac{8a}{27Rb}\ \therefore\ \frac{T_b}{T_c}=\frac{27}{8}$$

54. (c) The higher the value of 'a', more the value of T_c, easy is the liquefaction

55. (a) Ideal gas does not exhibit Joule Thomson effect. Hence

$\left(\frac{\delta T}{\delta P}\right)_H$, the Joule-Thomson coefficient is zero

56. (b) $T_i=\frac{2a}{Rb}$ Where T_i is inversion temperature.

57. (a) At exact inversion temperature there is neither heating nor cooling or no Joule Thomson effect

58. (c) Mean free path $\propto \frac{1}{(\text{Radius})^2}$

59. (b) Formula for mean free path. is $\lambda=\frac{1}{\sqrt{2}.\pi\sigma^2 N}$

60. (a) Avogadro number is 6.023×10^{23}

61. (a) At higher attitudes, boiling point is low because atmospheric pressure is low.

62. (b) The strength of H-bonding is in the order N....H< O....H < F....H

63. (d) All the given phenomenon occurs due to surface tension

64. (b) Liquid drops assume spherical shape because a sphere has minimum surface area.

65. (b) Surface tension decreases with increase in temperature

66. (b) Water sticks to a glass surface due to force of adhesion.

67. (c) The internal resistance of a liquid to flow is called viscosity.

68. (b) Visocity $\propto$ 1/temperature

69. (b) Visocity $\propto$ molecular weight

EXERCISE 3

1. (b) $V_2=\frac{P_1}{P_2}\frac{T_2}{T_1}.V_1=\frac{1}{0.5}\times\frac{250}{300}\times 12000\ lit.=20000$ lit.

2. (c) At any constant temperature the K.E. of gaseous molecules remains same (K.E. $\propto$ T). Thus option (c) is correct answer.

3. (d) $P=\frac{nRT}{V}=\frac{6}{16}\frac{\times 8.314\times 402}{0.03\times 10^3}\simeq 41777$ Pa

4. (d) Average velocity = $\sqrt{\frac{8RT}{\pi M}}$

i.e., $v\propto\sqrt{T}$

$$\therefore\ \frac{v_2}{v_1}=\sqrt{\frac{2T}{T}}=1.41$$

5. (b) $\frac{r_A}{r_B}=\sqrt{\frac{M_B}{M_A}}$

$$\frac{\frac{V}{20}}{\frac{V}{10}}=\sqrt{\frac{M_B}{49}}\ \Rightarrow\ \frac{1}{2}=\sqrt{\frac{M_B}{49}}$$

$$M_B=\frac{1}{4}\times 49=12.25$$

6. (a) Given $n_{CO}=n_{N_2}$

$P_{CO}+P_{N_2}=1$ atm

Partial pressure of a gas

= mole fraction of gas × total pressure

$$\therefore\ P_{N_2}=\frac{n_{N_2}}{n_{CO}+n_{N_2}}\times 1=\frac{n_{N_2}}{2n_{N_2}}\times 1=\frac{1}{2}=0.5\ \text{atm.}$$

7. **(a)** Given

$P_1 = 1.5 \text{ bar } T_1 = 273 + 15 = 288 \text{ K } V_1 = V$

$P_2 = 1.0 \text{ bar } T_1 = 273 + 25 = 298\text{K } V_2 = ?$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{1.5 \times V}{288} = \frac{1 \times V_2}{298}$$

$V_2 = 1.55$ V i.e., volume of bubble will be almost 1.6 time to initial volume of bubble.

8. **(c)** $\dfrac{V_A}{t_A} \Big/ \dfrac{V_B}{t_B} = \sqrt{\dfrac{M_B}{M_A}}$

$$\Rightarrow \frac{200}{150} = \sqrt{\frac{36}{M_A}} \Rightarrow \frac{4}{3} = \sqrt{\frac{36}{M_A}}$$

$$\Rightarrow \frac{16}{9} = \frac{36}{M_A} \Rightarrow M_A = \frac{81}{4} = 20.25$$

9. **(b)** t_1 - Time taken by unknown gas

t_2 - Time taken by helium

M_1 - Molar mass of unknown gas

M_2 - Molar mass of helium

$t_1 = 3t_2$

$$\frac{t_1}{t_2} = \sqrt{\frac{M_1}{M_2}} \Rightarrow \frac{3t_2}{t_2} = \sqrt{\frac{M_1}{4}}$$

$$9 = \frac{M_1}{4}$$

$M_1 = 36$

10. **(c)** Higher the critical temperature more easily will be the gas liquify. Now since most easily liquifiable gas show larger deviation, NH_3 will show maximum deviation from ideal behaviour.

11. **(c)** PV = nRT (number of moles = n/V)

∴ n/V = P/RT

12. **(c)** $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

13. **(d)**

14. **(b)** The heat rquired to raise the temperature of body by 1K is called thermal capacity or heat capacity.

15. **(a)** No. of moles of boron $= \dfrac{21.6}{10.8} = 2$ for BCl_3

∴ 1mole of Boron = 3 mole of Cl

∴ 2 mole of Boron = 6 mole of Cl

$H_2 + Cl_2 \rightarrow 2HCl$

⇒ 3 moles of Hydrogen is required

= 3 × 22.4 = 67.2 Litre

16. **(b)** According to kinetic theory the gas molecules travel in a straight line path but show zig-zag motion due to collisions.

17. **(a)** $\dfrac{\text{K.E of neon at } 40°\text{C}}{\text{K.E of neon at } 20°\text{C}} = \dfrac{\frac{3}{2}\text{K} \times 313}{\frac{3}{2}\text{K} \times 293} = \dfrac{313}{293}$

18. **(a)** In van der waal's equation 'b' is for volume correction

19. **(c)** As temperature rises the most probable speed increases and the fraction of molecules possessing most probable speed decreases.

20. **(a)** Particle size of colloidal particle = 1mμ to 100 mμ (suppose 10 ml)

$$V_c = \frac{4}{3}\pi r^3$$

$$= V_c = \frac{4}{3}\pi(10)^3$$

Particle size of true solution particle = 1mμ

$$V_s = \frac{4}{3}\pi(1)^3$$

hence now $\dfrac{V_c}{V_s} = 10^3$

21. **(d)** Let the mass of methane and oxygen = m gm.

Mole fraction of O_2

$$= \frac{\text{Moles of } O_2}{\text{Moles of } O_2 + \text{Moles of } CH_4}$$

$$= \frac{m/32}{m/32 + m/16} = \frac{m/32}{3m/32} = \frac{1}{3}$$

Partial pressure of O_2 = Total pressure × mole fraction of O_2, $P_{O_2} = P \times \dfrac{1}{3} = \dfrac{1}{3}P$

22. **(d)** From the ideal gas equation :

$PV = nRT$

or $n = \dfrac{PV}{RT} = \dfrac{3170 \times 10^{-3}}{8.314 \times 300} = 1.27 \times 10^{-3}$

23. **(a)** $r \propto \dfrac{P}{\sqrt{m}}$

$$\frac{r_A}{r_B} = \frac{P_A}{P_B}\sqrt{\frac{M_B}{M_A}}$$

24. **(c)** The different type of molecular velocities possessed by gas molecules are

(i) Most probable velocity (α) $=\sqrt{\frac{2RT}{M}}$

(ii) Average velocity $\overline{v}=\sqrt{\frac{8RT}{\pi M}}$

(iii) Root mean square velocity in all three cases

$$v=\sqrt{\frac{3RT}{M}}$$

In all the above cases

Velocity $\propto \sqrt{T}$

25. **(c)** $\left(P+\frac{a}{V^2}\right)(V-b)=RT$ at high pressure $\frac{a}{V^2}$ can be neglected

$PV-Pb=RT$ and $PV=RT+Pb$

$$\frac{PV}{RT}=1+\frac{Pb}{RT}$$

$Z=1+\frac{Pb}{RT}$; $Z>1$ at high pressure

26. **(c)** Most probable speed (C*) $=\sqrt{\frac{2RT}{M}}$

Average Speed $(\overline{C})=\sqrt{\frac{8RT}{\pi M}}$

Root mean square velocity $(C)=\sqrt{\frac{3RT}{M}}$

$$C^*:\overline{C}:C=\sqrt{\frac{2RT}{M}}:\sqrt{\frac{8RT}{\pi M}}:\sqrt{\frac{3RT}{M}}$$

$$=1:\sqrt{\frac{4}{\pi}}:\sqrt{\frac{3}{2}}=1:1.128:1.225$$

27. **(d)** $\frac{D_A}{D_B}=\sqrt{\frac{\rho_B}{\rho_A}}=\left[\frac{\rho_B}{\rho_A}\right]^{1/2}$; $\therefore\ D_A=D_B\left(\frac{\rho_B}{\rho_A}\right)^{1/2}$

28. **(d)** We know that

$$Z=\frac{PV}{nRT}\Rightarrow 0.5=\frac{100\times V}{1\times 0.0821\times 273}\Rightarrow V=0.112\text{ lit.}$$

According to van der Waals equation

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

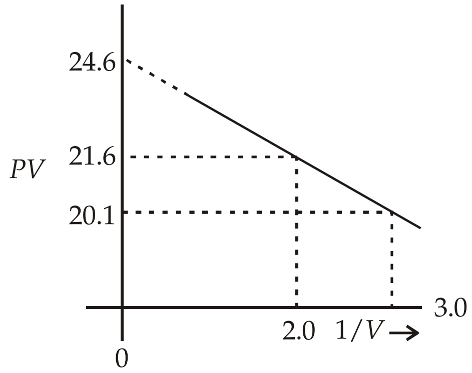
$$\left(100+\frac{a}{(0.112)^2}\right)(0.112-0)=0.0821\times 273$$

$a=1.253\ \text{L}^2\ \text{mol}^{-2}\ \text{atm}$

29. **(b)**

30. **(b)** Correction factor for attractive force for *n* moles of real gas is given by the term mentioned in (b).

31. **(c)**



$$\left(P+\frac{a}{V^2}\right)(V)=RT$$

$PV+a/V=RT$

$PV=RT-\frac{a}{V}$

$y=RT-a(x)$

So, slope $=-a=\frac{21.6-20.1}{2-3}=-a=-1.5$

$a=1.5$

EXERCISE 4

1. **(a)** $N_2O_4 \rightleftharpoons 2NO_2$

1-0.2 0.4

Total moles after dissociation = 1 –0.2+0.4 = 1.2

Molecular weight of mixture, $M=\frac{0.8\times 92}{1.2}+\frac{0.4\times 46}{1.2}=74$

Density $=\frac{PM}{RT}=\frac{75\times 1}{0.0821\times 300}=3.1\ g/\ell$

2. **(b)** $\overline{KE}=\frac{3}{2}\frac{n}{N_o}RT$. Average $\overline{KE}$ is the same for all gaseous molecules

3. **(b)**

4. **(c)** Gas equation is $PV=\frac{m}{M}RT$ (i)

Again $\frac{P}{2}V=\frac{m_1}{M}R.\frac{2}{3}T$ (ii) Divide (i) by (ii)

$2=\frac{m}{m_1}\times\frac{3}{2}\ \therefore m_1=\frac{3}{4}m$. Gas escaped is then $=\frac{1}{4}m$

5. **(c)** Moles of $H_2=\frac{2.06}{2}$; Moles of $O_2=\frac{96.0}{16}=6$ Total moles = 8

$P_{H_2}=\frac{2}{8}P=\frac{1}{4}$ (partial pressure = Mole fraction × Total pressure)

6. **(b)** Let the original volume be V then $\frac{V_1}{T_1}=\frac{V_2}{T_2}$ at constant

$P, \frac{V}{300\times 2}=\frac{V}{T_2}$ $\therefore T_2 = 600K = 327°C$

7. **(c)** When vessels are joined the volume is doubled and pressure is reduced to half \ Pressure of mixture

$=\frac{200}{2}+\frac{400}{2}=300mm$

8. **(b)** P, V and R are constant

$\therefore n_1T_1 = n_2T_2, 100\times 300 = n_2\times 500, : n_2 = 60$

Air escaped is 40%.

9. **(c)** Pressure of gas = (Total pressure of gas - aqueous tension) = 751-21 = 730 mm = 0.96 atm.

10. **(d)** Moles of 0.5 litre of $N_2 = \frac{1}{22.4}\times 0.5 = 0.02,$

moles of atoms = 0.04 (N_2 is diatomic),

Moles or atoms of He $=\frac{1}{22.4}=0.04$

11. **(b)** Apply

$\frac{P_1}{d_1T_1}=\frac{P_2}{d_2T_2}; \frac{1}{2.86\times 273}=\frac{2}{1092\times d}; d = 1.43\ kg\ m^{-3}$

12. **(c)** When a gas is present above the inversion temperature, heating is observed.

13. **(c)** Find the value of volume at STP,

$\frac{260}{290}\times 100.4\times 10^3 = \frac{V\times 101.325\times 10^3}{273}, \therefore = 242.5cm^3$

wt of 11200 cm^3 is equal to vapour density

$\therefore V.D = \frac{0.160}{242.5}\times 11200 = 7.4\ g$

14. **(d)** One mole of a substance contains the number of molecules which is independent of pressure.

15. **(b)** Density of N_2 at 25°C, $d=\frac{28p}{R\times 298}$ and density of

O_2 at, 75°C, $d=\frac{44p}{R\times 348}$

$\frac{r_{N2}}{r_{CO2}}=\sqrt{\frac{44p/R348}{28p/R298}}=1.16$

16. **(a)** 28g of CO $=\frac{28}{28}=1$ mole; 2g $H_2=\frac{2}{2}=1$ mole

Since the temperature and moles are the same, the average kinetic energy will also be the same.

17. **(d)** Critical temperature of water is higher than O_2 because H_2O molecule has dipole moment which is due to its V-shape.

18. **(d)** Let V be the original volume of bubble. The final volume will be 8 V. Let p be the atmospheric pressure and p_1 the pressure at the bottom

$\therefore \quad p\times 8V = p_1\times V;$

$8p = p_1$

p_1 = atmospheric pressure + pressure due to water lake

= p + 7p

The p = 10 m high, the 7p will be = 70 m high

So the depth = 70 m

19. **(a)** $\frac{r_{SO_2}}{r_{He}}=\frac{P_1}{P_2}\sqrt{\frac{M_{He}}{M_{SO_2}}}$

$=\frac{P_1}{P_2}\sqrt{\frac{4}{64}}=\frac{P_1}{4P_2} \quad \therefore \quad \frac{P_1}{P_2}=4$

20. **(a)** Since b = 4 × volume occupied by molecules of 1 mol of a gas

$b = 4\ N_A\left(\frac{4}{3}\pi r^3\right)$

$\therefore\ r=\left(\frac{3b}{16N_A\pi}\right)^{\frac{1}{3}}=\left[\frac{3\times 24cm^3mol^{-1}}{16(6.023\times 10^{23}mol^{-1}\times 3.14)}\right]^{\frac{1}{3}}$

$=1.335\times 10^{-8}$ cm = 133.5 pm

Molecular diameter, d = 2r = 267 pm.

21. **(c)** Mass of 1L water vapour = 0.6g, $V=\frac{m}{d}=0.6cm^3$

22. **(d)** The equation of state is PV = nRT $\therefore n\rightarrow\frac{1}{P}$ will not give straight line.

23 **(a)** If n is the total number of moles of gas and n_1 moles are in the larger shpere and n_2 moles in the smaller shpere. Then $n = n_1 + n_2$ and pV = nRT

$\frac{pV}{RT_1}=\frac{p'V}{RT_1}+\frac{p'V}{2RT_2}$

$p'=\frac{2pT_2}{2T_2+T_1}$

24 (d) $U_1 \propto \sqrt{\frac{1}{m_1}}$ and $U_2 \propto \sqrt{\frac{1}{m_2}}$

$\therefore \frac{U_1^2}{U_2^2} = \frac{m_2}{m_1}$ $\therefore m_1U_1^2 = m_2U_2^2$

25. (a) van der Waals eqation is $\left(p+\frac{a}{V_m^2}\right)(V_m - b) = RT$

Where $V_m = \frac{V}{n}$ = molar volume. At low pressure V_m is high and b can be ignored

$\therefore \left(p+\frac{a}{V_m^2}\right)V_m = RT$ or $pV_m + \frac{a}{V_m} = RT$

$\therefore pV_m = RT - \frac{a}{V_m}$ or $\frac{pV_m}{RT} = 1 - \frac{a}{RTV_m}$

or $Z = 1 - \frac{a}{RTV_m} = 1 - \frac{aP}{RT}$ $\left(\text{since } V \propto \frac{1}{P}\right)$

26. (d) The given equation is cubic equation in the variable V and, therefore, for a single value of P and T, there should be three values of V, all of which may be real or one real and two imaginary.
At T_c there values of V become identical.

27.(d) $PV = \frac{1}{3}NmU_{rms}^2$

$\therefore \quad U_{rms} = \left(\frac{3KT}{m}\right)^{\frac{1}{2}}$

$KE = \frac{1}{2}mv^2 = \frac{3}{2}KT$

28. (c) $PV^{\frac{3}{2}}$ = constant.

Again $P = \frac{nRT}{V}$

$\therefore \quad \frac{nRT}{V} \times V^{\frac{3}{2}}$ = constant (K)

or, $TV^{\frac{1}{2}} = \frac{K}{nR}$ = K' (constant)

For two states, $T_1V_1^{\frac{1}{2}} = T_2V_2^{\frac{1}{2}}$

$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\frac{1}{2}}$

But $V_2 = \frac{V_1}{2}$ (given)

$\therefore \quad T_2 = T_1\left(\frac{V_1}{\frac{V_1}{2}}\right)^{\frac{1}{2}} = T_1\sqrt{2}$

29. (b) Let the difference in two columns be h. Since the atmospheric pressure is more.

$\therefore \quad 60 = 74 - h$

or, $h = 74 - 60 = 14$ cm

Thus Hg will stand in column B = 84.5 – 14 = 70.5 cm

30. (a) The final volume will be $V_1 + V_2 + V_3$ (Amagat's law).

31. (b) The volume of the balloon = $\frac{4}{3}\pi r^3$

$= \frac{4}{3} \times \frac{22}{7} \times \left(\frac{21}{2}\right)^3 = 4851$ ml

Volume of the cylinder = 2820 ml

Volume of H_2 at NTP = $\frac{20 \times 2820 \times 273}{300 \times 1}$ ml

= 51324 ml

After filling the cylinder will have H_2 equal to its volume = 2820 ml

$\therefore$ Volume of H_2 for filling balloons = 51324 – 2820

= 48504 ml

Hence no. of balloon to be filled = $\frac{51324}{2820} = 10$

32. (a) 15 L (20°C, 740 mm) = $\frac{15 \times 273 \times 740}{293 \times 760} = 13.61$ L (NTP)

70% $N_2 = \frac{13.61}{100} \times 70 = 9.527$ L (NTP)

9.527 L (NTP) of $N_2 = \frac{28 \times 9.527}{22.4} = 11.91$ g

33. (b) $p_{N_2} = \rho - \rho_{O_2} = 90 - 63 = 27$ cm

p_{N_2} = mole fraction of $N_2 \times P$

$\therefore \quad 27 = X_{N_2} \times 90$

$\therefore \quad X_{N_2} = 0.3$

34. (a) Let the distance be x metre.

$$\therefore \quad \frac{R_{NH_3}}{R_{HBr}} = \frac{x}{1-x} = \sqrt{\frac{M_{HBr}}{M_{NH_3}}} = \sqrt{\frac{81}{17}}$$

$$\therefore \quad x = 0.6856 = 68.56 \text{ cm}$$

35. (b) $PV = \frac{4TR}{M}$ and $PV = \frac{3.2}{M}(T+50)R$

$$\therefore \quad \frac{4TR}{M} = \frac{3.2}{M}(T+50)$$

$$\therefore \quad T = 200 \text{ K}$$

36. (b) $V_0 = \sqrt{\frac{2RT}{M}} = \sqrt{R(273+t)}$

$$U_{rms} = \sqrt{\frac{3(2t+273+273)R}{1}}$$

$$= \sqrt{6(t+273)R} = \sqrt{6}.V_0$$

37. (c) $\frac{x}{32} + \frac{x}{28} = \frac{60x}{32 \times 28}$,

$PV = nRT$;

$$P_1V = \frac{x}{32}RT \; ; \; P_2V = \frac{x}{28}RT$$

$$\therefore \quad 32P_{O_2} = 28P_{N_2}$$

or, $\quad P_{O_2} = 0.875\, N_2$

38. (c) Wt. of compound is 96 g. The compound exists as 50% monomer and 50% dimer.

$$\text{Moles of monomer} = \frac{48}{48} = 1,$$

$$\text{Moles of dimer} = \frac{48}{96} = 0.5$$

$$\therefore \quad P = \frac{1.5 \times 0.0821 \times (273+273)}{33.6} = 2.00 \text{ atm}$$

39. (b) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

Since the HCl is highly soluble in water and no gas is left, the pressure in flask will be only due to water vapour at 27°C.

40. (a) % Relative humidity

$$= \frac{\text{Partial pressure of water in air} \times 100}{\text{Aqueous tension}}$$

$$\therefore \; p_{H_2O} \text{ in air} = \frac{27 \times 80}{100} = 21.60 \text{ mm Hg}$$

41. (a) Since the ratio of He and O_3 atoms is 1 : 1. The ratio of moles will be $1 : \frac{1}{3}$.

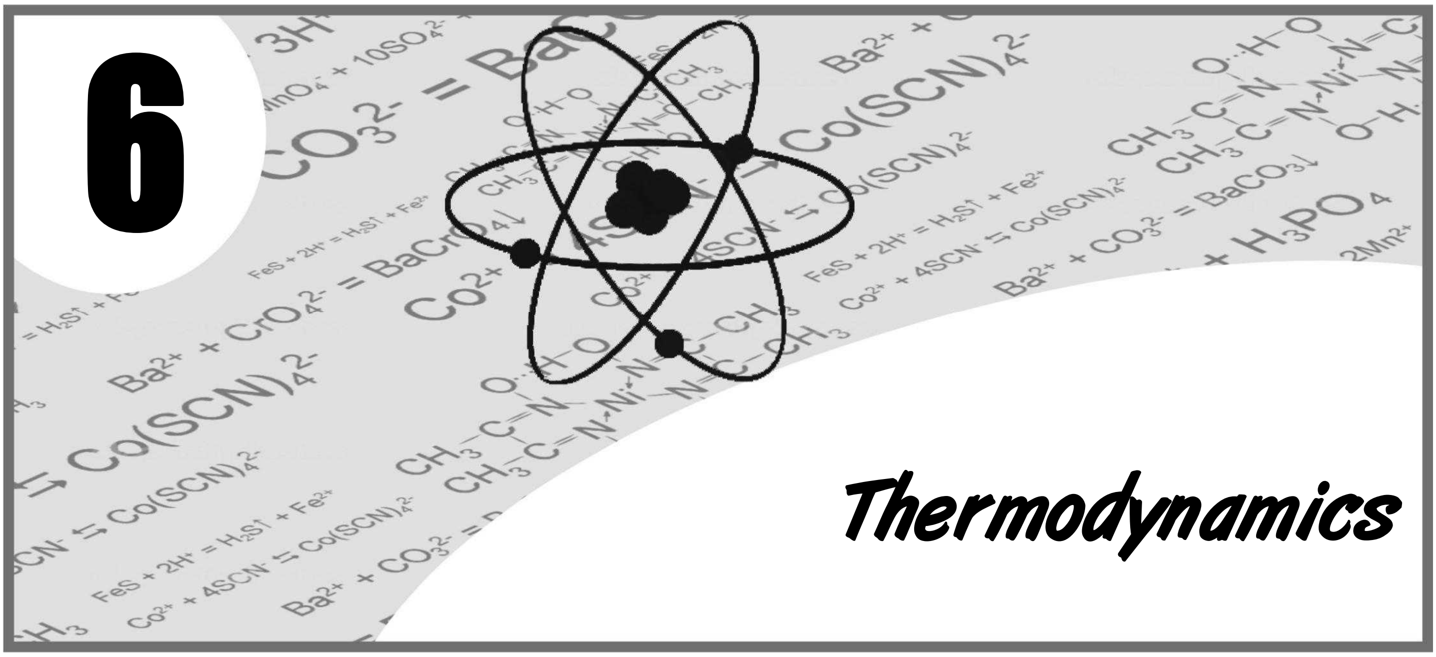
Total moles = $1 + \frac{1}{3} = \frac{4}{3}$. Total pressure P.

$$\text{Hence } p_{O_3} = \frac{\frac{1}{3}}{\frac{4}{3}}.P = 0.25\,P$$

42. (c)

43. (d) Molar volume of a gas or vapour (say at STP) is independent of molecular mass of the gas.

44. (d) Intermolecular H-bonding exists in ethanol unlike other liquids, hence it has strongest intermolecular attractions and highest viscosity.



6

Thermodynamics

It is the branch of chemistry which deals with the energy changes taking place during physical and chemical changes.

Terminology used in thermodynamics :-

SYSTEM :

A system is that part of universe which is under investigation .

SURROUNDINGS :

The part of the universe other than the system is known as surroundings.

Thus universe = system + surroundings

In simple case surroundings implies air or water both.

TYPES OF SYSTEM :

- **(i) Open system -** A system which can exchange matter as well as energy with surroundings.
- **(ii) Closed system –** A system which can exchange energy and not matter with surroundings.
- **(iii) Isolated system -** A system which can exchange neither matter nor energy with surroundings.
- **(iv) Homogeneous system –** A system consisting of one phase only e.g. pure solid, a liquid or a mixture of gases.
- **(v) Heterogeneous system –** It may consists of two or more phases e.g. a solid in contact with liquid etc.

STATE OF SYSTEM :

The condition of existence of a system when its macroscopic properties have definite values is known as state of system e.g. at 1 atm pressure H_2O is (a) Solid below 0°C, (b) liquid between 0°C - 100°C and (c) gas above 100°C.

MACROSCOPIC PROPERTIES :

The properties which arise out of collective behaviour of large number of chemical entities e.g. ***pressure, volume, temperature, composition, colour, refractive index*** etc.

EXTENSIVE PROPERTIES :

The properties which depend upon the quantity of the substance or substances present in the system e.g. ***volume, enthalpy, free energy, entropy, heat capacity***.

INTENSIVE PROPERTIES :

The properties which are independent of the quantity of the substance present in the system e.g. ***density, molar volume, temperature, melting point, boiling point, freezing point*** etc.

Note – Any ***extensive property*** if expressed as per mole or per gm becomes ***intensive property*** e.g. mass and volume are extensive properties but density is an intensive property.

STATE VARIABLES AND STATE FUNCTIONS :

These are the macroscopic properties of the system which change with the change in the state of system. They depend upon the initial and final state of system. They are ***temperature, pressure, volume, chemical composition, energy, entropy, free energy***.

INTERNAL ENERGY, INHERENT ENERGY OR HIDDEN ENERGY (IE) :

It is the sum of all types of energies (as given below) associated with a system or substance.

- (i) Translational energy of the molecules, $\mathbf{E_t}$
- (ii) Rotational energy, $\mathbf{E_r}$
- (iii) Vibrational energy, $\mathbf{E_v}$
- (iv) Electronic energy, $\mathbf{E_e}$
- (v) Nuclear energy, $\mathbf{E_n}$
- (vi) Interaction energy of molecules, $\mathbf{E_i}$

$$E = E_t + E_r + E_v + E_e + E_n + E_i$$

It is a state function, depends upon chemical nature of the substance, amount, temperature, pressure etc. Its absolute value cannot be determined but change during a chemical process can be determined.

$$\Delta E = E_{products} - E_{reactants} = E_P - E_R$$

If $E_P > E_R$ $\Delta E = +ve$ change is endothermic

If $E_P < E_R$ $\Delta E = -ve$ change is exothermic

Internal energy depends on temperature, pressure, volume and quantity of matter. In most stable form the internal energy of an element is zero.

INTERNAL ENERGY CHANGE (ΔE) :

It is the amount of heat evolved or absorbed when a chemical reaction is carried out at constant volume and constant temperature. It is measured in bomb calorimeter.

$$\Delta E = \frac{C \times \Delta T \times M}{W}$$

Where, C= Heat capacity of calorimeter
ΔT = Rise in temperature
M = Molecular mass of the substance
W = Mass of the substance taken

MODES OF THE TRANSFER OF ENERGY :

Exchange of energy between system and surroundings can take place by

(a) Heat (b) Work
(c) Electrical Energy (d) Radiations

EXPRESSION FOR PV WORK:

The mathematical expression for pressure-volume work is $W_{PV} = -P_{ext.}\Delta V$

SIGN CONVENTIONS :

(i)	Heat absorbed by the system is positive	+ve
(ii)	Heat evolved by the system is negative	–ve
(iii)	Work done on the system is positive	+ve
(iv)	Work done by the system is negative	–ve

PROCESSES AND THEIR TYPES:

(i) **Process** – The operation by which a system changes from one state to another state is called process

(ii) **Reversible process** – If the driving force is only infinitesimally greater than the opposing force and process can be reversed at any instant, it is known as reversible process.

(iii) **Irreversible process** - It does not take place infinitesimally slow.

THERMODYNAMIC PROCESSES :

(i) **Isothermal process ($\Delta T = 0$) :** During each stage of process, the temperature remains constant. If the process is exothermic heat is given out to surroundings, If the process is endothermic heat is absorbed from surroundings.

(ii) **Adiabatic process (dq=0) :** No heat leaves or enter the system, temperature of a system rises in exothermic process, temperature falls in endothermic process.

(iii) **Isobaric process ($\Delta P = 0$) :** Pressure remains constant, only volume changes.

e.g. $O_2 + 2H_2 \rightarrow 2H_2O$ volume decreases

$N_2O_4 \rightarrow 2NO_2$ volume increases

(iv) **Isochoric process ($\Delta V = 0$) :** Volume remains constant but pressure changes.

$O_2 + 2H_2 \rightarrow 2H_2O$ pressure decreases

$N_2O_4 \rightarrow 2NO_2$ pressure increases

(v) **Cyclic process ($\Delta E = 0$) :** After undergoing a number of changes, the system returns to its original state. In cyclic process $\Delta E = 0; \Delta H = 0; \Delta S = 0$

THERMODYNAMIC EQUILIBRIUM :

When there is no change in macroscopic properties with time. The types are :

(i) **Thermal equilibrium -** The temperature of the system remains constant throughout and no heat flows from one part to another part of system.

(ii) **Mechanical equilibrium -** The pressure remains constant and no mechanical work is done by one part of system on another part.

(iii) **Chemical equilibrium -** The composition of various phases remains the same.

FIRST LAW OF THERMODYNAMICS :

(i) Law of equivalence of different forms of energies

(ii) Energy can neither be created nor destroyed but can be transformed from one form to another.

(iii) Total energy of universe is conserved (fixed, constant)

MATHEMATICAL EXPRESSION OF FIRST LAW :

If q is the amount of heat absorbed by the system and w is the work done on the system, the change in internal energy,

$\Delta E = q + w$

$\Delta E = q + P\Delta V$ (work is pressure volume work)

If volume remains constant, no work is done then $\Delta E = q_v$

Note :- q and w are not state functions but the sum of the two (q + w) which represents ΔE is a state function

DISCUSSION OF EQUATION :

(i) when $w = 0$, $\Delta E = q_v$

If heat is absorbed by system, internal energy increases.
If heat is lost by system, internal energy decreases.

(ii) when $q = 0$, $\Delta E = W$

If work is done on the system, internal energy increases.
If work is done by the system, internal energy decreases.
In adiabatic process work is done by the system at the expense of internal energy.

(iii) when $\Delta E = 0$ $q = -w$

Heat absorbed by the system is equal to work done by the system
If we write $w = -q$

If work is done on the system (when $\Delta E = 0$) heat flows from system to surroundings.

(iv) Cyclic process, $\Delta E = 0$, $q = -w$
Work done by the system is equal to heat absorbed.

SIGNIFICANCE OF ΔE :

It represents the heat change taking place during the process occuring at constant volume and constant temperature.

$$q_v = \Delta E$$

ENTHALPY (H) AND ENTHALPY CHANGE (ΔH) :

Enthalpy is the heat content of the system and related to internal energy as follows.

$$H = E + PV$$

We can measure change in enthalpy and not absolute value of enthalpy. It is a state function.

$$\Delta H = H_{products} - H_{Reactants} = H_P - H_R$$

If $H_P > H_R$, the change is endothermic. If $H_R > H_P$, the change is exothermic.

SIGNIFICANCE OF ΔH :

The enthalpy H is given by

$H = E + PV$

the change in enthalpy is given by when pressure is kept constant

$$\Delta P = 0,\ \Delta H = \Delta E + \Delta(PV) = \Delta E + P\Delta V + V\Delta P$$

$$\Delta H = \Delta E + P\Delta V\ ;\ \Delta H = q_{(p)}\quad \text{(From first law of thermodynamics)}$$

The enthalpy change represents the heat change taking place during the process occuring at constant pressure and constant temperature.

FACTORS AFFECTING THE ΔH

(i) Physical state of reactants and products

(ii) Quantities of reactants and products

(iii) Allotropic forms

(iv) Temperature

(v) Conditions of constant P and Constant V at a particular temperature.

KIRCHOFF'S EQUATION :

If reaction takes place at constant pressure, the variation of ΔH with temperature is given by this equation

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$$

ΔC_p = Difference in the heat capacities of products and the reactants at constant pressure.

If the reaction takes place at constant volume.

$$\frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_v$$

ΔC_v = Difference in the heat capacities of products and the reactants at constant volume.

STANDARD ENTHALPY :

The enthalpy change at the standard conditions i.e. at 1 atm pressure and 298K temperature is called standard enthalpy of the reaction and is denoted by $\Delta H°$

RELATION BETWEEN ΔH AND ΔE:

It is given by $\mathbf{\Delta H = \Delta E + \Delta nRT}$, where

Δn = (Number of moles of products - number of moles of reactants) gaseous only.

ΔE AND ΔH FOR MONOATOMIC GAS :

For such a gas

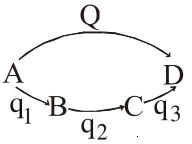
$$\text{Internal Energy} = KE = \frac{3}{2}RT \text{ per mole and}$$

$$\text{Enthalpy} = \frac{3}{2}RT + PV$$

$$= \frac{3}{2}RT + RT = \frac{5}{2}RT \text{ per mole} \quad (\because PV = RT)$$

APPLICATIONS OF FIRST LAW OF THERMODYNAMICS :

***Hess's law of constant heat summation* -** Law is based upon the first law of thermodynamics and states that if a chemical change can be made to take place in two or more ways involving one or more steps, the net amount of heat change in the complete process is the same regardless of the method employed.



$$Q = q_1 + q_2 + q_3$$

Applications of Hess's law

(i) Calculation of heats of reactions

(ii) Determination of heat changes of slow reactions

(iii) Calculation of enthalpies of formation

(iv) Calculation of bond energies

WORK DONE IN ISOTHERMAL REVERSIBLE EXPANSION (MAXIMUM WORK) :

It is given by the expression

$$W_{max} = -\ 2.303nRT\log\frac{V_2}{V_1} = -2.303nRT\log\frac{P_1}{P_2}$$

WORK DONE IN ADIABATIC REVERSIBLE EXPANSION :

It is given by the expression

$$W = \frac{nR(T_2 - T_1)}{\gamma - 1} \text{ where } \gamma \text{ is Poisson's ratio which is}$$

equal to $\frac{C_p}{C_v}$ and $C_p - C_v = R$

If we put the value of γ we get the expression for workdone

$$W = nC_v(T_2 - T_1)$$

Relation between temperature, volume and **pressure** in **reversible adiabatic expansion**

$$\text{(I)}\ TV^{\gamma-1} = \text{Const.}\quad \text{(II)}\ PV^{\gamma} = \text{Const.}\quad \text{(III)}\ TP^{\left(\frac{1-\gamma}{\gamma}\right)} = \text{Const.}$$

or $T^{\gamma} \cdot P^{1-\gamma} = \text{const.}$

Work done in adiabatic irreversible expansion

$$w_{irr} = -P_{ext}\Delta V = -P_{ext}(V_2 - V_1)$$

$$= -P_{ext}\left[\frac{RT_2}{P_2} - \frac{RT_1}{P_1}\right] = -P_{ext}\frac{R[P_1T_2 - P_2T_1]}{P_1P_2}$$

During expansion in vacuum

$P_{ext} = 0$, work done = 0, $\Delta E = w = 0$ also $\Delta T = 0$ and $\Delta H = 0$

If $V_2 > V_1$ then $W_{irr} = -ve$ i.e. expansion work or work done by system.

If $V_2 < V_1$ then W_{irr} is +ve i.e. compression work or work done on the system.

HEAT CAPACITY OF A SYSTEM :

It is the amount of heat required to raise the temperature of the system by 1 degree (K or °C)

$$C = \frac{q}{m(T_2 - T_1)}.$$

In case of single substance, when m=1 g, C is the **specific heat** of system; when m = Mg or 1 mole, it is **molar heat capacity**. Since heat capacity varies with temperature its true value is given by

$$C = \frac{dq}{dt}\text{(differenti al equation)};$$

Heat capacity at constant volume $C_V = \frac{dE}{dt} = \left(\frac{\delta E}{\delta T}\right)_V$

Heat capacity at constant pressure

$$C_p = \frac{dq}{dt} = \frac{dH}{dt} = \left(\frac{\delta H}{\delta T}\right)_p$$

Also $C_p = c_p \times M$ and $C_V = c_V \times M$

where $c_P \,\&\, c_V$ are specific heats at constant pressure and constant volume respectively.

$C_P \,\&\, C_V$ are molar heat capacities at constant pressure and constant volume respectively.

Dulong and Petit's rule : Atomic mass × specific heat = 6.4
The rule is valid for solid elements except Be, B, Si and C.

Units : In SI units the specific heat or molar heat is expressed in terms of Joules (1 Cal = 4.184 J)

MOLAR HEAT CAPACITY OF A MONOATOMIC GAS AT CONSTANT :

$$\text{volume } C_V = \frac{3}{2}R$$

MOLAR HEAT CAPACITY OF A MONOATOMIC GAS AT CONSTANT PRESSURE :

$$C_p = \frac{5}{2}R$$

MOLAR HEAT CAPACITY FOR POLYATOMIC GAS AT CONSTANT VOLUME :

$$C_V = \frac{3}{2}R + X$$

MOLAR HEAT CAPACITY FOR POLYATOMIC GAS AT CONSTANT PRESSURE :

$$C_p = \frac{5}{2}R + X$$

For monoatomic gas X=0, for diatomic gas X=R and for triatomic gas $X = \frac{3}{2}R$

LIMITATION OF FIRST LAW OF THERMODYNAMICS:

It fails to predict the feasibility and the direction of the change

SPONTANEOUS PROCESS :

A process which has an urge or a natural tendency to occur either of its own or after proper initiation under a given set of conditions. It is irreversible process and may only be reversed by some external agents.

(i) Spontaneous processes that need no initiation

(a) Evaporation of water $H_2O\,(l) \rightarrow H_2O\,(g)$

(b) Dissolution of sugar

$C_{12}H_{22}O_{11}(s) \rightarrow C_{12}H_{22}O_{11}$ (aq.)

(c) Intermixing of gases

(ii) Spontaneous processes that need initiation

(a) $2H_{2(g)} + O_{2(g)} \xrightarrow{\text{Electric, discharge}} 2H_2O(l)$

(b) Electrolysis of water $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

It requires continuous supply of energy.

SECOND LAW OF THERMODYNAMICS :

The entropy of the universe increases in every spontaneous (natural) change. The entropy of the universe is continuously increasing.

Other statements of second law of thermodynamics

(i) **Clausius :** Heat cannot itself pass from a colder body to a hotter body.

(ii) **Kelvin :** It is impossible to get a continuous supply of work from a body or engine which can transfer heat from a single heat reservoir.

(iii) **Planck :** It is impossible to construct a device which will work in a single complete cycle and convert heat into work without producing any change in the surroundings.

(iv) All natural and spontaneous processes take place in one direction and thus are irreversible in nature.

(v) In a reversible process the entropy of the universe is constant. In an irreversible process the entropy of the universe increases.

ENTROPY (S) :

It is a measure of degree of disorder or randomness in a system. More the disorder or randomness, the more is entropy. Heat added to a system increases randomness and hence the entropy. Heat added to a system at lower temperature causes greater randomness than the system at higher temperature. At higher temperature the system already has higher randomness. Thus entropy change is inversly proportional to temperature.

$$\Delta S = \frac{q_{rev}}{T}$$

For a spontaneous process

$$\Delta S_{\text{Total}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} > 0$$

or $\Delta S_{\text{universe}} > 0$

UNITS OF ENTROPY :

$\text{Jmol}^{-1}\text{K}^{-1}$; It is a state function. The change in entropy is represented by

$\Delta S = (S_{\text{final}} - S_{\text{initial}}) = q_{rev}/T$

q_{rev} is the heat absorbed by the system in a reversible manner and isothermally.

ENTROPY CHANGE FOR AN IDEAL GAS UNDER DIFFERENT CONDITIONS: WITH CHANGE IN P, V AND T :

$$\Delta S = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1} \quad \text{(when T and V are two variables)}$$

$$\Delta S = C_P \ln\frac{T_2}{T_1} + R\ln\frac{P_1}{P_2} \quad \text{(when T and P are two variables)}$$

For isothermal process $(\Delta T = 0)$, $\Delta S = R\ln\frac{V_2}{V_1} = R\ln\frac{P_1}{P_2}$

For isobaric process $(\Delta P = 0)$, $\Delta S = C_P \ln\frac{T_2}{T_1}$

For isochoric process $(\Delta V = 0)$, $\Delta S = C_V \ln\frac{T_2}{T_1}$

GIBB'S FREE ENERGY :

(G) - It is the maximum amount of energy which can be converted into the useful work (other than PV work). It is related to enthalpy (H) and entropy (S) as follows.

$G = H - TS$ and change is given by

$\Delta G = \Delta H - T\Delta S$

$-\Delta G = W_{max} - P\Delta V =$ Useful work

HELMHOLTZ FREE ENERGY (WORK FUNCTION) (A): The maximum work obtainable from a system is given by this energy.

$A = E - TS$; E= Internal energy, S = Entropy, T= Temperature

CRITERIA FOR FEASIBILITY OR SPONTANEITY OF A PROCESS :

Enthalpy or entropy alone cannot predict the spontaneity of a change. Gibb's free energy is very useful factor for this

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S \text{ (at constant } T)$$

$$\Delta S_{\text{Total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

$$\Delta S_{\text{surr}} = \frac{\Delta H_{\text{surr}}}{T} = -\frac{\Delta H_{\text{sys}}}{T} \quad \text{since}$$

Heat lost by system = Heat gained by surroundings and vice versa.

$$\Delta S_{\text{Total}} = \Delta S_{\text{sys}} + \left(-\frac{\Delta H_{\text{sys}}}{T}\right)$$

$$\begin{aligned} T\Delta S_{\text{Total}} &= T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} \\ &= -(\Delta H_{\text{sys}} - T\Delta S_{\text{sys}}) \\ &= -(\Delta G) \end{aligned}$$

Hence,

(i) If ΔG is negative, the process is spontaneous

(ii) If ΔG is zero, the process is in equilibrium

(iii) If ΔG is Positive the process does not occur

STANDARD FREE ENERGY CHANGE ($\Delta G°$) AND EQUILIBRIUM CONSTANT (K) :

They are related as follows $\Delta G^{o} = -2.303\ RT \log K$

FREE ENERGY CHANGE AND CELL POTENTIAL :

$\Delta G^{o} = -nFE^{o}$

VARIATION OF FREE ENERGY WITH TEMPERATURE AND PRESSURE IN A REVERSIBLE PROCESS :

$$dG = VdP - SdT$$

The equation is called the total differential equation.

(a) If temperature is kept constant dT=0 we have

$$(dG)_T = (VdP)_T \quad \text{or} \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

(b) If pressure is kept constant dP = 0 we have

$$(dG)_P = -(SdT)_P \quad \text{or} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

CHANGE IN FREE ENERGY FOR ISOTHERMAL PROCESS :

$$(\Delta G)_T = nRT\ln\frac{P_2}{P_1} = nRT\ln\frac{V_1}{V_2}$$

CRITERIA OF FEASIBILITY OR SPONTANEITY IN TERMS OF :

(i) **Entropy:** $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$ or $\Delta S_{\text{total}} > 0$

$\Delta S_{\text{total}} = 0$, the process is reversible and system is in equilibrium when internal energy and volume are kept constant

$(\Delta S)_{E,V} > 0$ the process is irreversible and if $(\Delta S)_{E,V} = 0$, the process is reversible.

(ii) Internal energy : When entropy and volume kept constant

If $(\Delta E)_{S,V} < 0$, the process is irreversible and if $(\Delta E)_{S,V} = 0$, the process is reversible.

(iii) Enthalpy (H) : When entropy and pressure are kept constant

$(\Delta H)_{S,P} < 0$, the process is irreversible and if $(\Delta H)_{S,P} = 0$, the process is reversible.

(iv) Work function : (A) when temperature and volume are kept constant

$(\Delta A)_{T,V} < 0$, the process is irreversible and if $(\Delta A)_{T,V} = 0$, the process is reversible.

(v) Free energy (G) : When pressure and temperature are kept constant

$(\Delta G)_{P,T} < 0$, the process is irreversible and if $(\Delta G)_{P,T} = 0$, the process is reversible.

NOTE : Criteria of feasibility or spontaneity in terms of free energy is most important since most of the processes are carried out at constant temperature and pressure.

ZEROTH LAW OF THERMODYNAMICS :

If two bodies have separately equality of temperature with a third body, they also have equality of temperature with each other.

THIRD LAW OF THERMODYNAMICS :

At absolute zero temperature, the entropy of a perfectly crystalline substance is taken as zero. This law was formulated by Nernst in 1906.

Calculation of absolute value of entropy:

Let S_0 be the entropy of substance at 0 K and S be its entropy at T K.

$$\Delta S = S_0 - S = \int_0^T \frac{C_p}{T} dT$$

Where C_p is the heat capacity of the substance at constant pressure. According to the third law

$$S_0 = 0, \text{ thus } S = \int_0^T \frac{C_p}{T} dT.$$

The value of the integral can be obtained from a plot of C_p / T Vs T. The area under the curve between 0 and T K gives the value of the integral and hence of S at temperature T.

CLAPEYRON - CLAUSIUS EQUATION :

It gives the change in pressure dP accompanying change in temperature dT or vice versa for a system containing two phases of a pure substance in equilibrium, q is heat exchanged reversibly per mole of the substance during the phase transformation at temperature T.

$$\frac{dP}{dT} = \frac{q}{T(V_B - V_A)}$$

(i) For water (liquid) = water (vapour) we have

$$\frac{dP}{dT} = \frac{\Delta H_V}{T(V_g - V_l)};$$

ΔH_V = molar heat of vaporisation ,

(ii) For water (Solid, Ice) = water (liquid)

$$\frac{dP}{dT} = \frac{\Delta H_f}{T(V_l - V_s)};$$

ΔH_f = molar heat of fusion of ice

(iii) For solid = vapour equilibrium

$$\frac{dP}{dT} = \frac{\Delta H_s}{T(V_g - V_s)}; \ \Delta H_s = \text{molar heat of sublimation}$$

INTEGRATED FORM OF CLAPEYRON - CLAUSIUS EQUATION :

For Liquid = gas system in Equilibrium

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

APPLICATIONS OF CLAPEYRON CLAUSIUS EQUATION :

(i) Calculation of molar heat of vaporisation
(ii) Effect of temperature on vapour pressure of a liquid
(iii) Effect of pressure on boiling point
(iv) Calculation of molal elevation constant (k_b) and molal depression constant (k_f) of a solvent.

$$k_b = \frac{0.002T^2}{l_v}$$

l_v = latent heat of vaporisation per gram of solvent
T = boiling point of pure solvent

$$k_f = \frac{0.002T^2}{l_f}$$

T = freezing point of solvent
l_f = latent heat of fusion per gram of solvent

HEAT ENGINE :

Machine which converts heat into work is called heat engine.

EFFICIENCY OF HEAT ENGINE :

The fraction of the heat absorbed, converted into work is called the efficiency of machine.

$$\eta = \frac{W}{Q} = \frac{\text{Work done}}{\text{Heat absorbed}}$$

CARNOT CYCLE :

It is a process where a system after undergoing a number of successive changes returns to its original state. It consists of four different operations.

(i) Isothermal expansion
(ii) Adiabatic expansion
(iii) Isothermal compression
(iv) Adiabatic compression

EFFICIENCY OF CARNOT CYCLE OR ENGINE :

$$\eta = \frac{W}{Q} = \frac{T_2 - T_1}{T_2} = \frac{Q_2 - Q_1}{Q_2}$$

Since $\frac{T_2 - T_1}{T_2}$ is always less than unity, hence efficiency is always less than unity

CARNOT THEOREM :

Efficiency of reversible heat engine is independent of the nature of working substance and depends upon the temperature of source and sink.

Or

All machines working reversibly between the same temperature of source and sink have same efficiency.

RESONANCE ENERGY :

(Expected value of ΔH_f°) – (Observed value of ΔH_f°)

Example - Calculate the resonance energy of N_2O from the following data

ΔH_f° of $N_2O = 82$ kJ mol^{-1}, Bond energies of $N \equiv N$, N=N, O=O and N=O bands are 946, 418, 498 and 607 kJ mol^{-1} respectively

Sol. Calculated value of ΔH_f° of N_2O

$$N_2(g) + \frac{1}{2}O_2(g) \rightarrow N_2O(g)$$

$$N \equiv N(g) + \frac{1}{2}(O = O)(g) \rightarrow \overset{-}{\ddot{N}} = \overset{+}{N} = \ddot{O} \quad (g)$$

$$\Delta H_f^0 = [\text{Energy required for breaking of bonds}] - [\text{Energy released for forming of bonds}]$$

$$= (\Delta H_{(N \equiv N)} + \frac{1}{2}\Delta H(_{O=O}) - (\Delta H_{N=N} + \Delta H_{N=O})$$

$$= (946 + \frac{1}{2} \times 498) - (418 + 607) = 170 \text{ kJ mol}^{-1}$$

$$\text{Resonance energy} = 170 - 82 = 88 \text{ kJ mol}^{-1}$$

CALORIFIC VALUE :

The heat liberated on burning unit mass of a fuel is called calorific value.

$$\text{Calorific Value} = \frac{\text{Heat of combustion}}{\text{Molar mass of fuel}}$$

The more the calorific value the more the efficient is the fuel. Oxygen atoms present in a molecule reduce the calorific value. The more the number of hydrogen atoms per carbon atom, the more is the calorific value.

TYPES OF REACTIONS AND CORRESPONDING ENTHALPY CHANGES :

(i) Heat of reaction at constant volume and certain temperature

It is defined as the change in internal energy (ΔE) of the system when requisite number of molecules of reactants react to form the products. (ΔE) = $E_p - E_r = q_v$ = heat of reaction at constant volume

(ii) Heat of reaction at constant pressure and certain temperature

It is defined as the difference in enthalpies (ΔH) of products and reactants $\Delta H = H_p - H_r = q_p =$ heat of reaction at constant pressure

(iii) Relation between heat of reaction at constant volume (q_v) and at constant pressure (q_p)

$$\Delta H = \Delta E + P\Delta V$$

(iv) Sign of ΔH and ΔE : Negative sign of ΔH or ΔE shows that heat is evolved and reaction is exothermic while a positive sign of ΔH and ΔE shows that heat is absorbed and reaction is endothermic.

(v) Factors affecting the heat of reaction

(a) Physical state of the reactants and products
(b) Amount of the reactants
(c) Temperature
(d) Pressure

(vi) Thermochemical equation

Stoichiometrically balanced, mentioning the physical state of the reactants and products and showing the values of ΔE and ΔH equation is called thermochemical equation

(vii) Heat of formation (ΔH_f) : It is defined as the enthalpy change ΔH accompanying the formation of one mole of the compound from its elements.

$$2C + H_2 \rightarrow C_2H_2 \ ; \Delta H = 53.140 \text{ kcal}$$

(viii) Standard heat of formation ΔH_f° : It is the enthalpy change accompanying the formation of one mole of a compound from its elements. All substances being in their standard states. The condition of standard state is 25ºC and 1 atm pressure.

(ix) Heat of combustion : It is the change in enthalpy of the system, when 1 gram mole of the substance is completely oxidized

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O \ ; \Delta H = -890.3 \text{kJ}$$

The combustion is always exothermic process.

(x) Application of heat of combustion

(a) Calorific value of fuel
(b) Calculation of heat of formation
(c) Constitution of organic compounds

(xi) Heat of neutralization : It is defined as the enthalpy change (ΔH) accompanying the neutralization of one gram equivalent of the acid by a base in dilute solution at that temperature.

$$HCl\,(aq) + NaOH(aq) \rightarrow NaCl(s) + H_2O(aq); \quad \Delta H = -57.32 kJ$$

Heat of neutralization of every strong acid by a strong base is identical. When acid or alkali is weak the heat of neutralization is different because the reaction involves the dissociation of the weak acid or the weak alkali.

Heat of neutralization of weak acids with NaOH at 25°C

Acid	*Heat of neutralisation (kJ per g eq.)*	*Heat of dissociation (kJ per g eq.)*
Acetic acid	–55.23	+2.09
Formic acid	–56.06	+1.26
Hydrocyanic acid	–12.13	+45.19
Hydrogen sulphide	–15.90	+41.42

(xii) Heat of solution : The enthalpy change per mole of solute when it is dissolved in large excess of solvent (generally H_2O) so that further dilution of the solution produces no heat exchange.

$$KCl + aq \rightarrow KCl(aq)\ ;\ \Delta H = 4400\ cal\,(18.58 kJ)$$

$$MgSO_4 + aq \rightarrow MgSO_4(aq)\ ;\ \Delta H = -20280\,cal$$

(xiii) Heat of dilution : The enthalpy change when a solution containing one mole of a solute is diluted from one concentration to another.

(xiv) Heat of hydration : The enthalpy change when one mole of a substance combines with the required number of moles of water to form a specified hydrate.

Heat of hydration = Heat of solution of the hydrated compound – Heat of solution of the unhydrated compound

(xv) Heat of precipitation : The enthalpy change when one mole of a sparingly soluble substance precipitates on mixing dilute solutions of stable electrolytes is called heat of precipitation.

$$BaCl_2(aq.) + Na_2SO_4(aq.) \longrightarrow BaSO_4(s) + 2NaCl(aq.)\ ; \quad \Delta H = -19.50\ kJ$$

(xvi) Bond enthalpy : It is defined as the average amount of energy required to break all the bonds of a particular type in one mole of the substance. It is also known as bond energy and expressed in kJ mol^{-1}.

In a diatomic molecule the bond energy and bond dissociation energy are the same.

In polyatomic molecules the bond dissociation energy is not the same for successive bonds though the bonds are of the same type.

$$H_3C-H = +425\ kJ\ mol^{-1}\ ;$$

$$H_2C-H = +470\ kJ\ mol^{-1}$$

$$HC-H = +416\ kJ\ mol^{-1}\ ;$$

$$C-H = +335\ kJ\ mol^{-1}$$

$$\text{Hence } C-H \text{ Bond energy } = \frac{425+470+416+335}{4} = 411.5 kJ\ mol^{-1}$$

(xvii) Use of bond enthalpy :

(1) Calculating standard enthalpy of reactions

ΔH =[sum of bond energies of reactants] – [sum of bond energies of products]

= [Total energy required for breaking the bonds] – [Energy given out in forming the bonds]

(2) Calculation of bond energy of some specific bond in the molecule

THE LAWS OF THERMOCHEMISTRY :

(1) ***Lavosier and Laplace law :*** The heat evolved or absorbed in the course of a chemical reaction is equal to the heat absorbed or evolved when the reaction is reversed.

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g)\ ;\ \Delta H = -92.0 kJ$$

$$HCl(g) \rightarrow \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)\ ;\ \Delta H = +92.0 kJ$$

(2) ***Hess's law of constant heat summation***

TROUTON'S RULE :

Fredrick Trouton (1884) found that for many liquids molar heat of vaporization in calories per mole divided by the normal boiling point in degree kelvin is a constant.

$$\frac{\Delta H_v}{T_b} = 21\ cal/kmol\ = 88\ J/K\ mol$$

The quantity $\frac{\Delta H_v}{T_b}$ is also called entropy of vaporization ΔS_v.

ENDOTHERMIC COMPOUNDS :

The compounds having positive values of formation are called endothermic compounds. Ozone is an example.

Miscellaneous Solved Examples

1. Six moles of an ideal gas expand isothermally and reversibly from a volume of 1 litre to a volume of 10 litres at 27° C. What is the maximum work done? Express the results in various units.

Sol. Work done

$$W = nRT\ \ln\frac{V_2}{V_1} = 2.303nRT\log\frac{V_2}{V_1}$$

$$= 2.303\times6\times0.0821\times300\log\frac{10}{1} = 340.3 \text{ lit. atm.}$$

If we put the value of

$R = 8.314\ J\ K^{-1}\ mol^{-1}$ $\quad W = 34464.8J$

$R = 8.314\times10^{7}\ ergs\ K^{-1}mol^{-1}$ $\quad W = 3.44\times10^{11}$ ergs

$R = 1.987\ cal\ K^{-1}\ mol^{-1}$ $\quad W = 8236.91$ cal

2. A system performs 101.3J of work on its surroundings and absorbs 15 kJ of heat from surroundings. What is the change in internal energy of the system.

Sol. Work done by the system is taken as negative

$W = -101.3J$

Heat absorbed by the system is taken as positive $q = 15kJ = 15000\ J$

$\Delta E = q + w$ (First law of thermodynamics) $= 15000J - 101.3J = 14898.7J$

3. One mole of liquid water at its boiling point vapourises against a constant external pressure of 1 atm. at the same temperature. Assuming ideal behaviour and initial volume of water vapours as zero, calculate the work done by the system.

Sol. For ideal behaviour of water vapour PV = nRT can be applied to find the volume.

$1 \times V = 1 \times 0.0821 \times 373$

$V = 30.62$ lit.

$\Delta V = V_2 - V_1 = 30.62 \text{ lit.} - 0 \text{ lit.} = 30.62 \text{ lit.}$

work done $= -P\Delta V = -1 \times 30.62 = -30.62$ lit atm.

$= -30.62 \times 101.3J = -3101.8\ J$

4. A gas expands from 3 dm^3 to 5 dm^3 against a constant pressure of 3 atm. The work done during expansion is used to heat 10 mole of water of temperature 290 K. Calculate the final temperature of water. Specific heat of water is $4.184\ Jg^{-1}K^{-1}$

Sol. Work done is irreversible as at constant pressure,

$\Delta V = 5 - 3 = 2\ dm^3 = 2$ lit.

$W = -P\Delta V = -3 \times 2 = -6$ atm. lit. $= -6 \times 101.3J = 607.8J$

This work is used for heating water $W = m \times s \times \Delta T$

$607.8 = 10 \times 18 \times 4.184 \times \Delta T$

Therefore $\Delta T = 0.807$

Hence final temperature $= 290 + 0.807 = 290.807$ K

5. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27° C from 10 litres to 5 litres. Calculate q, w, ΔE and ΔH for this process. R=2.0 cal K^{-1} mol^{-1} log 2 = 0.3010

Atomic weight of Argon = 40

Sol. $W = -2.303\,nRT\log\frac{V_2}{V_1} = -2.303\times\frac{10}{40}\times2\times300\ \log\frac{5}{10}$

$W = 103.635$ cal

For isothermal proccess $\Delta E = 0$, $q = -W = -103.635$ cal

$\Delta H = 0$

6. Show that in an isothermal expansion of an ideal gas

(a) $\Delta E = 0$ and (b) $\Delta H = 0$

Sol. (a) For one mole of a gas $C_v = [\delta E / \delta T]_v$

For finite change $\Delta E = C_v\ \Delta T$

For isothermal process $\Delta T = 0$ therefore $\Delta E = 0$

(b) We know that $\Delta H = \Delta E + \Delta(PV) = \Delta E + \Delta(RT)$

(PV = RT)

Therefore $\Delta H = \Delta E + R\Delta T$. Since $\Delta T = 0, \Delta E = 0$, therefore $\Delta H = 0$.

7. Calculate the change in free energy at 25° C for the reaction

$$CO(g) + \frac{1}{2}O_2\ (g) \rightarrow CO_2(g) \qquad \Delta H = -67.37 \text{ kcal}$$

and the change in entropy accompanying the process is – 20.7 cal deg^{-1} mol^{-1}

Sol. $\Delta G = \Delta H - T\Delta S$

$= -67.37 - 298\ (-20.7 \times 10^{-3})$

$= -61.2014 \text{ kcal mol}^{-1}$

8. Calculate ΔH, ΔS, ΔG and ΔE when 1 mole of water is vapourised at 100° C and 1 atm pressure. The latent heat of vapourisation of water is 540 cal g^{-1}

Sol. (i) 1 mole of water is 18 g therefore enthalpy change

$\Delta H = 18 \times 540$ cal $= 9720$ cal

(ii) Entropy change $\Delta S = \Delta H/T = 9720/373$

$= 26.06$ cal K^{-1}

(iii) Free energy change $\Delta G = \Delta H - T\Delta S$

$\Delta G = 9720 - 373 \times 26.06 = 0$

(iv) $\Delta H = \Delta E + P\Delta V$

therefore $\Delta E = \Delta H - P\Delta V = \Delta H - P(V_2 - V_1)$

V_1 = Volume of 1 mole of liquid water = 18 cm^3

V_2 = Volume of 1 mole of steam at 373 K

Applying ideal gas equation,

$$V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{1 \times 22400 \times 373}{1 \times 273}$$

$$V_2 = 30600 \text{ cm}^3$$

$\Delta V = V_2 - V_1 = (30600 - 18)\text{ cm}^3 = 30600 \text{ cm}^3$

(18 negligible)

$$P\Delta V = 1\,\text{atm} \times 30600\,\text{cm}^3 = 1 \times 30.6\,\text{lit.} = 30.6\,\text{lit atm.}$$

30.6×24.2 cal $= 740.5$ cal (1atm lit = 24.2 cal)

Hence $\Delta E = \Delta H - P\Delta V = 9720 - 740.5 = 8979.5$ cal

9. A certain volume of dry air at NTP is expanded reversibly to three times its volume (a) isothermally (b) adiabatically. Calculate the final pressure and temperature in each case, assuming ideal behaviour. (C_p/C_v for air is 1.4)

Sol. Let V_1 be the initial volume of dry air at NTP

(a) Isothermal expansion. Since

$\Delta T = 0$ hence $P_1V_1 = P_2V_2$

$$\therefore P_2 = \frac{P_1V_1}{V_2} = \frac{1 \times V_1}{3V_1} = 0.333 \text{ atm}$$

(b) Adiabatic expansion we have

$$\frac{T_1}{T_2} = \left[\frac{V_2}{V_1}\right]^{\gamma-1} \quad \text{or} \quad \frac{273}{T_2} = \left[\frac{3V_1}{V_1}\right]^{1.4-1}$$

$$T_2 = 176\text{K} = -97^\circ\text{C}$$

Final pressure under adiabatic conditions

$$\frac{P_1}{P_2} = \left[\frac{V_2}{V_1}\right]^{\gamma} \qquad \frac{1}{P_2} = \left[\frac{3V_1}{V_1}\right]^{1.4} \qquad P = 0.217 \text{ atm}$$

10. The latent heat of fusion of ice is 5.99kJ/mol at its melting point. Calculate.

(i) ΔS for fusion of 900g ice

(ii) ΔS for freezing of liquid water

Sol. $H_2O(s) \xrightleftharpoons{273K} H_2O(l)$

(i) Latent heat of fusion for 900 g ice

$$\Delta H_{\text{fus}} = \frac{900 \times 5.99}{18} \text{ kJ} = 299.5\text{kJ}$$

$$\Delta S = \frac{\Delta H_{\text{fus}}}{T} = \frac{299.5 \times 1000}{273} = 1097\text{JK}^{-1}$$

(ii) ΔS for freezing of liquid water $= -\dfrac{\Delta H_{\text{fus}}}{T}$

when liquid water freezes heat is evolved

$$\Delta S = -\frac{5.99 \times 1000}{273} = -21.94\,\text{Jmol}^{-1}\text{K}^{-1}$$

11. Calculate the entropy change in isothermal reversible expansion of 5 moles of an ideal gas from a volume of 10 litres to a volume of 100 litres at 300 K.

Sol. For isothermal process $T_1 = T_2$ hence the equation

$\Delta S = C_v \ln\dfrac{T_2}{T_1} + nR\ln\dfrac{V_2}{V_1}$ is reduced to

$$\Delta S = nR\ln\frac{V_2}{V_1} = 2.303nR\log\frac{V_2}{V_1}$$

Given n = 5,

$V_1 = 10$ litres, $V_2 = 100$ litres, $R = 8.314\text{JK}^{-1}\text{mol}^{-1}$

$$\Delta S = 2.303 \times 5 \times 8.314 \log\frac{100}{10} = 95.75\text{JK}^{-1}$$

12. Calculate the temperature at which the reaction

$Ag_2O(s) \rightarrow 2Ag(s) + \frac{1}{2}O_2(g)$ at 1 atmospheric pressure will be in equilibrium. The value of ΔH and ΔS for the reaction are 30.58 kJ and 66.11JK^{-1} respectively and these value do not change much with temperature.

Sol. $\Delta G = \Delta H - T\Delta S$ for equilibrium $\Delta G = 0$

$$\therefore \Delta S = \frac{\Delta H}{T} \quad \therefore T = \frac{\Delta H}{\Delta S} = \frac{30580}{66.1} = 462.6\text{ K}$$

13. Calculate the standard entropy change for the reaction $A \rightleftharpoons B$ if the value of $\Delta H^\circ = 28.40\text{kJ mol}^{-1}$ and equilibrium constant is 1.8×10^{-7} at 298K

Sol. $\Delta G^\circ = -2.303RT\log K_c$

$= -2.303 \times 8.31\text{JK}^{-1}\text{mol}^{-1} \times 298 \log 1.8 \times 10^{-7}$

$= 38466\,\text{J mol}^{-1}$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{28400 - 38466}{298} = -33.78\,\text{JK}^{-1}\text{mol}^{-1}$$

14. Calculate the equilibrium constant for the following reaction at 400 K

$2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$

$\Delta H^\circ = 77.2\,\text{kJmol}^{-1}$; $\Delta S^\circ = 122\,\text{JK}^{-1}\text{mol}^{-1}$ at 400K

Sol. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$= 77.2 \times 10^3 - 400 \times 122$

$= 28.4 \times 10^3\ \text{J mol}^{-1}$

$$\Delta G^o = -2.303\,RT\ \log K_c$$

$$\log k_c = -\frac{\Delta G^o}{2.303 \times RT} = \frac{-28.4\times 10^3}{2.303\times 8.314\times 400} = -3.708$$

taking antilog, we get

$$K_c = 1.995\times 10^{-4}$$

15. Show that the reaction $CO(g)+\frac{1}{2}O_2(g) \rightarrow CO_2(g)$ at 300 K is spontaneous and exothermic, when the standard entropy change is – 0.094 kJ mol^{-1} K^{-1}. The standard Gibb's free energies of formation of CO_2 and CO are – 394.4 and –137.2 KJ mol^{-1} respectively.

Sol. The given reaction is

$$CO(g)+\frac{1}{2}O_2(g) \rightarrow CO_2(g)$$

$$\Delta G^\circ \text{ (for reaction)} = G^\circ \text{ products} - \Delta G^\circ \text{ reactants}$$

$$= G^\circ_{CO_2} - (G^\circ_{CO} + G^\circ_{O_2})$$

$$= -394.4 - (-137.2 + 0) = -257.2$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$-257.2 = \Delta H^o + 298\ (0.094) \text{ or } \Delta H^o = -285.2\,KJ$$

Since ΔG^o is negative the process is spontaneous and ΔH^o is also negative the process is exothermic.

16. The heat of combustion of gaseous methane CH_4 at constant volume measured in bomb calorimeter at 298.2 K is found to be – 885389 J/mol. Find the value of enthalpy change.

Sol. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Given $\Delta E = -885389\ J\ mol^{-1}$

$\Delta n = 1-(1+2) = -2 \quad T = 298.2\,K;\ R = 8.314\ JK^{-1}mol^{-1}$

$\therefore \Delta H = \Delta E + \Delta nRT$

$= -885389 + (-2)\ 8.314 \times 298.2$

$= -890.34\,kJ$

For solving the heat of reaction follow the following rules

(i) When standard enthalpy of formation of compounds are given, apply the equation

$$\Delta H = \Sigma\Delta H^o{}_f\text{ (products)} - \Sigma\Delta H^o{}_f\text{ (reaction).}$$

(ii) When heat of combustion of compounds are given apply the equation

$$\Delta H = \Sigma\,\Delta H_{comb}\text{ of reactants} - \Sigma\,\Delta H_{comb}\text{ of products.}$$

17. The molar heats of combustion of C_2H_2 (g) , C(graphite) and H_2 (g) are – 310.62, – 94.05 and – 68.32 kcal respectively. Calculate the heat of formation of C_2H_2.

Sol. The desired equation is

$$2C\text{(graphite)} + H_2(g) \rightarrow C_2H_2(g)$$

$\Delta H = \Sigma$ Heats of combustion of reactants

$- \Sigma$ Heats of combustion of products

$= 2(-94.05) + (-68.32) - (-310.62) = 54.2\,kcal$

18. The heats of combustion of $C_2H_4(g), C_2H_6(g)$ and $H_2(g)$ are –1409.5, –1558.3 and –285.6 kJ respectively. Calculate the heat of hydrogenation of ethylene.

Sol. The desired equation is

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

$\Delta H = \Sigma$ Heat of combustion of reactants

– Σ Heat of combustion of products

$= -1409.5 + (-285.6) - (-1558.3) = -136.8\,KJ$

19. At 300 K the standard enthalpies of formation of $C_6H_5COOH(s), CO_2(g)$, and $H_2O(l)$ are respectively $-408, -393$ and $-286\,kJ\,mol^{-1}$. Calculate the heat of combustion of benzoic acid at (i) Constant pressure (ii) Constant volume

$(R = 8.314\,J\ mol^{-1}K^{-1})$

Sol. $\Delta H = \Sigma$ Enthalpies of formation of products

$-\Sigma$ Enthalpies of formation of reactants.

Desired equation is

$$C_6H_5COOH(s) + \frac{15}{2}O_2(g) \rightarrow 7CO_2(g) + 3H_2O(l)$$

$$\Delta H = 7(-393) + 3(-286) - (-408 - 0) = -\ 3201\,kJ$$

Also $\quad \Delta H = \Delta E + \Delta nRT$

or $-3201\ kJ = \Delta E + (-0.5)\times 8.314\times 10^{-3}\times 300$

$\Rightarrow \quad \Delta E = -3199.75\,kJ$

20. Given that the bond enthalpies for C– H, Cl –Cl, C – Cl and H– Cl are respectively 99, 58, 78 and 103 k cal / mol, determine ΔH for the reaction

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

Sol. ΔH (reaction) = Bond energy of (bond broken in reactants – bond formed in products).

$= \text{Bond energy of}\left[(C-H+Cl-Cl)-(C-Cl+H-Cl)\right]$

$= \left[(99+58)-(78+103)\right] = -\,24\,kcal$

21. Estimate the S – F bond energy in SF_6. The standard heat of formaton values of SF_6(g), S(g) and F(g) are –1100, 275 and 80 kJ mol^{-1} respectively.

Sol. $SF_6(g) \rightarrow S(g) + 6F(g)$

$\Delta H = (\Delta H_S + 6\Delta H_F) - \Delta H_{SF_6}$

$= 275 + 6\times 80 - (-1100) = 1855$

$$\therefore \text{ Average bond energy} = \frac{1855}{6} = 309.17\,kJ$$

22. The heat of reaction (ΔH) for the formation of water at 25°C is -68.4 kcal. Find the value at 90°C. The moler heat capacities of $H_2(g)$, $H_2O\,(l)$ are 6.62, 6.76 and 18 cal respectively.

Sol. $\Delta H_2 - \Delta H_1 = \Delta C_p\,(T_2 - T_1)$

ΔC_p = molar heat capacities of products

$-$molar heat capacities of reactants

The formation of water is $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

$$\Delta C_p = 18 - (6.62 + \frac{1}{2}(6.67) = 8\ \text{cal} = 8 \times 10^{-3}\ \text{k cal}$$

$$\Delta H_2 = -68.4 + 8 \times 10^{-3}(363 - 298) = -67.88\ \text{k cal}$$

23. The heat of solution of $MgSO_4$ and $MgSO_4.7H_2O$ are -20.3 and 3.8 kcal respectively. Find heat of hydration of $MgSO_4$.

Sol. Heat of hydration = Heat of solution of anhydrous salt

$-$Heat of solution of hydrated salt.

$= -20.3 - (3.8) = -24.1$ k cal.

24. Integral heat of solution (ΔH) for 1 mole of KCl dissolved in 20 moles of water is + 15.90 kJ. When 1 mole is dissolved in 200 moles of water, ΔH is 18.58 kJ. Calculate heat of dilution.

Sol. $KCl(s) + 20H_2O \rightarrow KCl(20\,H_2O)\ \Delta H_1 = 15.90\ \text{kJ}$

$KCl(s) + 200H_2O \rightarrow KCl(200H_2O)\ \Delta H_2 = 18.58\ \text{kJ}$

Heat of dilution $= \Delta H_2 - \Delta H_1 = 18.58 - 15.90 = 2.68\ \text{kJ}$

25. At what temperature will water boil when the atmospheric pressure is 528 mm Hg. Latent heat of vaporisation of water is 545.5 cal g^{-1}

Sol. The integrated form of Clapeyron equation is

$$\log\frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Here $P_1 = 528$ mm Hg; $P_2 = 1\,\text{atm} = 760\,\text{mm Hg}$; $T_1 = ?$;

$T_2 = 100°C = 373K$

$\Delta H_v = 545.5\ \text{cal g}^{-1} = 545.5 \times 18 = 9819\ \text{cal mol}^{-1}$

$$\log\frac{760}{528} = \frac{9819}{2.303 \times 1.987}\left[\frac{1}{T_1} - \frac{1}{373}\right] \quad \text{or } T_1 = 363\ \text{K}$$

26. Calculate the maximum efficiency of a steam engine working between 110°C and 25°C.

Sol. Efficiency of a heat engine is given by

$$\eta = \frac{T_2 - T_1}{T_2} \quad \text{or} \quad \eta = \frac{383 - 298}{383} = 0.222 \text{ or } 22.2\%$$

27. Calculate the useful work done by the heat engine which works between 10°C and 100°C. Heat supplied to engine is 1897.86 kJ

Sol. $W = \dfrac{q(T_2 - T_1)}{T_2} = 1897.86 \times \dfrac{373 - 283}{373} = 457.92\ \text{kJ}$

28. Calculate ΔH at 358 K for the reaction

$$Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(l)$$

Given that $\Delta H_{298} = -33.29\ \text{kJ mol}^{-1}$ and C_p for $Fe_2O_3(s)$, Fe(s), $H_2O\,(l)$ and $H_2(g)$ are 103.8, 25.1, 75.3 and 28.85 J/K mol.

Sol. $\Delta C_p = (2 \times 25.1 + 3 \times 75.3) - (103.8 + 3 \times 28.8)$

$= 85.9$ J/Kmol

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p \quad \text{(Kirchoff's equation)}$$

$$\frac{\Delta H_{358} - (-33290)}{358 - 298} = 85.9$$

$\Delta H_{358} = -28136$ J/mol

$= -28.136$ kJ/mol

29. K_a for CH_3COOH at 25°C is 1.754×10^{-5} at 50°C. K_a is 1.633×10^{-5}. What are $\Delta H°$ and $\Delta S°$ for the ionisation of CH_3COOH ?

Sol. $(\Delta G°)_{298} = -2.303\ RT\log K_a$

$= -2.303 \times 8.314 \times 298 \times \log 1.754 \times 10^{-5}$

$= -27194$ J

$(\Delta G°)_{323} = -2.303 \times 8.314 \times 323 \times \log 1.623 \times 10^{-5}$

$= -29605$ J

$\Delta G° = \Delta H° - T\,\Delta S°$

$27194 = \Delta H° - 298\,\Delta S°$

$29605 = \Delta H° - 323\,\Delta S°$

$\Delta H° = -1.55$ KJ/mol

$\Delta S° = -96.44$ J/mol

30. Calculate the heat of neutralisation from the following data 200 ml of 1 M HCl is mixed with 400 ml of 0.5 M NaOH. The temperature rise in the calorimeter was found to be 4.4°C. Water equivalent of calorimeter is 12 g and specific heat is 1 cal/ml/degree for solution

Sol. When HCl and NaOH are mixed (neutralised) the heat produced is taken up by calorimeter and solution in it

$\therefore\ \Delta H_1 = m_1s_1\Delta T + m_2s_2\Delta T$

$= 12 \times 1 \times 4.4 + 600 \times 1 \times 4.4$

(Total sol. = (200 + 400) ml

$= 2692.8$ cal

$= -2692.8$ cal

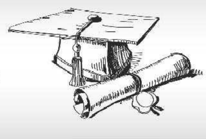
This is neutralisation of 200 Meq

Neutralisation of 1000 Meq. or one equivalent

$= -2692.8 \times 5 = -13464$ cal

$= -13.464$ kcal

Exercise-1 | NCERT Based Questions



Very Short/ Short Answer Questions

1. Predict $\Delta H > \Delta U$ or $\Delta H < \Delta U$ or $\Delta H = \Delta U$.

(a) $C\ (\textit{graphite}) + O_2\ (g) \rightarrow CO_2(g)$

(b) $PCl_5\ (g) \rightarrow PCl_3(g) + Cl_2\ (g)$.

2. In the equation $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, what whould be the sign of work done?

3. Give an example of following energy conversions:

(i) Radiation energy into chemical energy.

(ii) Radiation energy into electrical energy.

4. A system is changed from an initial state to a final state by a manner such that $\Delta H = q$. If the change from the initial state to a final state were made by a different path, would ΔH be the same as that for the first path? would q too be the same?

5. What property of enthalpy provides the basis of Hess's law?

6. A chemist while studying the properties of gaseous $C_2Cl_2F_2$, a chlorofluorocarbon refrigerant, cooled 1.25 g sample at constant atmospheric pressure of 1.0 atm from 320 K to 293 K. During cooling, the sample volume decreased from 274 to 248 ml. Calculate ΔH and ΔU for the chlorofluorocarbon for this process.

The value of molar heat capacity is 80.7 J mol^{-1} K^{-1}.

7. Gobar gas obtained by bacterial fermentation of animal refuse contains mainly methane. The heat of combustion of methane to CO_2 and water as gas is given by

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) + 809\ kJ$

How much gobar gas would have to be produced per day for a small village community of 100 families, if we assume that each family has to be supplied 20000 kJ of energy per day to meet all its needs and that the methane content in the gobar gas is 80 percent by weight.

8. Why is it more convenient to predict the direction of reaction in terms of ΔG_{sys} instead of ΔS_{total}? Under what conditions can ΔG_{sys} be used to predict the spontaneity of a reaction?

9. Which of the following processes are accompanied by increase of entropy ?

(a) Stretching of rubber band,

(b) Boiling of an egg

(c) A deodrant is sprayed.

10. Comment on the following statements :

(a) An exothermic reaction is always thermodynamically spontaneous.

(b) The entropy of a substance increases in going from the liquid to the vapour state at any temperature.

(c) Reaction with $\Delta G° < 0$ always have an equilibrium constant greater than 1.

11. Give reasons for the following :

(a) Why the heat produced be different if same mass of diamond and graphite are burnt in oxygen?

(b) The dissolution of ammonium chloride in water is endothermic still it dissolves in water

(c) A real crystal has more entropy than an ideal crystal.

12. Calculate the value of log K_p for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 25°C. The standard enthalpy of formation of $NH_3(g)$ is – 46 kJ mol^{-1} and standard entropies of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are 191, 130, 192 JK^{-1} mol^{-1} respectively.

Long Answer Questions

13. Define the following terms :

(a) System

(b) Isothermal processes

(c) Adiabatic processes

(d) State variables/state functions

(e) Work

14. **(i)** Calculate the standard molar entropy change for the following reactions at 298 K.

(a) $4\,Fe\,(s) + 3\,O_2\,(g) \longrightarrow 2\,Fe_2O_3(s)$.

(b) $Ca\,(s) + 2\,H_2O\,(l) \longrightarrow Ca(OH)_2\,(aq) + H_2\,(g)$

Given:

$S°\ Fe(s) = 27.28$, $S°O_2(g) = 205.14$, $S°\ Fe_2O_3\ (s) = 87.4$

$S°Ca(s) = 41.42$, $S°H_2O(l) = 69.9$, $S°Ca(OH)_2(aq) = 74.5$,

$S°H_2(g) = 130.68$,

(ii) Calculate the standard molar Gibbs energy of formation of CS_2, given that its standard enthalpy of formation is 89.7 kJ mol^{-1} and the standard molar entropies of graphite, S and CS_2 are 5.7, 31.8 and 151.3$JK^{-1}mol^{-1}$ respectively.

15. For the reaction

$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$

at 25°C, the equilibrium constant is 7.0×10^{-84}.

(i) Calculate the standard Gibbs energy formations of water at 25°C.

(ii) $\Delta_r\ H°_{H_2O} = -\ 280$ kJ mol^{-1}. Calculate the entropy change for the reaction.

Multiple Choice Questions

16. Thermodynamics is not concerned about____.

(a) energy changes involved in a chemical reaction.

(b) the extent to which a chemical reaction proceeds.

(c) the rate at which a reaction proceeds

(d) the feasibility of a chemical reaction.

17. Which of the following statements is correct?

(a) The presence of reacting species in a covered beaker is an example of open system.

(b) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.

(c) The presence of reactants in a closed vessel made up of copper is an example of a closed system.

(d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

18. Which one of the following statements is false?

(a) Work is a state function

(b) Temperature is a state function

(c) Change in the state is completely defined when the initial and final states are specified

(d) None of the above

19. A heat engine absorbs heat Q_1 at temperature T_1 and heat Q_2 at temperature T_2. Work done by the engine is J ($Q_1 + Q_2$). This data

(a) violates 1st law of thermodynamics

(b) violates 1st law of thermodynamics if Q_1 is –ve

(c) violates 1st law of thermodynamics of Q_2 is –ve

(d) does not violate 1st law of thermodynamics.

20. The pressure-volume work for an ideal gas can be calculated by using the expression $w = -\int_{V_i}^{V_f} p_{ex} dV$. The work can also be calculated from the pV–plot by using the area under the curve within the specified limits. When an ideal gas is compressed (a) reversibly or (b) irreversibly from volume V_i to V_f. Choose the correct option.

(a) w (reversible) = w (irreversible)

(b) w (reversible) < w (irreversible)

(c) w (reversible) > w (irreversible)

(d) w (reversible) = w (irreversible) + $p_{ex} . \Delta V$

21. During complete combustion of one mole of butane, 2658 kJ of heat is released. The thermochemical reaction for above change is

(a) $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$ $\quad \Delta_cH = -2658.0 \text{ kJ mol}^{-1}$

(b) $C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$ $\quad \Delta_cH = -1329.0 \text{ kJ mol}^{-1}$

(c) $C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$ $\quad \Delta_cH = -2658.0 \text{ kJ mol}^{-1}$

(d) $C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$ $\quad \Delta_cH = +2658.0 \text{ kJ mol}^{-1}$

22. On the basis of thermochemical equations (1), (2) and (3), find out which of the algebric relationships given in options (a) to (d) is correct.

(1) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g); \quad \Delta_rH = x \text{ kJ mol}^{-1}$

(2) $C(\text{graphite}) + \frac{1}{2} O_2(g) \rightarrow CO(g); \quad \Delta_rH = y \text{ kJ mol}^{-1}$

(3) $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g); \quad \Delta_rH = z \text{ kJ mol}^{-1}$

(a) $z = x + y$ (b) $x = y - z$

(c) $x = y + z$ (d) $y = 2z - x$

Exercise-2 | CONCEPTUAL MCQs

1. Which of the following is closed system ?
(a) Jet engine
(b) Tea placed in a steel kettle
(c) Pressure cooker
(d) Rocket engine during propulsion

2. An isolated system is that system in which:
(a) There is no exchange of energy with the surroundings
(b) There is exchange of mass and energy with the surroundings
(c) There is no exchange of mass or energy with the surroundings
(d) There is exchange of mass with the surroundings

3. The intensive property among these quantities is
(a) mass (b) volume
(c) enthalpy (d) mass/volume

4. Which is an extensive property of the system ?
(a) Volume (b) Viscosity
(c) Temperature (d) Refractive index

5. Internal energy and pressure of a gas of unit volume are related as :
(a) $P = \frac{2}{3}E$ (b) $P = \frac{1}{2}E$
(c) $P = \frac{3}{2}E$ (d) $P = 2E$

6. The latent heat of vapourization of a liquid at 500 K and 1 atm pressure is 10.0 kcal/mol. What will be the change in internal energy (ΔU) of 3 moles of liquid at the same temperature
(a) 13.0 kcal/mol (b) –13.0 kcal/mol
(c) 27.0 kcal mol (d) –7.0 kcal/mol

7. Mechanical work is specially important in systems that contain
(a) solid–liquid (b) liquid–liquid
(c) solid –solid (d) gases

8. In a closed insulated container a liquid is stirred with a paddle to increase the temperature. Which of the following is true?
(a) $\Delta E = W \neq 0$ (b) $\Delta E = W, q = 0$
(c) $\Delta E = 0, W = q \neq 0$ (d) $W = 0, \Delta W = q \neq 0$

9. An adiabatic expansion of an ideal gas always has
(a) decrease in temperature (b) $q = 0$
(c) $w = 0$ (d) $\Delta H = 0$

10. For the reaction $C + O_2 \rightarrow CO_2$
(a) $\Delta H > \Delta E$ (b) $\Delta H < \Delta E$
(c) $\Delta H = \Delta E$ (d) None of these

11. Enthalpy of a reaction ΔH is expressed as
(a) $\Delta H = \Sigma\Delta H_P - \Sigma\Delta H_R$ (b) $\Delta H = \Delta H_P + \Delta H_R$
(c) $\Delta H = \frac{\Delta H_P}{\Delta H_R}$ (d) $\Delta H = \frac{\Sigma H_P}{\Delta H_R}$

12. The enthalpy change of a reaction does not depend on
(a) The state of reactants and products
(b) Nature of reactants and products
(c) Different intermediate reactions
(d) Initial and final enthalpy change of a reaction.

13. Enthalpy change (ΔH) of a system depends upon its
(a) Initial state
(b) Final state
(c) Both on initial and final state
(d) None of these

14. The relationship between enthalpy change and internal energy change is
(a) $\Delta H = \Delta E + P\Delta V$ (b) $\Delta H = (\Delta E + V\Delta P)$
(c) $\Delta H = \Delta E - P\Delta V$ (d) $\Delta H = P\Delta V - \Delta E$

15. If a reaction involves only solids and liquids which of the following is true ?
(a) $\Delta H < \Delta E$ (b) $\Delta H = \Delta E$
(c) $\Delta H > \Delta E$ (d) $\Delta H = \Delta E + RT\Delta n$

16. C (diamond) $\rightarrow$ C (graphite), $\Delta H = -ve$. This shows that
(a) Graphite is more stable
(b) Graphite has more energy than diamond
(c) Both are equally stable
(d) Stability cannot be predicted

17. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) $\rightarrow$ (4.0 atm, 5.0 L, 245 K) with a change in internal energy, $\Delta U = 30.0$ L atm. The change in enthalpy ΔH of the process in L atm is.
(a) 40.0
(b) 42.3
(c) 44.0
(d) Not defined because pressure is not constant

18. The enthalpy of vapourisation of water from the following two equations is.

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O\,(l),\ \Delta H = -286\,kJ$$

$$H_2\,(g) + \frac{1}{2}O_2\,(g), \rightarrow H_2O\,(g),\ \Delta H = -245.5\,kJ$$

(a) 6.02 kJ (b) 40.5 kJ
(c) 62.3 kJ (d) 1.25 kJ

19. In the process $Cl(g)+e^- \xrightarrow{\Delta H} Cl^-(g)$, ΔH is

(a) positive (b) negative

(c) zero (d) unpredictable

20. The variation of heat of reaction with temperature is given by :

(a) Van't Hoff equation

(b) Clausius- Clapeyron equation

(c) Nernst equation

(d) Kirchoff's equation

21. Kirchoff's equation is :

(a) $k = Ae^{-E_a/RT}$

(b) $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

(c) $E_{cell} = \frac{2.303\ RT}{nF}\log\frac{C_2}{C_1}$

(d) $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$

22. Hess's law deals with :

(a) changes in heats of reaction

(b) rates of reactions

(c) equilibrium constants

(d) influence of pressure on the volume of a gas

23. If a chemical change is brought about by one or more methods in one or more steps, then the amount of heat absorbed or evolved during the complete change is the same whichever method was followed. This rule is known as :

(a) Le Chatelier principle (b) Hess's law

(c) Joule Thomson effect (d) None of these

24. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litres. The ΔE for this process is ($R = 2$ cal mol^{-1} K^{-1})

(a) 163.7 cal (b) zero

(c) 1381.1 cal (d) 9 lit atm

25. One mole of an ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27ºC. If the work done during the process is 3 kJ, the final temperature will be equal to ($C_v = 20$ JK^{-1})

(a) 150 K (b) 100 K (c) 26.85 K (d) 295 K

26. 2 moles of an ideal gas at 27ºC temperature is expanded reversibly from 2 lit to 20 lit. Find entropy change (R = 2 cal/mol K)

(a) 92.1 (b) 0 (c) 4 (d) 9.2

27. The heat required to raise the temperature of a body by 1K is called

(a) specific heat (b) thermal capacity

(c) water equivalent (d) none of these

28. For a reaction to occur spontaneously

(a) ΔS must be negative

(b) $(\Delta H - T\Delta S)$ must be negative

(c) $(\Delta H + T\Delta S)$ must be negative

(d) ΔH must be negative

29. The enthalpy and entropy change for a chemical reaction are – 2.5×10^3 cal and 7.4 cal deg^{-1} respectively. The reaction at 298K will be

(a) spontaneous (b) reversible

(c) irreversible (d) non – spontaneous.

30. Heat exchanged in a chemical reaction at constant temperature and constant pressure is called

(a) internal energy (b) enthalpy

(c) entropy (d) free energy

31. For the process

Dry ice $\rightarrow CO_2$ (g)

(a) ΔH is positive and ΔS is negative

(b) Both ΔH and ΔS are negative

(c) Both ΔH and ΔS are positive

(d) ΔH is negative whereas ΔS is positive

32. The favourable conditions for a spontaneous reaction are

(a) $T\Delta S > \Delta H,\ \Delta H = +ve,\ \Delta S = +ve$

(b) $T\Delta S > \Delta H,\ \Delta H = +ve,\ \Delta S = -ve$

(c) $T\Delta S = \Delta H,\ \Delta H = -ve,\ \Delta S = -ve$

(d) $T\Delta S = \Delta H,\ \Delta H = +ve,\ \Delta S = +ve$

33. Identify the correct statement regarding entropy.

(a) At absolute zero temperature, entropy of a perfectly crystalline substance is taken to be zero

(b) At absolute zero temperature, the entropy of a perfectly crystalline substance is positive

(c) Absolute entropy of a substance cannot be determined

(d) At 0°C, the entropy of a perfectly crystalline substance is taken to be zero

34. For which of the following process, ΔS is negative?

(a) $H_2(g) \rightarrow 2H(g)$

(b) $N_2(g)(1atm) \rightarrow N_2(g)(8atm)$

(c) $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$

(d) $C_{(diamond)} \rightarrow C_{(graphite)}$

35. According to second law of thermodynamics a process (reaction)is spontaneous if during the process

(a) $\Delta S_{universe} > 0$ (b) $\Delta S_{universe} = 0$

(c) $\Delta H_{system} > 0$ (d) $\Delta S_{universe} = \Delta S_{system}$

36. The law formulated by Nernst is

(a) first law of thermodynamics

(b) second law of thermodynamics

(c) third law of thermodynamics

(d) Both (a) and (b)

37. If 900 J/g of heat is exchanged at boiling point of water, then what is increase in entropy?

(a) 43.4 J/mole (b) 87.2 J/mole

(c) 900 J/mole (d) Zero

38. Given the following entropy values (in JK^{-1} mol^{-1}) at 298 K and 1 atm :

$H_2(g)$: 130.6, $Cl_2(g)$: 223.0 and HCl (g) : 186.7. The entropy change (in JK^{-1} mol^{-1}) for the reaction

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ is

(a) +540.3 (b) 727.0

(c) –166.9 (d) 19.8

39. Entropy change involved in the conversion of 1 mole of liquid water at 373 K to vapour at the same temperature will be $(\Delta H_{vap.} = 2.257 kJ/g)$

(a) 0.119 kJ (b) 0.109 kJ

(c) 0.129 kJ (d) 0.12 kJ

40. Which relation is correct ?

(a) $\Delta G = \Delta H - T\Delta S$ (b) $\Delta G = \Delta H + T\Delta S$

(c) $\Delta G = T\Delta S - \Delta H$ (d) $\Delta G = \Delta H - SdT$

41. The value of free energy change at equilibrium is

(a) positive (b) negative

(c) zero (d) not definite.

42. The standard Gibb's free energy change, ΔG^0 is related to equilibrium constant, K_P as

(a) $K_P = -RT \ln \Delta G^o$ (b) $K_P = \left[\frac{e}{RT}\right]^{\Delta G^o}$

(c) $K_P = -\frac{\Delta G}{RT}$ (d) $K_P = e^{-\Delta G^o/RT}$

43. What is the free energy change 'ΔG' when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm. pressure

(a) 540 cal (b) –9800 cal

(c) 9800 cal (d) 0 cal

44. According to third law of thermodynamics, which one of the following quantities for a perfectly crystalline solid is zero at absolute zero.

(a) Entropy (b) Free energy

(c) Internal energy (d) Enthalpy.

45. The calorific value of fat is

(a) less than that of carbohydrate and protein

(b) less than that of protein but more than carbohydrate

(c) less than that of carbohydrate but more than that of protein

(d) more than that of carbohydrate and protein.

46. Heat of neutralisation of strong acid against strong base is constant and is equal to

(a) 13.7 kcal (b) 57 kJ

(c) 5.7×10^4 J (d) All of the above

47. The heat of formation of the compound in the following reaction is

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) + 44kcal$

(a) $-44 \, kcal \, mol^{-1}$ (b) $-22 \, kcal \, mol^{-1}$

(c) $11 \, kcal \, mol^{-1}$ (d) $-88 \, kcal \, mol^{-1}$

48. Given that $C + O_2 \rightarrow CO_2 \; \Delta H^o = -xkJ$

$2CO + O_2 \rightarrow 2CO_2 \; \Delta H^o = -ykJ$

the enthalpy of formation of carbon monoxide will be

(a) $\frac{2x - y}{2}$ (b) $\frac{y - 2x}{2}$

(d) $2x - y$ (d) $y = 2x$.

49. The enthalpy of neutralization of acetic acid and sodium hydroxide is –55.4 kJ. What is the enthalpy of ionization of acetic acid ?

(a) –1.9 kJ (b) +1.9 kJ (c) +5.54 kJ (d) –5.54 kJ

50. The neutralisation of a strong acid by a strong base liberates an amount of energy per mole of H^+

(a) depends upon which acid and base are involved

(b) depends upon the temperature at which the reaction takes place

(c) depends upon which catalyst is used

(d) is always the same

51. Equal volumes of methanoic acid and sodium hydroxide are mixed. If x is the heat of formation of water, then heat evolved on neutralization is

(a) more than x (b) equal to x

(c) less than x (d) twice x.

52. $S+\frac{3}{2}O_2 \rightarrow SO_3 + 2x\,\text{kcal}$

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 + y\,\text{kcal}$

Find out the heat of formation of SO_2

(a) (y-2x) (b) (2x+y)
(c) (x+y) (d) 2x/y

53. The enthalpy of neutralisation of a weak acid by a strong base is

(a) – 57.32 kJ
(b) +57.32 kJ
(c) equal to -57.32kJ + enthalpy of ionization of week acid
(d) more than –57.32 kJ

54. The enthalpy of formation for C_2H_4 (g), CO_2 (g) and H_2O (l) at 25° C and 1 atm pressure are 52, –394 and – 286 kJ mol^{-1} respectively. The enthalpy of combustion of C_2H_4 (g) will be

(a) +1412 kJ mol^{-1} (b) –1412 kJ mol^{-1}
(c) 141.2 kJ mol^{-1} (d) –141.2 kJ mol^{-1}

55. When water is added to quicklime, the reaction is

(a) explosive (b) endothermic
(c) exothermic (d) photochemical.

56. Mark the correct statement

(a) For a chemical reaction to be feasible, ΔG should be 0
(b) Entropy is a measure of order in a system
(c) For a chemical reaction to be feasible, ΔG should be positive
(d) The total energy of an isolated system is constant.

57. One mole of an ideal gas is allowed to expand freely and adiabatically into vaccum until its volume has doubled. The expression which is not true concerning statement is

(a) $\Delta H = 0$ (b) $\Delta S = 0$
(c) $\Delta E = 0$ (d) $W = 0$.

58. Which of the following statements is true ?

(a) ΔG may be lesser or greater or equal to ΔH
(b) ΔG is always proportional to ΔH
(c) ΔG is always greater than ΔH
(d) ΔG is always less than ΔH

59. Compounds with high heat of formation are less stable because

(a) it is difficult to synthesize them
(b) energy rich state leads to instability
(c) high temperature is required to synthesize them
(d) molecules of such compunds are distorted.

60. The heat of combustion of CH_4(g), C (graphite), H_2(g) are – 20 kcal, –40 kcal –10 kcal respectively. The heat of formation of methane is

(a) –40 kcal (b) + 40 kcal
(c) –80.0 kcal (c) + 80 kcal

61. $H_2 + Cl_2 \rightarrow 2HCl, \Delta H = -194$ kJ. In this reaction, heat of formation of HCl in kJ is

(a) + 194 kJ (b) + 97 kJ
(c) –97 kJ (d) – 194 kJ

62. Enthalpy of neutralisation of HCl with NaOH is x. The heat evolved when 500 ml of 2 N HCl are mixed with 250 ml of 4N NaOH will be.

(a) 500 x (b) 100x
(c) x (d) 10 x

63. When 1 M H_2SO_4 is completely neutralised by sodium hydroxide, the heat liberated is 114.64 kJ.
What is the enthalpy of neutralisation ?

(a) +114.64 kJ (b) –114.64 kJ
(c) –57.32 kJ (d) + 57.32 kJ

64. The amount of energy released when 20 ml of 0.5 M NaOH are mixed with 100 ml of 0.1 M HCl is x kJ. The heat of neutralisation (in kJ mol^{-1}) is

(a) –100x (b) –50x
(c) + 100 x (d) +50x

65. The ΔH_f^0 for CO_2 (g), CO(g) and H_2O (g) are–393.5, –110.5 and –241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction

$CO_2\,(g) + H_2\,(g) \rightarrow CO\,(g) + H_2O\,(g)$ is

(a) 524.1 (b) 41.2
(c) –262.5 (d) -41.2

66. $H_2\,(g) + Cl_2\,(g) \rightarrow 2\,HCl(g)\ \Delta H = -44$ kcal

$2\,Na\,(s) + 2\,HCl(g) \rightarrow 2\,NaCl\,(s) + H_2(g)$

$$\Delta H = -152\text{kcal}$$

For the reaction

$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s) \quad \Delta H = ?$

(a) –180 kcal (b) –196 kcal
(c) –98 kcal (d) 54 kcal

67. The heat required to decompose a compound into its elements is equal to the heat evolved when the compound is formed from its elements. This is in accordance with :

(a) Lavosier and laplace law
(b) Second law of thermodynamics
(c) Joule- Thomson law
(d) Kirchoff's law

Exercise-3 | PAST COMPETITION MCQs

1. Consider the following reactions: **[CBSE-PMT 2007]**

(i) $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$,
$\Delta H = -X_1$ kJ mol^{-1}

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$,
$\Delta H = -X_2$ kJ mol^{-1}

(iii) $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O$,
$\Delta H = -X_3$ kJ mol^{-1}

(iv) $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$,
$\Delta H = +\ 4X_4$ kJ mol^{-1}

Enthalpy of formation of $H_2O\ (l)$ is

(a) $+X_3$ kJ mol^{-1} (b) $-X_4$ kJ mol^{-1}
(c) $+X_1$ kJ mol^{-1} (d) $-X_2$ kJ mol^{-1}

2. Given that bond energies of H – H and Cl – Cl are 430 kJ mol^{-1} and 240 kJ mol^{-1} respectively and $\Delta_f H$ for HCl is – 90 kJ mol^{-1}, bond enthalpy of HCl is **[CBSE-PMT 2007]**

(a) 380 kJ mol^{-1} (b) 425 kJ mol^{-1}
(c) 245 kJ mol^{-1} (d) 290 kJ mol^{-1}

3. Which of the following are *not* state functions ? **[CBSE-PMT 2008]**

(I) $q + w$ (II) q
(III) w (IV) $H - TS$
(a) (I) and (IV) (b) (II), (III) and (IV)
(c) (I), (II) and (III) (d) (II) and (III)

4. For the gas phase reaction, **[CBSE-PMT 2008]**

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

which of the following conditions are correct ?

(a) $\Delta H = 0$ and $\Delta S < 0$
(b) $\Delta H > 0$ and $\Delta S > 0$
(c) $\Delta H < 0$ and $\Delta S < 0$
(d) $\Delta H > 0$ and $\Delta S < 0$

5. Bond dissociation enthalpy of H_2, Cl_2 and HCl are 434, 242 and 431 kJ mol^{-1} respectively. Enthalpy of formation of HCl is : **[CBSE-PMT 2008]**

(a) 93 kJ mol^{-1} (b) – 245 kJmol^{-1}
(c) – 93 kJmol^{-1} (d) 245 kJmol^{-1}

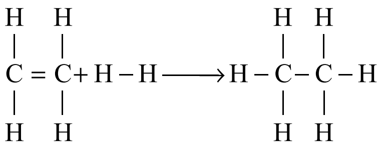
6. The values of ΔH and ΔS for the reaction, C(graphite) + $CO_2\ (g) \rightarrow 2CO(g)$ are 170 kJ and 170 JK^{-1}, respectively. This reaction will be spontaneous at **[CBSE-PMT 2009]**

(a) 910 K (b) 1110 K
(c) 510 K (d) 710 K

7 From the following bond energies: **[CBSE-PMT 2009]**

H – H bond energy: 431.37 kJ mol^{-1}
C = C bond energy: 606.10 kJ mol^{-1}
C – C bond energy: 336.49 kJ mol^{-1}
C – H bond energy: 410.50 kJ mol^{-1}

Enthalpy for the reaction,



$$H_2C{=}CH_2 + H{-}H \longrightarrow H{-}CH_2{-}CH_2{-}H$$

will be:

(a) – 243.6 kJ mol^{-1} (b) –120.0 kJ mol^{-1}
(c) 553.0 kJ mol^{-1} (d) 1523.6 kJ mol^{-1}

8. Standard entropies of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1}mol^{-1} respectively. For the reaction **[CBSE-PMT 2010]**

$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3$, $\Delta H = -30$ kJ

to be at equilibrium, the temperature should be:

(a) 750 K (b) 1000 K
(c) 1250 K (d) 500 K

9. For vaporization of water at 1 atmospheric pressure, the values of ΔH and ΔS are 40.63 kJmol^{-1} and 108.8 JK^{-1} mol^{-1}, respectively. The temperature when Gibbs energy change (ΔG) for this transformation will be zero, is: **[CBSE-PMT 2010]**

(a) 293.4 K (b) 273.4 K
(c) 393.4 K (d) 373.4 K.

10. Match List -I (Equations) with List-II (Type of processes) and select the correct option. **[CBSE-PMT 2010]**

List I **Equations**	**List II** **Type of processes**
(1) $K_p > Q$	(i) Non spontaneous
(2) $\Delta G^\circ < RT \ln Q$	(ii) Equilibrium
(3) $K_p = Q$	(iii) Spontaneous and endothermic
(4) $T > \frac{\Delta H}{\Delta S}$	(iv) Spontaneous

Options:

	(1)	(2)	(3)	(4)
(a)	(ii)	(i)	(iv)	(iii)
(b)	(i)	(ii)	(iii)	(iv)
(c)	(iii)	(iv)	(ii)	(i)
(d)	(iv)	(i)	(ii)	(iii)

11. The following two reactions are known : **[CBSE-PMT 2010]**

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g);\ \Delta H = -26.8\text{ kJ}$$

$$FeO(s) + CO(g) \longrightarrow Fe(s) + CO_2(g);\ \Delta H = -16.5\text{ kJ}$$

The value of Δ H for the following reaction

$Fe_2O_3(s) + CO(g) \longrightarrow 2FeO(s) + CO_2(g)$ is;

(a) $+6.2$ kJ (b) $+10.3$ kJ
(c) -43.3 kJ (d) -10.3 kJ

12. Three moles of an ideal gas expanded spontaneously into vacuum. The work done will be : **[CBSE-PMT 2010]**

(a) Zero (b) Infinite (c) 3 Joules (d) 9 Joules

13. If the enthalpy change for the transition of liquid water to steam is 30 kJ mol^{-1} at 27ºC, the entropy change for the process would be : **[CBSE-PMT 2011]**

(a) 10 J mol^{-1} K^{-1} (b) 1.0 J mol^{-1} K^{-1}
(c) 0.1 J mol^{-1} K^{-1} (d) 100 J mol^{-1} K^{-1}

14. Enthalpy change for the reaction, **[CBSE-PMT 2011]**

$4H(g) \longrightarrow 2H_2(g)$ is $-$ 869.6 kJ.

The dissociation energy of H–H bond is :

(a) -434.8 kJ (b) -869.6 kJ
(c) $+434.8$ kJ (d) $+217.4$ kJ

15. Consider the following processes :

	ΔH (kJ/mol)
$1/2\,A \rightarrow B$	+150
$3B \rightarrow 2C + D$	–125
$E + A \rightarrow 2D$	+350

For $B + D \rightarrow E + 2C$, ΔH will be : **[CBSE-PMT 2011 M]**

(a) 525 kJ/mol (b) -175 kJ/mol
(c) -325 kJ/mol (d) 325 kJ/mol

16. In which of the following reactions, standard entropy change (ΔS°) is positive and standard Gibb's energy change (ΔG°) decreases sharply with increase in temperature ? **[CBSE-PMT 2012 S]**

(a) $C\,(graphite) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

(b) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

(c) $Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$

(d) $\frac{1}{2}C\,(graphite) + \frac{1}{2}O_2(g) \rightarrow \frac{1}{2}CO_2(g)$

17. The enthalpy of fusion of water is 1.435 kcal/mol. The molar entropy change for the melting of ice at 0°C is : **[CBSE-PMT 2012 S]**

(a) 10.52 cal / (mol K) (b) 21.04 cal / (mol K)
(c) 5.260 cal / (mol K) (d) 0.526 cal / (mol K)

18. Standard enthalpy of vapourisation Δ_{vap} H° for water at 100°C is 40.66 kJ mol^{-1}. The internal energy of vaporisation of water at 100°C (in kJ mol^{-1}) is : **[CBSE-PMT 2012 S]**

(a) $+37.56$ (b) -43.76
(c) $+43.76$ (d) $+40.66$

(Assume water vapour to behave like an ideal gas).

19. Equal volumes of two monoatomic gases, A and B, at same temperature and pressure are mixed. The ratio of specific heats (C_p/C_v) of the mixture will be : **[CBSE-PMT 2012]**

(a) 0.83 (b) 1.50
(c) 3.3 (d) 1.67

20. A reaction having equal energies of activation for forward and reverse reaction has : **[NEET 2013]**

(a) $\Delta G = 0$ (b) $\Delta H = 0$
(c) $\Delta H = \Delta G = \Delta S = 0$ (d) $\Delta S = 0$

21. If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, then **[AIEEE 2002]**

(a) ΔH is –ve, ΔS is +ve
(b) ΔH and ΔS both are +ve
(c) ΔH and ΔS both are –ve
(d) ΔH is +ve, ΔS is -ve

22. A heat engine abosrbs heat Q_1 at temperature T_1 and heat Q_2 at temperature T_2. Work done by the engine is J (Q_1 + Q_2). This data **[AIEEE 2002]**

(a) violates 1st law of thermodynamics
(b) violates 1st law of themodynamics if Q_1 is –ve
(c) violates 1st law of thermodynamics of Q_2 is –ve
(d) does not violate 1st law of themodynamics.

23. For the reactions, **[AIEEE 2002]**

$C + O_2 \rightarrow CO_2$; ΔH = -393 J
$2Zn + O_2 \rightarrow 2\,ZnO$; ΔH = -412 J

(a) carbon can oxidise Zn
(b) oxidation of carbon is not feasible
(c) oxidation of Zn is not feasible
(d) Zn can oxidise carbon.

24. The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy ? **[AIEEE 2003]**

(a) >40 kJ (b) <40 kJ
(c) Zero (d) 40 kJ

25. If at 298 K the bond energies of C — H, C — C, C = C and H — H bonds are respectively 414, 347, 615 and 435 kJ mol^{-1}, the value of enthalpy change for the reaction

$$H_2C = CH_2(g) + H_2(g) \rightarrow H_3C — CH_3(g)$$

at 298 K will be **[AIEEE 2003]**

(a) -250 kJ (b) $+125$ kJ
(c) -125 kJ (d) $+250$ kJ

26. In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done, the change in Gibbs free energy (dG) and change in entropy (dS), satisfy the criteria **[AIEEE 2003]**

(a) $(\Delta S)_{V,E}>0, (\Delta G)_{T,P}<0$
(b) $(\Delta S)_{V,E}=0, (\Delta G)_{T,P}=0$
(c) $(\Delta S)_{V,E}=0, (\Delta G)_{T,P}>0$
(d) $(\Delta S)_{V,E}<0, (\Delta G)_{T,P}<0$

27. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_c is **[AIEEE 2003]**

(a) $-\Delta G = RT\, ln\, K_c$
(b) $\Delta G^o = RT\, ln\, K_c$
(c) $-\Delta G^o = RT\, ln\, K_c$
(d) $\Delta G = RT\, ln\, K_c$

28. The enthalpy change for a reaction does **not** depend upon **[AIEEE 2003]**

(a) use of different reactants for the same product
(b) the nature of intermediate reaction steps
(c) the differences in initial or final temperatures of involved substances
(d) the physical states of reactants and products

29. An ideal gas expands in volume from 1×10^{-3} to $1\times10^{-2}\ m^3$ at 300 K against a constant pressure of $1\times10^5\ Nm^{-2}$. The work done is **[AIEEE 2004]**

(a) 270 kJ
(b) – 900 kJ
(c) – 900 kJ
(d) 900 kJ

30. The enthalpies of combustion of carbon and carbon monoxide are – 393.5 and – 283 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide per mole is **[AIEEE 2004]**

(a) – 676.5 kJ
(b) 676.5 kJ
(c) 110.5 kJ
(d) – 110.5 kJ

31. For a spontaneous reaction the ΔG, equilibrium constant (K) and E^o_{Cell} will be respectively **[AIEEE 2005]**

(a) –ve, >1, –ve
(b) –ve, <1, –ve
(c) +ve, >1, –ve
(d) –ve, >1, +ve

32. Consider the reaction : $N_2 + 3H_2 \rightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔU are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ? **[AIEEE 2005]**

(a) $\Delta H > \Delta U$
(b) $\Delta H < \Delta U$
(c) $\Delta H = \Delta U$
(d) $\Delta H = 0$

33. If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and ΔH_f for the formation of XY is – 200 kJ $mole^{-1}$. The bond dissociation energy of X_2 will be **[AIEEE 2005]**

(a) 400 kJ mol^{-1}
(b) 300 kJ mol^{-1}
(c) 200 kJ mol^{-1}
(d) 100 kJ mol^{-1}

34. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct? **[AIEEE 2006]**

(a) $(T_f)_{rev} = (T_f)_{irrev}$
(b) $T_f = T_i$ for both reversible and irreversible processes
(c) $(T_f)_{irrev} > (T_f)_{rev}$
(d) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process

35. The standard enthalpy of formation $(\Delta_f H^o)$ at 298 K for methane, CH_4 (g) is –74.8 kJ mol^{-1}. The additional information required to determine the average energy for C – H bond formation would be **[AIEEE 2006]**

(a) the first four ionization energies of carbon and electron gain enthalpy of hydrogen
(b) the dissociation energy of hydrogen molecule, H_2
(c) the dissociation energy of H_2 and enthalpy of sublimation of carbon
(d) latent heat of vapourization of methane

36. The enthalpy changes for the following processes are listed below : **[AIEEE 2006]**

$Cl_2(g) = 2Cl(g)$, 242.3 kJ mol^{-1}
$I_2(g) = 2I(g)$, 151.0 kJ mol^{-1}
$ICl(g) = I(g) + Cl(g)$, 211.3 kJ mol^{-1}
$I_2(s) = I_2(g)$, 62.76 kJ mol^{-1}

Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation for ICl(g) is : **[AIEEE 2006]**

(a) +16.8 kJ mol^{-1}
(b) +244.8 kJ mol^{-1}
(c) –14.6 kJ mol^{-1}
(d) –16.8 kJ mol^{-1}

37. $(\Delta H - \Delta U)$ for the formation of carbon monoxide (CO) from its elements at 298 K is **[AIEEE 2006]**
$(R = 8.314\ J\ K^{-1}\ mol^{-1})$

(a) –2477.57 J mol^{-1}
(b) 2477.57 J mol^{-1}
(c) –1238.78 J mol^{-1}
(d) 1238.78 J mol^{-1}

38. In conversion of lime-stone to lime, **[AIEEE 2007]**
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ the values of ΔH° and ΔS° are + 179.1 kJ mol^{-1} and 160.2 J/K respectively at 298 K and 1 bar. Assuming that ΔH° and ΔS° do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is

(a) 1118 K
(b) 1008 K
(c) 1200 K
(d) 845 K.

39. Assuming that water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vapourised at 1 bar pressure and 100°C, (given : molar enthalpy of vapourisation of water at 1 bar and 373 K = 41 kJ mol^{-1} and R = 8.3 J mol^{-1} K^{-1}) will be **[AIEEE 2007]**

(a) 41.00 kJ mol^{-1}
(b) 4.100 kJ mol^{-1}
(c) 3.7904 kJ mol^{-1}
(d) 37.904 kJ mol^{-1}

40. Identify the correct statement regarding a spontaneous process: **[AIEEE 2007]**

(a) Lowering of energy in the process is the only criterion for spontaneity.

(b) For a spontaneous process in an isolated system, the change in entropy is positive.

(c) Endothermic processes are never spontaneous.

(d) Exothermic processes are always spontaneous.

41. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below: **[AIEEE 2008]**

$$\frac{1}{2}Cl_2(g) \xrightarrow{\frac{1}{2}\Delta_{diss}H^{\ominus}} Cl(g) \xrightarrow{\Delta_{eg}H^{\ominus}} Cl^-(g)$$

$$\xrightarrow{\Delta_{Hyd}H^{\ominus}} Cl^-(aq)$$

(using the data,

$\Delta_{diss}H^{\ominus}_{Cl_2} = 240\ kJ\ mol^{-1}$, $\Delta_{eg}H^{\ominus}_{Cl} = -349\ kJ\ mol^{-1}$,

$\Delta_{hyd}H^{\ominus}_{Cl^-} = -381\ kJ\ mol^{-1}$), will be

(a) $+152\ kJ\ mol^{-1}$ (b) $-610\ kJ\ mol^{-1}$

(c) $-850\ kJ\ mol^{-1}$ (d) $+120\ kJ\ mol^{-1}$

42. On the basis of the following thermochemical data : $[\Delta_f H°(H^+_{(aq)}) = 0)]$ **[AIEEE 2009]**

$$H_2O(l) \rightarrow H^+(aq) + OH^-(aq); \Delta H = 57.32 kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell);\ \Delta H = -286.20 kJ$$

The value of enthalpy of formation of OH^- ion at 25° C is:

(a) –228.88 kJ (b) +228.88 kJ

(c) –343.52 kJ (d) –22.88 kJ

43. The standard enthalpy of formation of NH_3 is $-46.0\ kJ\ mol^{-1}$. If the enthalpy of formation of H_2 from its atoms is $-436\ kJ\ mol^{-1}$ and that of N_2 is $-712\ kJ\ mol^{-1}$, the average bond enthalpy of N – H bond in NH_3 is **[AIEEE 2010]**

(a) $-964\ kJ\ mol^{-1}$ (b) $+352\ kJ\ mol^{-1}$

(c) $+1056\ kJ\ mol^{-1}$ (d) $-1102\ kJ\ mol^{-1}$

44. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when

(a) $T_e > T$ (b) $T > T_e$ **[AIEEE 2010]**

(c) T_e is 5 times T (d) $T = T_e$

45. The value of enthalpy change (ΔH) for the reaction

$$C_2H_5OH(\ell) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$$

at 27° C is $-1366.5\ kJ\ mol^{-1}$. The value of internal energy change for the above reaction at this temperature will be : **[AIEEE 2011 RS]**

(a) – 1369.0 kJ (b) – 1364.0 kJ

(c) – 1361.5 kJ (d) – 1371.5 kJ

46. Consider the reaction : **[AIEEE 2011 RS]**

$$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g),$$

$\Delta_r H = -111\ kJ$.

If $N_2O_5(s)$ is formed instead of $N_2O_5(g)$ in the above reaction, the $\Delta_r H$ value will be :

(given, ΔH of sublimation for N_2O_5 is $-54\ kJ\ mol^{-1}$)

(a) + 54 kJ (b) + 219 kJ

(c) – 219 J (d) – 165 kJ

47. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be: **[JEE M 2013]**

(R = 8.314 J/mol K) (ln 7.5 = 2.01)

(a) q = + 208 J, w = – 208 J

(b) q = – 208 J, w = – 208 J

(c) q = – 208 J, w = + 208 J

(d) q = + 208 J, w = + 208 J

48. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is

(Given : $\Delta_r H^{\circ}_{298K} = -54.07\ kJ\ mol^{-1}$,

$\Delta_r S^{\circ}_{298K} = 10\ JK^{-1}\ mol^{-1}$ and $R = 8.314\ JK^{-1}\ mol^{-1}$;

$2.303 \times 8.314 \times 298 = 5705$) **[IIT-JEE 2007]**

(a) 5 (b) 10

(c) 95 (d) 100

49. For the process $H_2O(l)$ (1 bar, 373 K) $\rightarrow$ $H_2O(g)$ (1 bar, 373 K), the correct set of thermodynamic parameters is **[IIT-JEE 2007]**

(a) $\Delta G = 0, \Delta S = +ve$ (b) $\Delta G = 0, \Delta S = -ve$

(c) $\Delta G = +ve, \Delta S = 0$ (d) $\Delta G = -ve, \Delta S = +ve$

50. The species which by definition has **ZERO** standard molar enthalpy of formation at 298 K is **[IIT-JEE 2010]**

(a) $Br_2(g)$ (b) $Cl_2(g)$

(c) $H_2O(g)$ (d) $CH_4(g)$

51. Using the data provided, calculate the multiple bond energy ($kJ\ mol^{-1}$) of a C ≡ C bond in C_2H_2. That energy is (take the bond energy of a C – H bond as $350\ kJ\ mol^{-1}$)

$$2C(s) + H_2(g) \longrightarrow HC \equiv CH(g);\quad \Delta H = 225\ kJ\ mol^{-1}$$

$$2C(s) \longrightarrow 2C(g); \Delta H = 1410\ kJ\ mol^{-1}$$

$$H_2(g) \longrightarrow 2H(g); \Delta H = 330\ kJ\ mol^{-1}$$ **[IIT-JEE 2012]**

(a) 1165 (b) 837

(c) 865 (d) 815

52. The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 25°C are –400 kJ/mol, –300 kJ/mol and –1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is **[JEE Advanced 2013]**

(a) +2900 kJ (b) –2900 kJ

(c) –16.11 kJ (d) +16.11 kJ

Exercise-4 | Applied MCQs

1. For determining the spontaneity of a process which of the following is considered ?
(a) ΔS system
(b) ΔS surroundings
(c) ΔS system + ΔS surroundings
(d) ΔS system – ΔS surroundings

2. Which of the following is always true for a spontaneous change at all temperatures ?
(a) $\Delta H > 0 ; \Delta S < 0$
(b) $\Delta H < 0 ; \Delta S < 0$
(c) $\Delta H < 0 ; \Delta S > 0$
(d) $\Delta H > 0 ; \Delta S > 0$

3. What is the change in entropy when ice melts at 0°C, enthalpy of fusion of one mole of ice is 6.02 kJ ?
(a) $6.02\ kJ\ K^{-1}\ mol^{-1}$
(b) $22.1\ J\ K^{-1}\ mol^{-1}$
(c) $41.6\ J\ K^{-1}\ mol^{-1}$
(d) $22.0 J\ K^{-1}\ mol^{-1}$

4. In which of the following processes, the entropy decreases ?
(a) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
(b) $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$
(c) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
(d) $O_3(g) \rightarrow O_2(g) + O(g)$

5. For which one of the processes represented by the following equations the enthalpy (heat) change is likely to be negative
(a) $Cl^-(g) + aq \rightarrow Cl^-(aq)$
(b) $Cl(g) \rightarrow Cl^+(g) + e^-$
(c) $1/2Cl_2(g) \rightarrow Cl(g)$
(d) $Cl_2(l) \rightarrow Cl_2(g)$

6. The enthalpy change of formation of CO_2 (g) is – 393 $kJmol^{-1}$ and that of H_2O (l) is – 286 $kJmol^{-1}$. The enthalpy of combustion of one mole of ethanol (C_2H_5OH) is –1360. The enthalpy change for the formation of one mole of ethanol form its constituent elements is
(a) –681 kJ
(b) –284 kJ
(c) +965 kJ
(d) 1360 kJ

7. What is Δn_{gas} for the combustion of 1 mole of benzene, when both the reactants and the products are at 298 K ?
(a) 0
(b) 1/2
(c) 3/2
(d) –3/2

8. Which of the following statements is false ?
(a) For 1 mole of an ideal gas, $C_p - C_v = R$
(b) $\left(\dfrac{\partial E}{\partial T}\right)_T = 0$ for an ideal gas
(c) $\Delta q = \Delta w + p\Delta V$
(d) For reversible isothermal expansion of 1 mole of an ideal gas from volume V_1 to V_2, work done is equal to RT ln (V_2/V_1)

9. What is the free energy change for the conversion of 1 mole of water into steam at 373.2 K . The heat of vaporization (ΔH_v) of water of 373.2 K is 9.1 kcal. mol^{-1}. The entropy change is 25.5 cal/mol deg.
(a) –401.6 cal/mol
(b) –416.6 cal/mol
(c) 516.5 cal/mol
(d) –516.5 cal/mol

10. The 'thermite reaction' involving the reaction between ferric oxide and metallic aluminium produces molten iron. Given that

$$2Al + 3/2O_2 \rightarrow Al_2O_3; \Delta H_1 = -400\ kcal/mol$$

$$2Fe + 3/2O_2 \rightarrow Fe_2O_3; \Delta H_2 = -200\ kcal/mol.$$

What is ΔH for the formation of 1 mole of iron ?
(a) –100 kcal
(b) –200 kcal
(c) +100 kcal
(d) +200 kcal

11. Given the reaction at 927°C and 1 atm. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ ΔH= 176 kJ/mol; then ΔE equals
(a) 100 kJ
(b) 166.03 kJ
(c) 180.0 kJ
(d) 186.4 kJ

12. What is the enthalpy change for the reaction

$$H_2(g) + C_2H_4(g) \rightarrow C_2H_6(g)$$

The bond energies are given below:

$\in(H-H) \rightarrow 103; \in(C-H) \rightarrow 99, \in(C-C) \rightarrow 80$ and $\in(C=C) \rightarrow 145$ kcal/mol respectively
(a) $-10\ kcal\ mol^{-1}$
(b) $+10\ kcal\ mol^{-1}$
(c) $-30\ kcal\ mol^{-1}$
(d) $+30\ kcal\ mol^{-1}$

13. For the process $H_2O(l) \rightleftharpoons H_2O(g)$ $\Delta H = 45.0\ kJ\ mol^{-1}$ and $\Delta S = 1.20 \times 10^2\ J\ K^{-1}\ mol^{-1}$. At what temperature the above process is at equilibrium?
(a) 273 K
(b) 373 K
(c) 370 K
(d) 375 K

14. Third law of thermodynamics is used to determine the
(a) spontaneity of a process
(b) enthalpy of substance
(c) absolute values of entropy of a substance
(d) free energy of a substance

15. In thermodynamics, a process is called reversible when
(a) surroundings and system change into each other
(b) there is no boundary between system and surroundings
(c) the surroundings are always in equilibrium with the system
(d) the system changes into the surroundings spontaneously

16. Which one of the following statements is false?
(a) Work is a state function
(b) Temperature is a state function
(c) Change in the state is completely defined when the initial and final states are specified
(d) Work appears at the boundary of the system

17. The standard enthalpies of formation of H^+ and OH^- ions in water are zero and –229.6 kJ mol^{-1} respectively. The standard enthalpy of formation of liquid water is –285.6kJ mol^{-1}. Then the enthalpy of neutralization of HCl(aq) by KOH(aq) is
(a) 229.6 kJ mol^{-1} (b) –173.4 kJ mol^{-1}
(c) 56.0 kJ mol^{-1} (d) –56.0 kJ mol^{-1}

18. Which of the following salts should cause maximum cooling when 1 mole of it is dissolved in the same volume of water ?
(a) NaCl; $\Delta H^\circ = 5.35$ kJ mol^{-1}
(b) KNO_3; $\Delta H^\circ = 53.5$ kJ mol^{-1}
(c) KOH; $\Delta H^\circ = -56.0$ kJ mol^{-1}
(d) HBr; $\Delta H^\circ = -83.3$ kJ mol^{-1}

19. The molar enthalpies of combustion of isobutane and n-butane are –2870 kJ mol^{-1} & –2875 kJ mol^{-1} respectively at 298 K and 1 atm. Calculate ΔH° for the conversion of 1 mole of n-butane to 1 mole of isobutane
(a) –8 kJ mol^{-1} (b) +8 kJ mol^{-1}
(c) –5748 kJ mol^{-1} (d) +5748 kJ mol^{-1}

20. For the reaction

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g); \Delta H^\circ = -67650 \text{ cal at}$$

25 °C. Calculate ΔH° at 100°C, given that the required molar heat capacities are as follows.
$C_P(CO,g) = 6.97$ cal °C^{-1}
$C_P(CO_2,g) = 8.97$ cal °C^{-1}
$C_P(O_2,g) = 7.00$ cal °C^{-1}
(a) –54.6 cal (b) –67650.4 cal
(c) –67684.4 cal (d) –67762.5 cal

21. The heat of atomization of $PH_3(g)$ is 228 kcal mol^{-1} and that of $P_2H_4(g)$ is 335 kcal mol^{-1}. The energy of the P–P bond is
(a) 102 kcal mol^{-1} (b) 51 kcal mol^{-1}
(c) 26 kcal mol^{-1} (d) 204 kcal mol^{-1}

22. The enthalpy of solution of a substance is given by
(a) $\Delta H^\circ_{soln} = U_{(\text{lattice energy})} + \Delta H^\circ_{hydration}$
(b) $\Delta H^\circ_{soln.} = U_{(\text{lattice energy})} - \Delta H^\circ_{hydration}$
(c) $\Delta H^\circ_{soln.} = -U_{(\text{lattice energy})} + \Delta H^\circ_{hydration}$
(d) $\Delta H^\circ_{soln.} = -U_{(\text{lattice energy})} - \Delta H^\circ_{hydration}$

23. For the reaction

$$2C_6H_5CO_2H(s) + 15O_2(g) \longrightarrow 14CO_2(g) + 6H_2O(g)$$

$\Delta U^\circ = -772.7$ kJ mol^{-1} at 298 K. Calculate ΔH°
(a) +760.3 kJ mol^{-1} (b) –760.3 kJ mol^{-1}
(c) +670.3 kJ mol^{-1} (d) –790.3 kJ mol^{-1}

24. 1 gram equivalent of H_2SO_4 is treated with 112 g of KOH for complete neutralization. Which of the following statements is correct?
(a) 13.7 kcal of heat is evolved with the formation of 87 g of K_2SO_4, leaving no KOH.
(b) 27.4 kcal of heat is evolved with the formation of 87 g of K_2SO_4, leaving 4 gram equivalent of KOH.
(c) 15.7 kcal of heat is evolved with the formation of 1 gram equivalent of K_2SO_4, leaving 56 g of KOH.
(d) 13.7 kcal of heat is evolved with the formation of 87g of K_2SO_4, leaving 1 gram equivalent of KOH.

25. From the following data ΔH of the following reactions

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g); \quad \Delta H = -110 \text{ kJ and}$$

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g); \Delta H = 132 \text{ kJ}$$

Calculate the mole composition of the mixture of steam and oxygen on being passes over coke at 1273 K, keeping the temperature constant.
(a) 1 : 0.6 (b) 0.6 : 1
(c) 2 : 3 (d) 3 : 2

26. ΔH_f^o of water is – 285.8 $kJmol^{-1}$. If enthalpy of neutralisation of monoacidic strong base is $-57.3\ kJmol^{-1}$. ΔH_f^o of OH^- ion will be
(a) $-114.25\ kJmol^{-1}$ (b) $114.25\ kJmol^{-1}$
(c) $228.5\ kJmol^{-1}$ (d) $-228.5\ kJmol^{-1}$

27. Temperature of 5 moles of a gas is decreased by 2K at constant pressure. Indicate the correct statement
(a) Work done by gas is = 5 R
(b) Work done over the gas is = 10 R
(c) Work done by the gas = 10 R
(d) Work done = 0

28. An ideal gas occuping a volume of 2dm³ and a pressure of 5 bar undergoes isothermal and irreversible expansion against external pressure of 1 bar. The final volume of the system and the work involved in the process is
(a) $10\ dm^3, 1000$ J (b) $8\ dm^3, -800$ J
(c) $10\ dm^3, -800$ J (d) $10\ dm^3, -1000$ J

29. At 25°C and 1 bar which of the following has a non-zero ΔH_f^o

(a) $Br_2(\ell)$
(b) C (graphite)
(c) $O_3(g)$
(d) $I_2(s)$

30. Bond enthalpies of H_2, X_2 and HX are in the ratio 2 : 1 : 2. If enthalpy of formation of HX is – 50 $kJmol^{-1}$, the bond enthalpy of X_2 is

(a) 100 $kJmol^{-1}$
(b) 300 $kJmol^{-1}$
(c) 200 $kJmol^{-1}$
(d) 400 $kJmol^{-1}$

31. When 1 mole of oxalic acid is treated with excess of NaOH in dilute aqueous solution, 106 kJ of heat is liberated. Predict the enthalpy of ionisation of the acid

(a) 4.3 $kJmol^{-1}$
(b) -4.3 $kJmol^{-1}$
(c) 8.6 $kJmol^{-1}$
(d) -8.6 $kJmol^{-1}$

32. An athlete is given 100 g of glucose $(C_6H_{12}O_6)$ of energy equivalent to 1560 kJ. He utilises 50% of this gained energy in the event. In order to avoid storage of energy in the body. Calculate the weight of water he would need to perspire. The enthalpy of evaporation of water is 44 $kJmol^{-1}$.

(a) 319.1 g
(b) 119.7 g
(c) 227.5 g
(d) 250.2 g

33. The enthalpy change for hydration

$$CuSO_4(s) + 5H_2O(g) \longrightarrow CuSO_4.5H_2O(s)$$

is -71.50 $kcal\,mol^{-1}$. If enthalpy of vaporisation of water is 10.5 $kcal\,mol^{-1}$ at 25°C, what would be the enthalpy change for the hydration

$$CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4.5H_2O(s)$$

(a) -19.0 $kcal\,mol^{-1}$
(b) 19.0 $kcal\,mol^{-1}$
(c) 61.0 $kcal\,mol^{-1}$
(d) -61.0 $kcal\,mol^{-1}$

34. The lattice energy of solid NaCl is 180 $kcal\,mol^{-1}$ and enthalpy of solution is 1 $kcal\,mol^{-1}$. If the hydration energies of Na^+ and Cl^- ions are in the ratio 3 : 2, what is the enthalpy of hydration of sodium ion ?

(a) -107.4 $kcal\,mol^{-1}$
(b) 107.4 $kcal\,mol^{-1}$
(c) 71.6 $kcal\,mol^{-1}$
(d) -71.6 $kcal\,mol^{-1}$

35. The ΔH at 358 K for the reaction

$$Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(l)$$

given that $\Delta H_{298} = -33.29$ $kJ\,mol^{-1}$ and C_p for $Fe_2O_3(s)$, Fe(s), $H_2O(l)$ and $H_2(g)$ and 103.8, 25.1, 75.3 and 28.8 J/K mol

(a) -28.136 $kJ\,mol^{-1}$
(b) -38.3 $kJ\,mol^{-1}$
(c) 42.5 $kJ\,mol^{-1}$
(d) 56.2 $kJ\,mol^{-1}$

36. ΔH_f° of NF_3 is – 113 $kJ\,mol^{-1}$ and N–F bond energy is 273.0 $kJ\,mol^{-1}$. If N ≡ N and F–F bond energies are in the rates 6 : 1, their magnitudes will be

(a) 780.0 $kJ\,mol^{-1}$, 130.0 $kJ\,mol^{-1}$
(b) 840 $kJ\,mol^{-1}$, 140 $kJ\,mol^{-1}$
(c) 950.0 $kJ\,mol^{-1}$, 158.3 $kJ\,mol^{-1}$
(d) 941.3 $kJ\,mol^{-1}$, 156.9 $kJ\,mol^{-1}$

37. The enthalpy of neutralisation of NH_4OH and CH_3COOH is – 10.5 $kcal\,mol^{-1}$ and enthalpy of neutralisation of CH_3COOH with strong base is – 12.5 $kcal\,mol^{-1}$. The enthalpy of ionisation of NH_4OH will be

(a) 3.2 $kcal\,mol^{-1}$
(b) 2.0 $kcal\,mol^{-1}$
(c) 3.0 $kcal\,mol^{-1}$
(d) 4.0 $kcal\,mol^{-1}$

38. Standard enthalpy of combustion of CH_4 is -890 $kJ\,mol^{-1}$ and standard enthalpy of vaporisation of water is 40.5 $kJ\,mol^{-1}$. The enthalpy change of the reaction

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

(a) -809.5 $kJ\,mol^{-1}$
(b) -890 $kJ\,mol^{-1}$
(c) 809 $kJ\,mol^{-1}$
(d) -971 $kJ\,mol^{-1}$

39. The enthalpy of combustion of 2 moles of benzene at 27°C differs from the value determined in bomb calorimeter by

(a) -2.494 kJ
(b) 2.494 kJ
(c) -7.483 kJ
(d) 7.483 kJ

40. The heats of neutralisation of CH_3COOH, HCOOH, HCN and H_2S are – 13.2, – 13.4, – 2.9 and – 3.8 kcal per equivalent respectively. Arrange the acids in increasing order of strength

(a) HCOOH > CH_3COOH > H_2S > HCN
(b) CH_3COOH > HCOOH > H_2S > HCN
(c) H_2S > HCOOH > CH_3COOH > HCN
(d) HCOOH > H_2S > CH_3COOH > HCN

41. When 1.8 g of steam at the normal boiling point of water is converted into water at the same temperature, enthalpy and entropy changes respectively will be ($\Delta H_{\text{Vaporisation}}$ for $H_2O = 40.8\ \text{kJ mol}^{-1}$)

(a) $4.08\,\text{kJ}, 10.93\ \text{JK}^{-1}$ (b) $-4.08\,\text{kJ}, -10.93\ \text{JK}^{-1}$

(c) $-4.08\,\text{kJ}, -40.8\ \text{JK}^{-1}$ (d) $4.08\,\text{kJ}, 40.8\ \text{JK}^{-1}$

42. The enthalpy of neutralisation of a weak acid in 1 M solution with a strong base is – 56.1 kJ mol^{-1}. If the enthalpy of ionisation of acid is 1.5 kJ mol^{-1} and enthalpy of neutralisation of the strong acid with a strong base is -57.3 kJ eq^{-1}. What is the % ionisation of the weak acid in molar solution (assume the acid is monobasic)

(a) 25 (b) 20

(c) 15 (d) 10

43. The enthalpy of atomisation of CH_4 and C_2H_6 are 360 and 620 kcal mol^{-1} respectively. The C – C bond energy is expected to be

(a) 210 k cal mol^{-1} (b) 80 k cal mol^{-1}

(c) 130 k cal mol^{-1} (d) 180 k cal mol^{-1}

44. A certain reaction is non spontaneous at 298K. The entropy change during the reaction is 121 JK^{-1}. Is the reaction is endothermic or exothermic ? The minimum value of ΔH for the reaction is

(a) endothermic, $\Delta H = 36.06\,\text{kJ}$

(b) exothermic, $\Delta H = -36.06\,\text{kJ}$

(c) endothermic, $\Delta H = 60.12\,\text{kJ}$

(d) exothermic, $\Delta H = -60.12\,\text{kJ}$

Hints & Solutions

EXERCISE 1

1. (a) $\Delta H = \Delta U$ because $\Delta n = 0$
   (b) $\Delta H > \Delta U$ because $\Delta n = 1$
2. The sign of work done will be +ve
3. (i) Photosynthesis
   (ii) Photoelectric effect.
4. ΔH is the same but q will be different.
5. (a) Enthalpy is a state function and (b) law of conservation of energy are the two basis of Hess's law.
6. $\Delta U = -20.48$ J
   $\Delta H = -23.11$ J
7. Amount of gobar gas produced per day = 49.44 kg
9. (b) and (c).
11. (a) because they have different crystal structure.
    (b) ΔG will be –ve. Hence, the process is spontaneous,
    (c) A real crystal has some disorder due to presence of defects
12. $\log K_p = 5.83 \times 10^{-3}$
14. **(i)** (a) $\Delta S° = -549.74\ JK^{-1}\ mol^{-1}$
    (b) $\Delta S° = 23.96\ JK^{-1}\ mol^{-1}$
    (ii) $65.27\ kJ\ mol^{-1}$.
15. (i) $\Delta_f G°_{H_2O} = -237.22\ kJ\ mol^{-1}$
    (ii) $\Delta_r S° = 327\ J\ mol^{-1}\ K^{-1}$

16. (c) 17. (c) 18. (a) 19. (d)
20. (b) 21. (c) 22. (c)

EXERCISE 2

1. **(c)** Closed system can exchange energy and not matter with surroundings. Pressure cooker provides closed system.
2. **(c)** Isolated system cannot exchange mass or energy.
3. **(d)** Mass/volume = density, hence it is intensive property.
4. **(a)** Volume depends upon mass. Hence it is extensive property.
5. **(a)** Kinetic gas equation,
   $PV = \frac{1}{3} m n U^2 = \frac{2}{3}$ KE. For unit volume, $P = \frac{2}{3} E$
6. **(c)** $3H_2O(l) \rightarrow 3H_2O(g)$;
   $\Delta n = 3,\ \Delta E = \Delta H - \Delta nRT = 30 - 3 \times \frac{2}{1000} \times 500 = 27\,kcal$
7. **(d)** Gases can undergo expansion hence perform mechanical work . (PΔV work)
8. **(a)** In insulated system no heat or matter is exchanged, $q = 0\ \therefore \Delta E = W$. The work done on the system increases internal energy.
9. **(b)** For adiabatic process q = 0
10. **(c)** $\Delta H = \Delta E + \Delta nRT$; $\Delta n = 0 \Rightarrow \Delta H = \Delta E$. In the given reaction C is solid.
11. **(a)** Enthalpy of reaction, $\Delta H = \sum \Delta H_{products} - \sum \Delta H_{Reactants}$
12. **(c)** In accordance with Hess's law
13. **(c)**
14. **(a)** $\Delta H = \Delta E + P\Delta V$
15. **(b)** $\Delta H = \Delta E + P\Delta V$, for solid and liquid, $\Delta V = 0$
    or $\Delta H = \Delta E + \Delta nRT$, for solids and liquids $\Delta n = 0$
16. **(a)** As heat is evolved, heat content of diamond > heat content of graphite. Hence graphite is more stable.
    $\therefore \Delta H = -245.5\ kJ - (-286\ kJ)$
    $= 40.5\ kJ$
17. **(c)** $\Delta H = H_2 - H_1 = (E_2 + P_2V_2) - (E_1 + P_1V_1)$
    $= (E_2 - E_1) + (P_2V_2 - P_1V_1)$
    $= 30 + 4 \times 5 - 2 \times 3 = 44\,L\ atm$
18. **(b)** Desired equation is $H_2O(l) \rightarrow H_2O(g),\ \Delta H = ?$
    (Equation II - Equation I)
    $\Delta H = -245.5\ kJ - (-286\ kJ) = 40.5\ kJ$
19. **(b)** This is electron affinity and exothermic process.
20. **(d)** Kirchoff's equation, $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$
21. **(d)**
22. **(a)** Hess's law deals with changes in heat of reaction.
23. **(b)** Hess's law
24. **(b)** For a finite change $\Delta E = C_V \Delta T$. For an isothermal process $\Delta T = 0$. Hence $\Delta E = 0$
25. **(a)** Work done during adiabatic expansion $= C_V(T_2 - T_1)$
    or $-3000 = 20(T_2 - 300) \Rightarrow T_2 = 150K$
26. **(d)** Entropy change at constant temperature
    $= 2.303nR \log \frac{V_2}{V_1} = 2.303 \times 2 \times 2 \log \frac{20}{2} = 9.2\ cal K^{-1} mol^{-1}$
27. **(b)** Concept of thermal capacity is, the heat required to raise the temperature of a body.
28. **(b)** $\Delta G = \Delta H - T\Delta S$, ΔG must be negative hence $\Delta H - T\Delta S$ must be negative
29. **(a)** $\Delta G = \Delta H - T\Delta S = -2.5 \times 10^3 - 298 \times 7.4 = -ve$, hence spontaneous.
30. **(b)** $q_p = \Delta H$ (Enthalpy)

31. (c) Endothermic process, increase in entropy, $\Delta H = +ve, \Delta S = +ve$

32. (a) $\Delta G = \Delta H - T\Delta S$, ΔH + ve, ΔS is + ve; $T\Delta S > \Delta H$ for spontaneous process. It will make ΔG, –ve

33. (a) Third law of Thermodynamics.

34. (b) High pressure reduces volume, decreases entropy, hence ΔS negative.

35. (a) For spontaneous process, ΔS_{total} is +ve.

36. (c) Third law of thermodynamics is due to Nernst.

37. (a) $\Delta S = \frac{\Delta H}{T} = \frac{900 \times 18}{373} = 43.4\,J\,K^{-1}\,mol^{-1}$

38. (d) $\Delta S^\circ = 2S^\circ_{HCl} - (S^\circ_{H_2} + S^\circ_{Cl_2})$

$= 2 \times 186.7 - (130.6 + 223.0)$

$= 19.8\,JK^{-1}mol^{-1}$

39. (b) $\Delta S = \frac{2.257 \times 18}{373} = 0.109\text{ kJ }K^{-1}mol^{-1}$

40. (a) $\Delta G = \Delta H - T\Delta S$

41. (c) At equilibrium, $\Delta G = 0$

42. (d) $\Delta G = -RT\ln K_p$ or $K_p = e^{-\Delta G/RT}$

43. (d) Condition of equilibrium, hence $\Delta G = 0$

44. (a) Statement of third law.

45. (d) Calorific value of fat > carbohydrate and protein; Butter 34, Sugar 16, Egg 14.

46. (d) All values are same

47. (b) For one mole the value is - 22 kcal mol^{-1}

48. (b) $C + O_2 \to CO_2;\ \Delta H^\circ = -x\,kJ$.......(1)

$2CO + O_2 \to 2CO_2;\ \Delta H^\circ = -y\,kJ$......(2)

multiply equation (1) by 2 and substract equation (2) and divide final equation by 2

49. (b) 57.3 – 55.4 = 1.9 kJ (57.3 kJ is heat of neutralisation of strong acid and strong base)

50. (d) It is infact the formation of one molecule of H_2O always

$(H^+ + OH^- \longrightarrow H_2O)$

51. (c) Neutralisation of weak acid with strong base hence < x. Extra heat is utilised to effect the ionisation of weak acid.

52. (a) Equation (1) – Equation (2) gives

$S + O_2 \to SO_2, \Delta H = (y - 2x)$

53. (c) It is always = – 57.32 + ionisation of weak acid

54. (b) Desired eqn; $C_2H_4 + 3O_2 \to 2CO_2 + 2H_2O$

$\Delta H = 2(-394) + 2(-286) - (52) = -1412\,kJ$

55. (c) $CaO + H_2O \to Ca(OH)_2$; Exothermic process.

56. (d) Energy of isolated system is constant.

57. (d)

58. (a) Depending upon the value of $T\Delta S$, ΔG can be lesser, equal or greater to ΔH

59. (b) The more the energy, the lesser is the stability.

60. (a) $CH_4 + 2O_2 \to CO_2 + 2H_2O; \Delta H = 20\,kcal$........(1)

$C + O_2 \to CO_2;\ \Delta H = -40\,kcal$.....(2)

$2H_2 + O_2 \to 2H_2O\ ; \Delta H = -20\,kcal$........(3)

(2) + (3) – (1) we have, $C + 2H_2 \to CH_4$

or $\Delta H = -20 + (-40) - (-20) = -40\,kcal$

61. (c) ΔH for two moles = –194kJ. For one mole $= \frac{-194}{2} = -97\,kJ$

62. (c) Enthalpy of neutralisation of HCl with NaOH is x. In question gev of HCl

$\left(\frac{500 \times 2}{1000} = 1\,gev\right)$ and NaOH $\left(\frac{250 \times 4}{1000} = 1\,gev\right)$ hence the value x.

63. (c) Enthalpy of neutralisation is enthalpy change when 1 gev of acid is neutralised by 1 gev of base. In question, 2 gev of H_2SO_4 is being neutralised. Hence enthalpy of neutralisation is $\frac{-114.64}{2} = -57.32\,kJ$

64. (a) In question 0.01 gev of NaOH is being neutralised by 0.01 gev of HCl and value is x kJ, for 1 gev the value is -100x (exothermic process).

65. (b) $\Delta H = H^\circ_f\text{ (products)} - H^\circ_f\text{ (reactants)}$

$= -110.5 + (-241.8) - (-393.5 + 0) = 41.2\,kJ$

66. (c) Add equation (I) and (II) divide by 2 the equation obtained $-44 + (-152) = \frac{.-196}{2} = -98\,kcal$

67. (a) Lavoisier and Laplace law.

EXERCISE 3

1. (d) This reaction shows the formation of H_2O, and the $-X_2$ represents the enthalpy of formation of H_2O because as the definition suggests that the enthalpy of formation is the heat evolved or absorbed when one mole of substance is formed from its constituent elements.

2. (b) $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow HCl$

$\Delta_f H_{HCl} = \sum \text{B.E. of reactants} - \sum \text{B.E. of products}$

$-90 = \frac{1}{2} \times 430 + \frac{1}{2} \times 240 - \text{B.E. of HCl}$

$\therefore$ B.E. of HCl = 215 + 120 + 90

$= 425\text{ kJ mol}^{-1}$

3. (d) We know that heat (q) and work (w) are not state functions but (q + w) is a state function. H – TS (i.e. G) is also a state function. Thus II and III are not state functions so the correct answer is option (d).

4. (b) For the reaction

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

The reaction given is an example of decomposition reaction and we know that decomposition reactions are endothermic in nature, i.e., $\Delta H > 0$.

Further

$\Delta n = (1+1) - 1 = +1$

Hence more number of gaseous molecules are present in products which shows more randomness i.e., $\Delta S > 0$ (ΔS is positive)

5. **(c)** The reaction for formation of HCl can be written as

$H_2 + Cl_2 \rightarrow 2HCI$

$H-H + Cl-Cl \rightarrow 2\,(H-Cl)$

Substituting the given values, we get enthalpy of formation of

$2HCl = (676 - 862) = -186$ kJ.

$\therefore$ Enthalpy of formation of HCl $= \frac{-186}{2}$ kJ $= -93$ kJ.

6. **(b)** $\Delta G = \Delta H - T\,\Delta S$

At equilibrium, $\Delta G = 0$

$\Rightarrow 0 = (170 \times 10^3\ J) - T\,(170\ JK^{-1})$

$\Rightarrow T = 1000\ K$

For spontaneity, ΔG is – ve, which is possible only if $T > 1000\ K$.

7. **(b)** Enthalpy of reaction

$= B.E_{(Reactant)} - B.E_{(Product)}$

$= \left[B.E_{(C=C)} + 4\,B.E._{(C-H)} + B.E._{(H-H)}\right]$

$-\left[B.E._{(C-C)} + 6\,B.E._{(C-H)}\right]$

$= [606.1 + (4 \times 410.5) + 431.37)] - [336.49 + (6 \times 410.5)]$

$= -120.0\ kJ\ mol^{-1}$

8. **(a)** ΔS for the reaction $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3$

$\Delta S = 50 - (30 + 60) = -40$ J

For equilibrium $\Delta G = 0 = \Delta H - T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{-30000}{-40} = 750\ K$$

9. **(d)** $H_2O(\ell) \xrightleftharpoons{1atm} H_2O(g)$

$\Delta H = 40630\ J\,mol^{-1}$

$\Delta S = 108.8\ JK^{-1}\ mol^{-1}$

$\Delta G = \Delta H - T\Delta S$ When $\Delta G = 0$,

$\Delta H - T\Delta S = 0$

$$T = \frac{\Delta H}{\Delta S} = \frac{40630\ J\,mol^{-1}}{108.8\ Jk^{-1}\ mol^{-1}} = 373.4\ K.$$

$\therefore$ Correct choice : (d)

10. **(d)**

(1)	$K_p > 0$	(iv)	Spontaneous
(2)	$\Delta G < RT\,\ln Q$	(i)	Non spontaneous
(3)	$K_p = 0$	(ii)	Equilibrium
(4)	$T > \frac{\Delta H}{\Delta S}$	(iii)	Spontaneous and endothermic

11. **(a)** $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$;
$\Delta H = -26.8$ KJ ...(i)

$FeO(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$;
$\Delta H = -16.5$ KJ ...(ii)

eq. (i) – 2 × eq. (ii), we get

$Fe_2O_3(s) + CO(g) \longrightarrow 2FeO(s) + CO_2(g)$

$\Delta H = -26.8 + 33.0 = +6.2$ kJ

12. **(a)** Ideal gas during spontaneous expansion into vacuum does not do any external work.

13. **(d)** Given $\Delta H = 30\ kJ\ mol^{-1}$ $T = 273 + 27 = 300\ K$

$$\Delta S_T = \frac{\Delta H_T}{T} = \frac{3 \times 10^4}{300}\ J\,mol^{-1}$$

$= 100\ J\ mol^{-1}\ K^{-1}$

14. **(c)** Given

$4H(g) \longrightarrow 2H_2(g);\ \Delta H = -869.6$ kJ

or $2H_2(g) \longrightarrow 4H(g);\ \Delta H = 869.6$ kJ

$H_2(g) \longrightarrow 2H(g);\ \Delta H = \frac{869.6}{2} = 434.8$ kJ

15. **(b)**

Given	ΔH	
$\frac{1}{2}A \longrightarrow B$	+150	...(1)
$3B \longrightarrow 2C + D$	–125	...(2)
$E + A \longrightarrow 2D$	+350	...(3)

To calculate ΔH operate

2 × eq. (1) + eq. (2) – eq. (3)

$\Delta H = 300 - 125 - 350 = -175$

16. **(a)** Since, in the first reaction value of Δn is positive.

$\Delta n = 1 - \frac{1}{2} = \frac{1}{2}$ hence entropy will increase i.e., $\Delta s = +ve$.

$C\,(gr.) + \frac{1}{2}\,O_2(g) \rightarrow CO(g);\ \Delta S° = +ve$

Since, $\Delta G° = \Delta H° - T\Delta S$ hence the value of ΔG decreases on increasing temperature.

17. **(c)** $\Delta S = \frac{\Delta H}{T} = \frac{1.435 \times 10^3}{273}$

$= 5.260$ cal / molK

18. **(d)** $H_2O\ (\ell) \rightleftharpoons H_2O\ (g)$ $\Delta H = 40.66\ KJmol^{-1}$

$T = 373\ K$

$\Delta E = \Delta H - \Delta nRT$

$= 40.66 \times 10^3\ Jmol^{-1} - 1 \times 8.314 JK^{-1} mol^{-1} \times 373\ K$

$\Delta E = 37558$ J / mol

$\Delta E = 37.56\ kJ\ mol^{-1}$

19. **(d)** $$\frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$$

20. **(b)** $\Delta H = E_{a_f} - E_{a_b} = 0$

21. (b) At low temperature the ΔS is – ve which makes ΔG positive ($\Delta G = \Delta H - T\Delta S$). But at higher temperature ΔS is +ve which makes the ΔG negative (condition for spontaneity)

22. (d) It violate 2nd law of thermodynamics, not 1st.

23. (d) ΔH negative shows that the reaction is spontaneous. Higher value for Zn shows that the reaction is more feasible.

24. (c) For a cyclic process the net change in the internal energy is zero because the change in internal energy does not depend on the path.

25. (c) $CH_2 = CH_2\,(g) + H_2\,(g) \rightarrow CH_3 - CH_3\,(g)$

$\Delta H = 1(C=C) + 4(C-H) + 1(H-H) - 1(C-C) - 6(C-H)$

$= 1(C=C) + 1(H-H) - 1(C-C) - 2(C-H)$

$= 615 + 435 - 347 - 2 \times 414 = 1050 - 1175 = -125\ \text{kJ}.$

26. (a) For spontaneous reaction, $dS > 0$ and ΔG and ΔG should be negative i.e. < 0.

27. (c) $\Delta G^o = -RT\ln K_c$ or $-\Delta G^o = RT\ln K_c$

28. (b) Enthalpy change for a reaction does not depend upon the nature of intermediate reaction steps.

29. (c) $W = -P\Delta V = -10^{-5}(1\times10^{-2} - 1\times10^{-3}) = -900\text{J}$

30. (b)

(i) $C + O_2 \rightleftharpoons CO_2;\ \Delta H = -393.5\ \text{kJmol}^{-1}$

(ii) $CO + \frac{1}{2}O_2 \rightleftharpoons CO_2;\ \Delta H - -283.0\ \text{kJmol}^{-1}$

After,
(i) - (ii),
We have

$$C + \frac{1}{2}O_2 \rightarrow CO \quad \Delta H = -110.5\ \text{kJmol}^{-1}$$

31. (d) For spontaneous reaction ΔG should be negative. Equilibrium constant should be more than one ($\Delta G = -2.303\,RT\log K_c$, If $K_c = 1$ then $\Delta G = 0$; If $K_c < 1$ then ΔG = +ve). Again $\Delta G = -nFE^o_{cell} \cdot E^o_{cell}$ must be +ve to have ΔG –ve.

32. (b) $\Delta H = \Delta U + \Delta nRT$ for $N_2 + 3H_2 \longrightarrow 2NH_3$

$\Delta n_g = 2 - 4 = -2$

$\therefore \Delta H = \Delta U - 2RT$ or $\Delta U = \Delta H + 2RT \quad \therefore \Delta U > \Delta H$

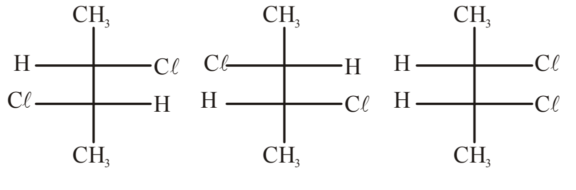
33. (N) $X_2 + Y_2 \longrightarrow 2XY,\ \Delta H = 2(-200).$

Let x be the bond dissociation energy of X_2.
Then

$$\Delta H = -400 = \xi_{x-x} + \xi_{y-y} - 2\xi_{x-y} = x + 0.5x - 2x = -0.5x$$

$$\text{or } x = \frac{400}{0.5} = 800\ \text{kJ mol}^{-1}$$

(In the question paper, this option was not mentioned. So the answer has been marked 'N')



34. (c) In a reversible process the work done is greater than in irreversible process. Hence the heat absorbed in reversible process would be greater than in the latter case. So

$$T_f(\text{rev.}) < T_f(\text{irr.})$$

35. (c) The standard enthalpy of formation of CH_4 is given by the equation :

$$C(s) + 2H_2(g) \longrightarrow CH_4(g)$$

Hence, dissociation energy of hydrogen and enthalpy of sublimation of carbon is required.

36. (a) $I_2(s) + Cl_2(g) \longrightarrow 2ICl(g)$

$\Delta H = [\Delta H_{I_2(s) \longrightarrow I_2(g)} + \Delta H_{I-I} + \Delta H Cl-Cl]$
$- [\Delta H I - Cl]$

$= 151.0 + 242.3 + 62.76 - 2 \times 211.3 = 33.46$

$$\Delta H^o_{f\,(ICl)} = \frac{33.46}{2} = 16.73\ \text{kJ/mol}$$

37. (d) $C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO\,(g)$

$\Delta H - \Delta U = \Delta nRT$

$$= \frac{1}{2} \times 8.314 \times 298 = 1238.78\ \text{J mol}^{-1}$$

38. (a) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

For a spontaneous reaction $\Delta G^\circ < 0$

or $\Delta H^\circ - T\Delta S^\circ < 0 \Rightarrow T > \frac{\Delta H^\circ}{\Delta S^\circ}$

$$\Rightarrow T > \frac{179.1\times10^3}{160.2} > 1117.9\text{K} \approx 1118\text{K}$$

39. (d) Given $\Delta H = 41\ \text{kJ mol}^{-1} = 41000\ \text{J mol}^{-1}$

$T = 100°C = 273 + 100 = 373\ \text{K}$

$n = 1$

$\Delta U = \Delta H - \Delta nRT = 41000 - (1 \times 8.314 \times 373)$

$= 37898.88\ \text{J mol}^{-1} \simeq 37.9\ \text{kJmol}^{-1}$

40. (b) Spontaneity of reaction depends on tendency to acquire minimum energy state and maximum randomness. For a spontaneous process in an isolated system the change in entropy is positive.

41. (b) The energy involved in the conversion of $\frac{1}{2}Cl_2(g)$ to $Cl^{-1}(aq)$ is given by

$$\Delta H = \frac{1}{2}\Delta_{diss}H^{\ominus}_{Cl_2} + \Delta_{eg}H^{\ominus}_{Cl} + \Delta_{hyd}H^{\ominus}_{Cl}$$

Substituting various values from given data, we get

$$\Delta H = \left(\frac{1}{2}\times240\right) + (-349) + (-381)\ \text{kJmol}^{-1}$$

$= (120 - 349 - 381)\ \text{kJ mol}^{-1} = -610\ \text{kJ mol}^{-1}$

i.e., the correct answer is (b)

42. (a) Given, for reaction

(i) $H_2O(\ell) \longrightarrow H^+(aq.) + OH^-(aq.);$

$$\Delta H_r = 57.32\ \text{kJ}$$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell);$

$$\Delta H_r = -286.20\ \text{kJ}$$

For reaction (i)

$$\Delta H_r = \Delta H^\circ_f(H^+.aq) + \Delta H^\circ_f(OH^-.aq) - \Delta H^\circ_f(H_2O, \ell)$$

$$57.32 = 0 + \Delta H^\circ_f(OH^-, aq) - \Delta H^\circ_f(H_2O, \ell) \quad ...(iii)$$

For reaction (ii)

$$\Delta H_r = \Delta H^\circ_f(H_2O, \ell) - \Delta H^\circ_f(H_2, g) - \frac{1}{2}\Delta H^\circ_f(O_2, g)$$

$$-286.20 = \Delta H^\circ_f(H_2O, \ell)$$

On replacing this value in eq. (iii) we have

$$57.32 = \Delta H^\circ_f(OH^-, aq) - (-286.20)$$

$$\Delta H^\circ_f(OH^-, aq) = -286.20 + 57.32$$

$$= -228.88 \text{ kJ}$$

43. (b) $N_2 + 3H_2 \longrightarrow 2NH_3 \quad \Delta H = 2 \times -46.0 \text{ kJ mol}^{-1}$

Let x be the bond enthalpy of N – H bond then

[**Note :** Enthalpy of formation or bond formation enthalpy is given which is negative but the given reaction involves bond breaking hence values should be taken as positive.]

$\Delta H = \Sigma$ Bond energies of reactants – Σ Bond energies of products

$2 \times -46 = 712 + 3 \times (436) - 6x$

$-92 = 2020 - 6x$

$6x = 2020 + 92$

$6x = 2112$

$x = +352$ kJ/mol

44. (b) At equilibrium $\Delta G = 0$

Hence, $\Delta G = \Delta H - T_e\Delta S = 0$

$$\therefore \Delta H = T_e\Delta S \quad \text{or} \quad T_e = \frac{\Delta H}{\Delta S}$$

For a spontaneous reaction

ΔG must be negative which is possible only if $\Delta H - T\Delta S < 0$

$\therefore \Delta H < T\Delta S$

$$\text{or } T > \frac{\Delta H}{\Delta S};\ T_e < T$$

45. (b) $C_2H_5OH(\ell) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$

$$\Delta n_g = 2 - 3 = -1$$

$$\Delta U = \Delta H - \Delta n_g RT$$

$$= -1366.5 - (-1) \times \frac{8.314}{10^3} \times 300$$

$$= -1366.5 + (1) \times \frac{8.314}{10^3} \times 300$$

$$= -1366.5 + 0.8314 \times 3 = -1364.006 \text{ kJ}$$

46. (d)

$$\begin{tikzcd}
4NO_2(g) + O_2(g) \arrow[r] \arrow[dr, "\Delta H'"'] & 2N_2O_5(g), \Delta_r H = -111 \text{ kJ} \arrow[d, "-54 \text{ kJ}"] \\
& 2N_2O_5(s)
\end{tikzcd}$$

$-111 - 54 = \Delta H'$

$\Delta H' = -165$ kJ

47. (a) Process is isothermal reversible expansion, hence $\Delta U = 0$, therefore $q = -W$.

Since $q = +208$ J, $W = -208$ J

48. (b) $A \rightleftharpoons B$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ = -2.303 \text{ RT} \log_{10} K$

$-2.303 \text{ RT} \log_{10} K = \Delta H^\circ - T\Delta S^\circ$

$2.303 \text{ RT} \log_{10} K = T\Delta S^\circ - \Delta H^\circ$

$$\log_{10} K = \frac{T\Delta S^\circ - \Delta H^\circ}{2.303RT} = \frac{298 \times 10 + 54.07 \times 1000}{2.303 \times 8.314 \times 298}$$

$= 9.998 \approx 10$

49. (a) Since, liquid is passing into gaseous phase so entropy will increase and at 373 K during the phase transformation it remains at equilibrium. So, $\Delta G = 0$.

50. (b) The species in its elemental form has zero standard molar enthalpy of formation at 298 K. At 298K, Cl_2 is gas while Br_2 is liquid.

51. (d) (i) $2C(s) + H_2(g) \longrightarrow H-C \equiv C-H(g)$

$\Delta H = 225 \text{ kJ mol}^{-1}$

(ii) $2C(s) \longrightarrow 2C(g)$

$\Delta H = 1410 \text{ kJ mol}^{-1}$

$$C(s) \longrightarrow C(g) \Delta H = \frac{1410}{2} = 705 \text{kJmol}^{-1}$$

(iii) $H_2(g) \longrightarrow 2H(g)$

$\Delta H = 330 \text{ kJ mol}^{-1}$

From equation (i) :

$$225 = \left[2 \times \Delta H_{C(s) \longrightarrow C(g)} + 1 \times BE_{H-H}\right] - [2 \times BE_{C-H} + 1 \times BE_{C\equiv C}]$$

$225 = [1410 + 1 \times 330] - [2 \times 350 + 1 \times BE_{C\equiv C}]$

$225 = [1410 + 330] - [700 + BE_{C\equiv C}]$

$225 = 1740 - 700 - BE_{C\equiv C}$

$BE_{C\equiv C} = 815 \text{ kJ mol}^{-1}$

52. (c) The standard enthalpy of the combustion of glucose can be calculated by the eqn.

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

$\Delta H_C = 6 \times \Delta H_f(CO_2) + 6 \times \Delta H_f(H_2O) - \Delta H_f[C_6H_{12}O_6]$

$\Delta H^\circ = 6(-400) + 6(-300) - (-1300)$

$\Delta H^\circ = -2900$ kJ/mol

For one gram of glucose, enthalpy of combustion

$$\Delta H^\circ = -\frac{2900}{180} = -16.11 \text{ kJ / gm}$$

EXERCISE 4

1. **(c)** The criteria for the spontaneity, ΔS system + ΔS surroundings, must be + ve
2. **(c)** $\Delta G = \Delta H - T\Delta S$. For spontaneous process $\Delta G < 0$. To get $\Delta G < 0$. we must have $\Delta H < 0$; $\Delta S > 0$
3. **(d)** $\Delta S = \frac{\Delta H_{\text{fusion}}}{T}; \Delta S = \frac{6.02\times10^3}{273} = 22.0 \text{ JK}^{-1} \text{ mol}^{-1}$
4. **(c)** Examine the chemical equations . If there is decrease in number of moles of gaseous products, the entropy will decrease and vice versa.
5. **(a)** Gaseous ions, when dissolved in water, get hydrated and heat is evolved (heat of hydration).

   $Cl^-(g) + aq \rightarrow Cl^-(aq)$ is such reaction .
6. **(b)** Write the proper chemical equations.

   $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$

   $\Delta H = -393\text{kJ}$ ....(i)

   $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

   $\Delta H = -286\text{kJ}$ ....(ii)

   $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
   $\Delta H = -1360\text{kJ}$ ....(iii)

   From $(2\times I + 3\times II) - (III)$ we get

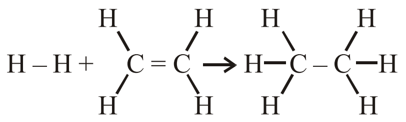
   $$2C + 3H_2 + \frac{1}{2}O_2 \rightarrow C_2H_5OH$$

   $\therefore 2(-393\text{kJ}) + 3(-286\text{kJ}) - (-1360\text{kJ}) = -284\text{kJ}$
7. **(d)** $C_6H_6\ (l) + \frac{15}{2}O_2\ (g) \rightarrow 6CO_2\ (g) + 3H_2O\ (l)$

   $\Delta n = 6 - 15/2 = -3/2$
8. **(c)** C is incorrect ; The correct is $\Delta E = \Delta q + \Delta w$
9. **(b)** $\Delta G = \Delta H - T\Delta S$

   $\therefore \Delta G = 9100 - 373.2\times25.5 = -416.6 \text{ cal mol}^{-1}$
10. **(a)** I – II, gives, $2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$

    we have $-400 - (-200) = -200$; For one mole of iron the value is –100 cal
11. **(c)**
12. **(b)** Enthalpy change = (Energy required for breaking of bonds – Energy evolved by formation of bonds)

    $$\begin{matrix} H{-}H \\ C{=}C \end{matrix}\begin{pmatrix} 103 \\ 145 \end{pmatrix} - \begin{pmatrix} 80 \\ 2\times99 \end{pmatrix}\begin{matrix} C{-}C \\ C{-}H \end{matrix} = -30 \text{ kcal mol}^{-1}$$
13. **(d)** $\Delta G = \Delta H - T\Delta S$; At equilibrium $\Delta G = 0$; $\Delta H = T\Delta S$;

    $$T = \frac{\Delta H}{\Delta S}$$

    $$T = \frac{45000}{1.2\times10^2} = 375\text{K}$$
14. **(c)** The third law of thermodynamics is about entropy.
15. **(c)** 16. **(a)**
17. **(d)** It is neutralisation of strong acid with strong base.
18. **(b)** Dissolution of KNO_3 is endothermic, hence heat is absorbed and cooling is observed.
19. **(a)** Isobutane + oxygen $\rightarrow CO_2 + H_2O$

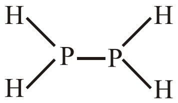
    $\Delta H = -2870 \text{ kJ mol}^{-1}$ ......(i)

    n-butane + oxygen $\rightarrow CO_2 + H_2O$

    $\Delta H = -2878 \text{ kJ mol}^{-1}$ ....(ii)

    (ii) - (i); n-butane – Isobutane,
    $\Delta H = (-2878 + 2870)$
    $= -8 \text{ kJ mol}^{-1}$.
20. **(d)** Apply Kirchoff's equation $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C_p - C_R = \Delta C_p$
21. **(b)** Bond dissociation energy of $PH_3(g) = 228 \text{ kcal mol}^{-1}$

    P – H bond energy $= \frac{228}{3} = 76 \text{ kcal mol}^{-1}$

    Bond energy of 4 (P – H) + (P –P) = 355 kcal mol^{-1}
    or 4 × 76 + (P – P) = 355 kcal mol^{-1}
    P–P bond energy = 51 kcal mol^{-1}
22. **(a)** ΔH° solution = U (lattice energy) + ΔH° hydration
23. **(b)** $\Delta H^\circ = \Delta U^\circ + \Delta nRT$

    $$\Delta H^\circ = -772.7 + \frac{5\times8.314\times298}{1000} = -760.3 \text{ kJ mol}^{-1}$$
24. **(d)** $\underset{\substack{98\\49}}{H_2SO_4} + \underset{\substack{112\\56}}{2KOH} \rightarrow \underset{\substack{174\\87}}{K_2SO_4} + \underset{\substack{2\text{ mole}\\1\text{ mole}}}{2H_2O}$

    13.7 kcal is the heat evolved when 1 gev of strong acid is neutralised by 1 gev of strong base.
25. **(a)** The first reaction is exothermic and the second reaction is endothermic. If on passing the mixture of O_2 and H_2O (steam) over coke while keeping the temperature constant ΔH of both the reactions must be same.

    Moles of O_2 needed to evolve 132 kJ

    $$= \frac{0.5\times132}{110} = 0.6$$

    Hence steam : O_2 ratio must be 1 : 0.6
26. **(d)** $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O\ (l)$;

    $\Delta H = -285.8\text{ kJ}$ .... (i)

    $H^+(aq) + OH^-(aq) \longrightarrow H_2O\ (l)$;

    $\Delta H = -57.3\text{ kJ}$ ... (ii)

    $\frac{1}{2}H_2(g) + aq \longrightarrow H^+\ (aq) + e^-$; $\Delta H = 0$

    (by convention) .... (iii)

(i) – (ii) – (iii) gives,

$$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) + e^- + aq \longrightarrow OH^-(aq)$$

$\Delta H = -285.8 + 57.3 = -228.5$ kJ

27. (b) For 5 moles of gas at temperature T,

$PV_1 = 5RT$

For 5 moles of gas at temperature T – 2,

$PV_2 = 5R(T-2)$

$\therefore \quad P(V_2 - V_1) = 5R(T-2-T);$

$P\Delta V = -10R,$

$-P\Delta V = 10R$

When ΔV is negative, W is + ve.

28. (d) $P_1V_1 = P_2V_2$

$$\therefore \quad V = \frac{5\text{bar} \times 2\text{dm}^3}{1\text{bar}} = 10 \text{ dm}^3$$

Work, $W = -P_{ext}((V_{final} - V_{initial})$

$= -1 \text{ bar}(10-2)$

$= -1 \times 10^5 \text{ Pa} \times 8 \times 10^{-3} \text{m}^3$

$= -800$ J

29. (c) Ozone is allotropic form of oxygen and is of higher energy (by 68 kcal mol^{-1}) than O_2. Hence it cannot be taken as the reference a standard state.

30. (a) $\frac{1}{2}H_2 + \frac{1}{2}X_2 \longrightarrow HX$

Let the bond enthalpy of X – X bond be x.

$$\Delta H_f(HX) = -50 = \frac{1}{2}\Delta H_{H-H} + \frac{1}{2}\Delta H_{X-X} - \Delta H_{H-X}$$

$$= \frac{1}{2}2x + \frac{1}{2}x - 2x = \frac{-x}{2}$$

$\therefore \quad x = 50 \times 2 = 100 \text{ kJ mol}^{-1}$

31. (c) $H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l); \Delta H = -57.3 \text{ kJ} \ldots \text{(i)}$

$H_2C_2O_4 + 2OH^- \rightleftharpoons C_2O_4^{--} + 2H_2O; \Delta H = -106 \text{ kJ}$ ...... (ii)

For the second reaction the value should have been $2 \times (-57.3) = -114.6$ kJ

The difference (114.6 – 106) = 8.6 kJ mol^{-1} is used to effect of the ionisation of oxalic acid.

32. (a) After the event the energy remained in the body of the athlete $= \frac{1560}{2} = 780$ kJ

$\therefore$ Weight of water to be evaporated by 780 kJ of energy

$$= \frac{18}{44} \times 780 = 319.1 \text{ g}$$

33. (a) $CuSO_4(s) + 5H_2O(g) \longrightarrow CuSO_4.5H_2O(s);$

$\Delta H = -71.5$ kcal .... (i)

$5H_2O(l) \rightarrow 5H_2O(g);$

$\Delta H = 5 \times 10.5$ k cal = 52.5 kcal .... (ii)

(i) + (ii),

$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4.5H_2O(s)$

$\Delta H = -71.5 + 52.5 = -19.0 \text{ kcal mol}^{-1}$

34. (a) $\Delta H_{hyd.} = \Delta H_{sol.} - \Delta H_{lattice}$

$= 1 - 180 = -179 \text{ kcal mol}^{-1}$

Then $\Delta H_{hyd.}(Na^+) + \Delta H_{hyd.}(Cl^-) = -179$

or $\quad \Delta H_{hyd.}(Na^+) + \frac{2}{3}\text{ hyd.}(Na^+) = -179$

or $\Delta H_{hyd.}(Na^+) = -107.4 \text{ kcal mol}^{-1}$

35. (a) $\Delta C_p = 2 \times 25.1 + 3 \times 75.3 - [103.8 + 3 \times 28.8]$

$= 85.9 \text{ J K}^{-1}\text{mol}^{-1}$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p;$$

$$\frac{\Delta H_2 - (-33290)}{358 - 298} = 85.9$$

$\Delta H = -28136 \text{ J mol}^{-1}$

$= -28.136 \text{ kJ mol}^{-1}$

36. (d) $\frac{1}{2}N_2(g) + \frac{3}{2}F_2(g) \longrightarrow NF_3; \ \Delta H = -113$ kJ

or $\quad \Delta H_{N\equiv N} + \frac{3}{2}\Delta H_{F-F} - 3\Delta H_{N-F} = -113$ kJ

Let x kJ mol^{-1} be the bond energy of F – F bond then bond energy of N ≡ N bond = 6x

$$\therefore \quad \frac{1}{2} \times 6x + \frac{3}{2} \times x - 3 \times 273 = -113 \text{ kJ}$$

On solving,

$x = 156.9 \text{ kJ mol}^{-1}$ and

$N \equiv N$ bond energy $= 6 \times 156.9 = 941.4 \text{ kJ mol}^{-1}$

37. (b) ΔH_N for strong base and strong acid

$= -13.7 \text{ kcal eq}^{-1}$

$\Delta H_{ion}(CH_3COOH)$

$= -12.5 - (-13.7) = 1.2 \text{ kcal mol}^{-1}$

$\Delta H_{ion}(NH_4OH)$

$= -10.5 - (-13.7) - \Delta H_{ion}(CH_3COOH)$

$= 13.7 - 10.5 - 1.2$

$= 2 \text{ kcal mol}^{-1}$

38. (a) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$\Delta H = -890\,kJ$ .... (i)

$2H_2O(l) \longrightarrow 2H_2O(g);$

$\Delta H = 2 \times 40.5 = 81\,kJ$ .... (ii)

From (i) + (ii), we get

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

$\Delta H = -890 + 81 = -809\,kJ$

39. (c) By bomb calorimeter we get ΔE.

$2C_6H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(l)$

$\Delta H - \Delta E = \Delta nRT$

$= (12 - 15) \times 8.314 \times 300 = -7.483\,kJ$

40. (a) The greater the (negative value) of heat of neutralisation, the more is the strength of the acid. Hence,

$HCOOH > CH_3COOH > H_2S > HCN$

41. (b) $H_2O(l) \longrightarrow H_2O(g) \quad \Delta H = 40.8\ kJ\,mol^{-1}$

Hence for

$H_2O(g) \longrightarrow H_2O(l) \quad \Delta H = -40.8\ kJ\,mol^{-1}$

$$\Delta H = -40.8 \times \frac{1.8}{18} = -4.08\,kJ$$

$$\Delta S = \frac{\Delta H}{T} = -\frac{4.08 \times 10^3}{373.15} = -10.93\ JK^{-1}$$

42. (b) The enthalpy of ionisation of weak acid is given by

$\Delta H_{ion(HA)}$

$= \Delta H_{N(weak\,acid/strong\,base)} - \Delta H_{N(strong\,acid/strong\,base)}$

$= -56.1 - (-57.3) = 1.2\ kJ\,mol^{-1}$

$\Delta H_{(ionisation)} = 1.5\ kJ\,mol^{-1}$

Hence % ionisation in 1 M solution

$$= \frac{(1.5 - 1.2)}{1.5} \times 100 = 20$$

43. (b) Atomisation of methane

$CH_4(g) \longrightarrow C(g) + 4H(g); \quad \Delta H = 360\,kcal$

$\therefore \quad C - H \text{ bond energy} = \frac{360}{4} = 90\,kcal\,mol^{-1}$

$C_2H_6(g) \longrightarrow 2C(g) + 6H(g); \quad \Delta H = 620\,kcal$

or $H_{C-C} + 6H_{C-H} = 620$

$\therefore \quad H_{C-C} = 620 - 6H_{C-H}$

$= 620 - 6 \times 90 = 80\,kcal$

44. (a) For non spontaneous reaction

$\Delta G = +ve$

$\Delta G = \Delta H - T\Delta S$ and

$\Delta S = 121\ JK^{-1}$

For $\Delta G = +ve$

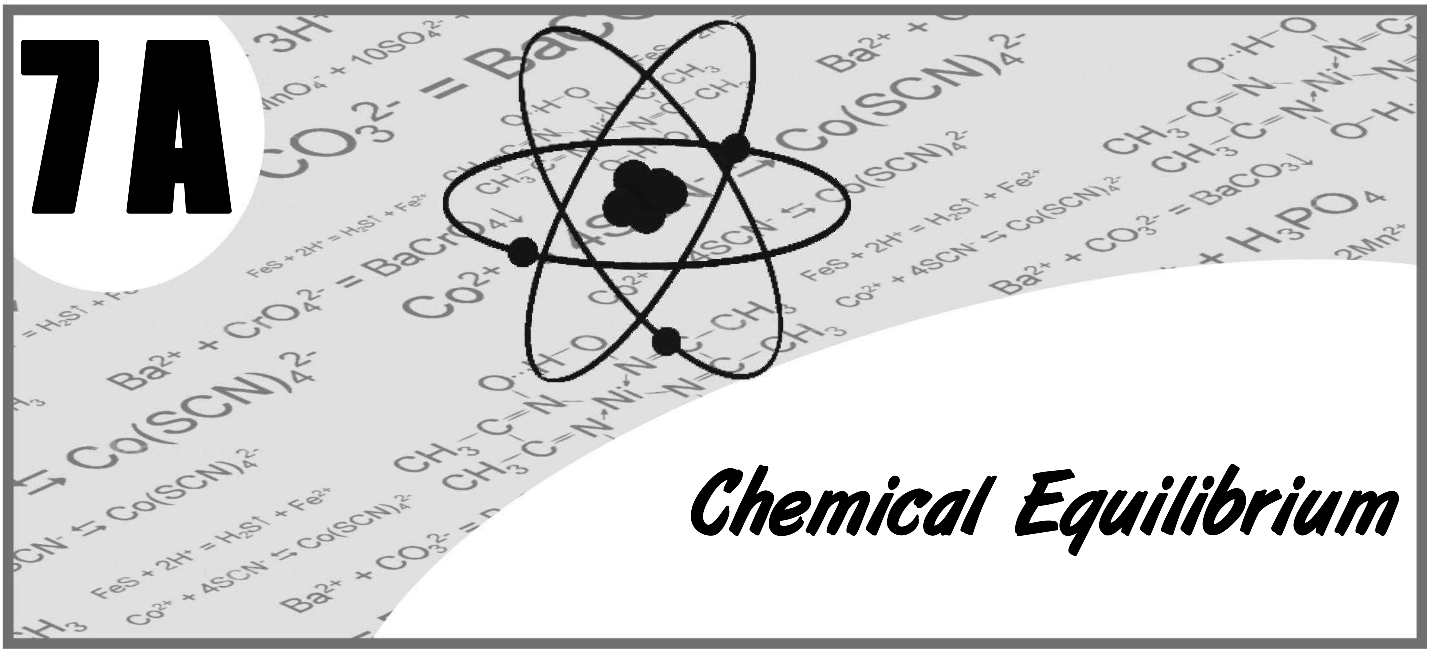
ΔH has to be positive. Hence the reaction is endothermic.

The minimum value of ΔH can be obtained by putting

$\Delta G = 0$

$\Delta H = T\Delta S = 298 \times 121\,J$

$= 36.06\,kJ$



7A

Chemical Equilibrium

REVERSIBLE REACTIONS :

Reactions which do not always proceed to completion and may be made to proceed in the opposite direction under suitable conditions are called reversible reactions e.g.

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

$$H_2 + I_2 \rightleftharpoons 2HI$$

$$N_2O_4 \rightleftharpoons 2NO_2$$

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

IRREVERSIBLE REACTIONS :

Reactions which always proceed to completion in one direction only are called irreversible reactions.

$$\left.\begin{aligned} AgNO_3 + HCl &\longrightarrow AgCl + HNO_3 \\ BaCl_2 + Na_2SO_4 &\longrightarrow BaSO_4 + 2NaCl \end{aligned}\right\} \text{Precipitation}$$

$$NaOH + HCl \longrightarrow NaCl + H_2O \quad \text{Neutralisation}$$

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2 \quad \text{Decomposition}$$

CHEMICAL EQUILIBRIUM :

When a reversible reaction is carried out in a closed vessel a stage reached when the speed of the forward reaction equals the speed of the backward reaction and chemical equilibrium is said to be established.

CHARACTERISTICS OF CHEMICAL EQUILIBRIUM :

(i) Equilibrium can be attained from either side.

(ii) Equilibrium is dynamic in nature i.e. at equilibrium, reaction does not stop.

(iii) At equilibrium there is no change in the concentration of various species.

(iv) The equilibrium state remains uneffected by the presence of catalyst. Catalyst helps to attain the equilibrium state rapidly.

(v) It can be achieved in a closed container.

(vi) The observable properties of the process become constant and remain unchanged.

EQUILIBRIUM STATE AND FREE ENERGY CHANGE:

At equilibrium ΔG is equal to zero and we have

$\Delta G = \Delta H - T\Delta S \qquad \therefore \ \Delta H = T\Delta S$

LAW OF MASS ACTION :

It was put forward by **Guldberg and Waage**. The law states that the rate at which a substance reacts is directly proportional to its active mass and the rate of a chemical reaction is directly proportional to the product of the active masses of the reacting substances. For a general reaction

$$aA + bB \rightleftharpoons cC + dD$$

Rate of forward reaction $\propto [A]^a[B]^b = K_f[A]^a[B]^b$

Rate of backward reaction $\propto [C]^c[D]^d = K_b[C]^c[D]^d$

where K_f and K_b are velocity constants for forward and backward reactions respectively. At equilibrium point,

Rate of forward reaction = Rate of backward reaction

$$K_f[A]^a[B]^b = K_b[C]^c[D]^d$$

$$\frac{K_f}{K_b} = K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

K_c is called the equilibrium constant.

FACTORS INFLUENCING EQUILIBRIUM CONSTANT:

(i) The equilibrium constant is not influenced by :

(1) Concentration of reactants and products.

(2) Presence of a catalyst.

(3) Pressure.

(4) Presence of inert materials.

(5) The direction from which the equilibrium state is reached.

(ii) The equilibrium constant is influenced by :

(A) Temperature : The variation of equilibrium constant is given by Van't Hoff equation.

$$\log\frac{(K_p)_2}{(K_p)_1}=\frac{\Delta H}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

where ΔH = Enthalpy change, $(K_p)_1$ and $(K_p)_2$ = Equilibrium Constant at temperature T_1 & T_2

R = Universal gas Constant

For exothermic reaction : K_p decreases with increase of temperature since K_f decreases. $\left(K_p=\frac{K_f}{K_b}\right)$

For endothermic reaction. K_p increases with increase of temperature since K_f increases.

(B) The mode of representing the reaction :

The reaction $A+B \rightleftharpoons C+D$ may be written as

$$C+D \rightleftharpoons A+B$$

$$K_c=\frac{K_f}{K_b}=\frac{[C][D]}{[A][B]}$$

$$K'_c=\frac{K'_f}{K'_b}=\frac{[A][B]}{[C][D]} \qquad \therefore K_c=\frac{1}{K'_c}$$

(C) Stoichiometric representation of equation :

(I) $N_2+3H_2 \rightleftharpoons 2NH_3$

$$K_c=\frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$\frac{1}{2}N_2+\frac{3}{2}H_2 \rightleftharpoons NH_3$$

$$K'_c=\frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$$

$$\therefore \sqrt{K_c}=K'_c$$

USE OF PARTIAL PRESSURE INSTEAD OF CONCENTRATIONS :

For gaseous reacting substances partial pressures are conveniently used since at any fixed temperature partial pressure is directly proportional to concentration. For a general reaction

$$aA+bB \rightleftharpoons cC+dD$$

$$K_p=\frac{[P_C]^c\times[P_D]^d}{[P_A]^a\times[P_B]^b}$$

RELATION BETWEEN K_c AND K_p :

$$K_p=K_c[RT]^{\Delta n}$$

where

Δn = [moles of products – moles of reactants] gaseous only.

RELATION BETWEEN K_c AND K_p FOR DIFFERENT TYPES OF REACTIONS :

(i) When $\Delta n = 0$, $K_p = K_c$ e.g. for reaction $A \rightleftharpoons B$.
$[H_2(g)+I_2(g) \rightleftharpoons 2HI(g)]$

(ii) When $\Delta n = +ve$, $K_p > K_c$ e.g. for reaction $A \rightleftharpoons 2B$.
$[PCl_5(g) \rightleftharpoons PCl_3(g)+Cl_2(g)]$

(iii) When $\Delta n = -ve$, $K_p < K_c$ e.g. for reaction $2A \rightleftharpoons B$.
$[N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)]$

THE UNITS OF K_p AND K_c :

(i) Unit of $K_p = (atm)^{\Delta n}$

(ii) Unit of $K_c = (mol\ lit^{-1})^{\Delta n}$

CHARACTERISTICS OF EQUILIBRIUM CONSTANT :

1. It has definite value for every chemical reaction at a particular temperature
2. The more is the value of K_c or K_p, the more is the completion of reaction or the more is the concentration of products.
3. When the reaction can be expressed as sum of two other reactions, the K_c of overall reaction is equal to the product of equilibrium constants of individual reactions.

Illustration :

If K_1, K_2 and K_3 are the quilibrium constants for the reaction (1), (2) and (3) respectively, then prove that $K_1\times K_2=K_3$.

$H_2S \rightleftharpoons HS^- + H^+$ ...(1)

$HS^- \rightleftharpoons S^{--} + H^+$ ...(2)

$H_2S \rightleftharpoons S^{--} + 2H^+$ ...(3)

Sol. $K_1=\frac{[HS^-][H^+]}{[H_2S]}$ $\qquad K_2=\frac{[S^{--}][H^+]}{[HS^-]}$

On multiplying $K_1\times K_2=\frac{[S^{--}][H^+]^2}{[H_2S]}=K_3$

4. The equilibrium constant is independent of initial concentrations of reacting species.
5. Independent of presence of catalyst.
6. K_c for backward reaction is inverse of K_c for forward reaction.
7. K_c changes with stoichiometric representation of reaction.

Illustration :

For the reaction $2SO_2+O_2 \rightleftharpoons 2SO_3$ the equilibrium constant is 49. Find the equilibrium constant for

$$SO_2+\frac{1}{2}O_2 \rightleftharpoons SO_3.$$

Sol. $49=\frac{[SO_3]^2}{[SO_2]^2[O_2]}$ (I)

$$K_c=\frac{[SO_3]}{[SO_2][O_2]^{1/2}} \qquad \text{(II)}$$

taking under root of (I)

$$7 = \frac{[SO_3]}{[SO_2][O_2]^{1/2}} = K_c$$

$\therefore$ K_c for second reaction = 7

HOMOGENEOUS EQUILIBRIUM :

In homogeneous equilibrium the reactants and products are present in the same phase (gaseous or liquid).

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$

HETEROGENEOUS EQUILIBRIUM :

In heterogeneous equilibrium the reactants and products are present in two or more phases.

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4\,(s) + 4H_2\,(g)$$

CHEMICAL EQUILIBRIUM APPLIED TO HOMOGENEOUS SYSTEM :

(a) Gaseous system : They are of two types

(i) Gaseous reactions in which the number of moles of products remain the same as that of reactants.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$
$$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

Hydrogen - iodine equilibrium : Suppose, a moles of H_2 and b moles of I_2 are present in a container of V litres. At equilibrium x moles of each have combined to form HI.

$$\begin{array}{lccc} & H_2 & + \; I_2 & \rightleftharpoons 2HI \\ \text{Initial molar conc.} & \frac{a}{V} & \frac{b}{V} & 0 \\ \text{Eqb. molar conc.} & \frac{a-x}{V} & \frac{b-x}{V} & \frac{2x}{V} \end{array}$$

Applying the law of chemical equilibrium

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\frac{a-x}{V} \times \frac{b-x}{V}} = \frac{4x^2}{(a-x)(b-x)} \qquad \text{..........(i)}$$

The equilibrium constant written as K_c indicates that active masses are expressed in terms of molar concentrations.

The eq. (i) does not contain the volume term. Thus equilibrium is independent of **volume** and therefore of **pressure**.

(ii) Gaseous reactions in which the number of moles of products and reactants are different.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
$$N_2O_4 \rightleftharpoons 2NO_2$$
$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

Dissociation of PCl_5 : Suppose 'a' moles of PCl_5 are present in a container of V litres. At equilibrium x moles have dissociated.

$$\begin{array}{lccc} & PCl_5 & \rightleftharpoons PCl_3 & + \; Cl_2 \\ \text{Initial molar Conc.} & \frac{a}{V} & 0 & 0 \\ \text{Eqb. molar Conc.} & \frac{a-x}{V} & \frac{x}{V} & \frac{x}{V} \end{array}$$

Applying the law of chemical equilibrium

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{a-x}{V}} = \frac{x^2}{V(a-x)} \qquad \text{.......(i)}$$

The eq.(i) contains the V term in denominator . If volume increases, the dissociation of PCl_5 must also increase to keep K_c constant. The decrease of pressure will cause increase in volume and so the dissociation.

If the value of x is small then $K_c = \left\|\frac{x^2}{V}\right\|$; $\qquad x \propto \sqrt{V} \propto \sqrt{1/p}$

(b) Liquid system : Examples are :

(i) Esterification of acetic acid

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

At equilibrium 2/3rd of acetic acid is converted into ester. Hence alcohol consumed will also be 2/3rd.

(ii) Reaction between amylene and tricholoroacetic acid

$$Cl_3C.COOH + C_5H_{10} \rightleftharpoons Cl_3CCOOC_5H_{11}$$

CHEMICAL EQUILIBRIUM APPLIED TO HETEROGENEOUS SYSTEM :

(i) Dissociation of calcium carbonate

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Applying the law of chemical equilibrium

$$K_p = \frac{p_{CaO} \times p_{CO_2}}{p_{CaCO_3}}$$

The active mass of a solid reactant and product is assumed to have a constant value and is taken as unity. The equilibrium constant is determined by gaseous substances only

$$\therefore\ K_p = p_{CO_2}$$

(ii) Reaction of steam on heated iron

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

$$K_p = \frac{\left[p_{Fe_3O_4}\right] \times \left[p_{H_2}\right]^4}{\left[p_{Fe}\right]^3 \times \left[p_{H_2O}\right]^4} = \frac{p_{H_2}^4}{p_{H_2O}^4}$$

Partial pressures of solid is taken unity.

(iii) Water gas reaction :

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

$$K_p = \frac{p_{CO} \times p_{H_2}}{p_C \times p_{H_2O}}$$

Since partial pressure of carbon (solid) is taken as unity, the equilibrium constant is given by

$$K_p = \frac{p_{CO} \times p_{H_2}}{p_{H_2O}}$$

VAN'T HOFF ISOCHORE :

A relationship between the equilibrium constant K_p, at any temperature T and constant pressure P, and heat of reaction $\Delta H°$.

$$\frac{d \log_e K_p}{dT} = \frac{\Delta H°}{RT^2}$$

The enthalpy change ΔH does not vary appreciably with change in partial pressures of reactants and products. Therefore ΔH^o can be taken as ΔH whatever may be the partial pressures of reactants and products

$$\frac{d \log_e K_p}{dT} = \frac{\Delta H}{RT^2}$$

The integrated form of the equation is

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Three important conditions may arise

(i) when $\Delta H = 0$ no heat is evolved or absorbed

$$\log \frac{K_{p_2}}{K_{p_1}} = 0 \text{ i.e. } \frac{K_{p_2}}{K_{p_1}} = 1 \text{ or } K_{p_2} = K_{p_1}$$

Equilibrium constant does not change when no change in temperature.

(ii) when $\Delta H = +ve$ i.e. heat is absorbed

$$\log \frac{K_{p_2}}{K_{p_1}} > 1 \qquad K_{p_2} > K_{p_1}$$

Equilibrium constant increases with increase of temperature.

(iii) when $\Delta H = -ve$ i.e. heat is evolved

$$\log \frac{K_{p_2}}{K_{p_1}} < 1 \qquad K_{p_2} < K_{p_1} \text{ ; Equilibrium constant}$$

decreases with increase of temperature

(iv) when $\Delta n = 0$ i.e. there is no change in volume during a reaction $K_P = K_c$. The variation of equilibrium constant with temperature is given by $\frac{d \log_e K_c}{dT} = \frac{\Delta E}{RT^2}$

ΔE heat of reaction at constant volume.

VAN'T HOFF REACTION ISOTHERM :

It gives the free energy change of a reaction at any given temperature, pressure and composition of the reacting system.

$$\Delta G = \Delta G° + RT \ln J$$

At equilibrium $\Delta G = 0$ then $\Delta G° = -RT \ln J_{eq}$

J stands for reaction quotient of partial pressure of products and reactants.

$$\text{viz. } \frac{\text{Concentration terms of products}}{\text{Concentration terms of reactants}}$$

J_{eq} means the partial pressure of the products and the reactants at the equilibrium. Hence J_{eq} can be replaced by K_p.

$\therefore \Delta G° = -RT \ln K_p$

HENRY'S LAW :

The mass of a gas dissolved per unit volume of solvent is proportional to the pressure of the gas in equilibrium with the solution at constant temperature.

- The volume of the gas dissolved remains the same inspite of increase in pressure.
- The dissolution of a gas in a liquid is spontaneous process ($\Delta G = 0$), accompanied by decrease in entropy ($\Delta S = -ve$). Since $\Delta G = \Delta H - T\Delta S$, ΔG can only be negative if ΔH is –ve. Therefore dissolution of a gas in a liquid is always exothermic in nature.

FACTORS ALTERING THE STATE OF EQUILIBRIUM - LE CHATELIER'S PRINCIPLE :

There are three main factors which alter the state of equilibrium. They are (I) **Concentration**, (II) **Temperature**, and (III) **Pressure**. Le Chatelier's principle states that if a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect of the change.

(1) Effect of change of concentration :

If at equilibrium the concentration of one of the reactants is increased, the equilibrium will shift in the forward direction and vice versa. Consider the following equilibrium

$$\underset{\text{Pale yellow}}{Fe^{3+}(aq)} + \underset{\text{Colourless}}{SCN^-(aq)} \rightleftharpoons \underset{\text{Dark brown}}{[Fe(SCN)]^{2+}(aq)}$$

If ferric salt is added the colour of the solution darkens immediately i.e. Fe^{3+} ions are consumed and more $[Fe(SCN)]^{2+}$ are formed. If some sulphocyanide salt is added the colour also darkens. If Potassium ferrisulphocyanide capable of giving complex ion $[Fe(SCN)]^{2+}$ is added the colour lightens to pale yellow.

(2) Effect of change in pressure :

(a) No effect of pressure on equilibria having same moles of reactants and products e.g.

(I) $N_2 + O_2 \rightleftharpoons 2NO$

(II) $H_2 + I_2 \rightleftharpoons 2HI$

(b) When there is change in the number of moles the equilibrium will shift in the direction having smaller number of moles when the pressure is increased and vice versa e.g.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

More pressure more ammonia

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

The more the pressure, the lesser the dissociation of PCl_5.

(3) Effect of temperature :

(I) When process is exothermic - Low temperature favours the formation of products.

(II) When process is endothermic - High temperature favours the formation of products

e.g. $N_2 + 3H_2 \rightleftharpoons 2NH_3 + 24.0$ kcal.

Since the production of NH_3 is exothermic low temperature favours its formation.

(4) Effect of addition of inert gas :

(I) **Addition of Inert gas at constant volume :** The total pressure of the system is increased, but the partial pressure of each reactant and product remains the same. Hence no effect on the state of equilibrium.

(II) **Addition of Inert gas at constant pressure :** The total volume is increased, the number of moles per unit volume of each reactant and product is decreased. Hence equilibrium will shift to the side where number of moles are increased e.g.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Introduction of inert gas at constant pressure will shift the equilibrium to right hand side.

(5) Effect of catalyst : The presence of catalyst does not change the position of equilibrium. It simply fastens the attainment of equilibrium.

LE CHATELIER'S PRINCIPLE APPLICABLE TO PHYSICAL EQUILIBRIUM :

(i) Effect of pressure on solubility : The increased pressure, will increase the solubility of a gas and vice versa.

(ii) Effect of temperature on solubility : The substances which dissolve with the absorption of heat, their solubility will increase with increase of temperature and vice versa e.g. dissolution of NH_4Cl, KCl, KNO_3 is endothermic which increases with increase of temperature. The dissolution of calcium acetate and Calcium hydroxide is exothermic, their solubility is lowered at higher temperature.

(iii) Effect of pressure on the melting point of ice :

$$\text{Ice} \rightleftharpoons \text{liquid water}$$

The ice occupy the more volume than liquid water, so increased pressure will result in melting of ice according to Le Chatelier's principle.

FAVOURABLE CONDITIONS FOR SOME IMPORTANT REACTIONS :

(1) Synthesis of ammonia (Haber's process) :

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22.4$ kcal.

(I) Low temperature (500°C)

(II) High pressure (200 – 1000 atm.)

(III) Excess of N_2 and H_2

(2) Synthesis of NO (nitric acid birkland eyde process)

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 43.2$ kcal

(I) High temperature

(II) Excess of N_2 and O_2

(III) No effect of pressure

(3) Formation of SO_3 (sulphuric acid contact process)

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3 + 42.0$ kcal

(I) Low temperature

(II) High pressure

(III) Excess of SO_2 and O_2

(4) Formation of nitrogen dioxide

$2NO + O_2 \rightleftharpoons 2NO_2 + 27.8$ kcal

(I) Low temperature

(II) High pressure

(III) Excess of NO and O_2

(5) Dissociation of nitrogen tetraoxide

$N_2O_4 \rightleftharpoons 2NO_2 - 14$ kcal

(I) High temperature

(II) Low pressure

(III) Excess of N_2O_4

(6) Oxidation of CO by steam (Bosch process)

$CO + H_2O \rightleftharpoons CO_2 + H_2 + x$ kcal

(I) Low temperature

(II) Excess of steam and CO

(III) No effect of pressure

(7) Dissociation of PCl_5

$PCl_5 \rightleftharpoons PCl_3 + Cl_2 - 15$ kcal

(I) High temperature

(II) Low pressure

(III) Excess of PCl_5

TRIPLE POINT :

The temperature and pressure at which the three states of a substance can exist in equilibrium is known as triple point e.g.

Ice (s) $\rightleftharpoons$ water (l) $\rightleftharpoons$ vapour (g) can exist at 0.0098°C and 4.58 mm.

DEGREE OF DISSOCIATION FROM DENSITY MEASUREMENT :

The density of one mole of gas is given by

$D = \frac{MP}{RT}$ where M = Mol. wt of gas; P = Total pressure.

The volume of the gas increases on dissociation in proportion to increase in the total number of moles, but total weight remains constant. Hence density decreases in the same proportion.

Consider dissociation of PCl_5. Let x be degree of dissociation

$PCl_5 \rightleftharpoons$	PCl_3	+ Cl_2	
$1-x$	x	x	Total moles $(1+x)$

$$\therefore \frac{D}{d}=\frac{1+x}{1} \qquad \therefore x=\frac{D-d}{d} \quad \left(\because D \propto \frac{1}{\text{moles}}\right)$$

where D is the theoretical vapour density and

$$D=\frac{1}{2}\text{ Molecular mass}$$

d is observed vapour density at temperature t°C.

If nx moles of products are formed, then total number of moles after dissociation

$$1-x+nx=1+x(n-1)$$

$$\therefore \frac{D}{d}=\frac{1+x(n-1)}{1} \qquad \therefore x=\frac{D-d}{d(n-1)}$$

Miscellaneous Solved Examples

1. A sample of air consisting of N_2 and O_2 was heated to 2500K until the equilibrium

$$N_2(g)+O_2(g) \rightleftharpoons 2NO(g)$$

was established with an equilibrium constant $K_c = 2.1 \times 10^{-3}$. At equilibrium, the mole % of NO was 1.8. Estimate the initial composition of air in mole fraction of N_2 and O_2.

Sol.

	N_2	+ O_2 $\rightleftharpoons$	$2NO$
Initial	a	$(100-a)$	0
Final	$(a-x)$	$(100-a-x)$	2x

Given $2x = 1.8$ $\qquad \therefore x = 0.9.$

$$K_c=\frac{[NO]^2}{[N_2][O_2]}=\frac{(2x)^2}{(a-x)(100-a-x)}$$

On substituting the value of x in the given eqn.

$$K_c=\frac{(2\times 0.9)^2}{(a-0.9)(100-a-0.9)}=2.1\times 10^{-3}$$

On solving the value of a, we get

$a = 79\%;\ \ 100-a = 21\%$

2. One mole of H_2, two moles of I_2 and three moles of HI are injected in one litre flask. What will be the concentration of H_2, I_2 and HI at equilibrium at 500°C. K_c for reaction.

$H_2 + I_2 \rightleftharpoons 2HI$ is 45.9.

Sol.

	H_2	+ I_2 $\rightleftharpoons$	$2HI$
Initial mole	1	2	3
Mole at equilibrium	$(1-x)$	$(2-x)$	$(3+2x)$

$$K_c=\frac{[HI]^2}{[H_2][I_2]}=\frac{(3+2x)^2}{(1-x)(2-x)}=49.5 \quad \text{On solving } x=0.684$$

$$\therefore [H_2]=1-0.684=0.316\text{ mol lit}^{-1}$$

$$[I_2]=2-0.684=1.316\text{ mol lit}^{-1}$$

$$[HI]=3+2(0.684)=4.368\text{ mol lit}^{-1}$$

3. At 700 K hydrogen and bromine react to form hydrogen bromide. The value of equilibrium constant for this reaction is 5×10^8. Calculate the amount of H_2, Br_2 and HBr at equilibrium if a mixture of 0.6 mole of H_2 and 0.2 mole of Br_2 is heated at 700K.

Sol.

	H_2	+ Br_2	$\rightleftharpoons$ $2HBr$
Initial moles	0.6	0.2	0
At equilibrium	0.6–x	0.2–x	2x

$$\therefore K_c=\frac{(2x)^2}{(0.6-x)(0.2-x)}$$

$$\text{or} \quad 5\times 10^8=\frac{4x^2}{(0.6-x)(0.2-x)}$$

$$\text{or} \quad 4x^2=5\times 10^8\left(x^2-0.8x+0.12\right)$$

On solving the equation we get

$x = 0.6$ or 0.2

But x can't be exceed than 0.2 because initial moles of Br_2 is 0.2

$\therefore x = 0.2$

Thus, at equilibrium

$$[H_2]=0.6-0.2=0.4\text{ mole}$$

$$[Br_2]=0.2-0.2=0.0\text{ mole}$$

$$[HBr]=2\times 0.2=0.4\text{ mole}$$

4. At 540 K 0.10 mole of PCl_5 are heated in a 8 litre flask. The pressure of the equilibrium mixture is found to be 1.0 atm. Calculate K_p and K_c for the reaction.

Sol.

	PCl_5	$\rightleftharpoons$ PCl_3	+ Cl_2
Moles before dissociation	0.1	0	0
Moles after dissociation	$0.1-x$	x	x

Given volume of container = 8 litre

$$\text{Now } K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{x}{8}\cdot\frac{x}{8}}{\frac{0.1-x}{8}} = \frac{x^2}{8(0.1-x)} \qquad \text{(I)}$$

Also PV = nRT for the equilibrium mixture at 540 K

$1\times 8 = (0.1+x)\times 0.082\times 540$ (II)

On solving the equation we get

$x = 0.08$

Now substitute the value of x in eqn (i)

$$K_c = \frac{0.08\times 0.08}{8(0.1-0.08)} = 4\times 10^{-2}\,\text{mol lit}^{-1};\ K_p = K_c\,(RT)^{\Delta n}$$

$$= 4\times 10^{-2}(0.082\times 540) = 1.77\text{ atm}\ \left[\text{where } \Delta n = 2-1 = 1\right]$$

5. The equilibrium constant K_p for the reaction

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.64×10^{-4} atm at 400°C. What will be the equilibrium constant at 500°C. If the heat of reaction in this temperature ranges –105185.8 J.

Sol. Van't Hoff equation is

$$\log\frac{K_p''}{K_p'} = \frac{\Delta H}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

$$\log K_p'' = \log K'_p + \frac{\Delta H}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

$$= \log 1.64\times 10^{-4} + \frac{-105185.8}{2.303\times 8.314}\left(\frac{773-673}{773\times 673}\right)$$

On solving we get $K''_p = 0.144\times 10^{-4}$ atm.

6. The vapour density of PCl_5 when in equilibrium with its dissociation products was found to be 90. Calculate its degree of dissociation. Also calculate the dissociation constant of PCl_5 at this temperature if the pressure is in atmosphere.

Sol. Theoretical density $D = \frac{31+177.5}{2} = 104.25$

Observed density d = 90

$$\text{Degree of dissociation } x = \frac{D-d}{d(n-1)} = \frac{104.25-90}{90} = 0.158$$

K_p can be calculated as $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$1-0.158 \quad 0.158 \quad 0.158$

Total moles $= 1-0.158+0.158+0.158 = 1.158$

$$K_p = \frac{p_{PCl_5}\times p_{Cl_2}}{p_{PCl_5}} = \frac{\frac{0.158}{1.158}\times 1\times\frac{0.158}{1.158}\times 1}{\frac{0.847}{1.158}} = 0.0256$$

7. The degree of dissociation of PCl_5 at 50 atm is 0.186. The degree of dissociation at 200 atm will be?

Sol. Degree of dissociation $x \propto \sqrt{v} \propto \sqrt{\frac{1}{p}}$

$$\frac{x_1}{x_2} = \sqrt{\frac{p_2}{p_1}} \qquad \therefore \frac{0.186}{x_2} = \sqrt{\frac{200}{50}}$$

$$\therefore x_2 = \frac{0.186}{2} = 0.093$$

8. 2.7 ml H_2 and 3.1 ml I_2 vapour react-at 444°C to form 4.5 ml HI. Calculate the K_c at this temperature

Sol.

	H_2	+ I_2	$\rightleftharpoons$ 2HI
Initial moles	2.7	3.1	0.0
Moles at equil.	2.7–x	3.1–x	2x

But 2x = 4.5 (given) ∴ x = 2.25

$[H_2] = 2.7-2.25 = 0.45$, $[I_2] = 3.1-2.25 = 0.85$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(4.5)^2}{0.45\times 0.85} = 52.94$$

9. A mixture of SO_2, SO_3, and O_2 gases present in a 10 litre flask at certain temperature at which K_c for the reaction

$2SO_2 + O_2 \rightleftharpoons 2SO_3$; is 100

(i) If the No. of moles of SO_2 and SO_3 in the flask are equal, how many moles of O_2 are present.

(ii) If the No. of moles of SO_3 in the flask is twice the No. of moles of SO_2, how many moles of O_2 are present.

Sol. (i) $2SO_2 + O_2 \rightleftharpoons 2SO_3$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left[\frac{1}{10}\right]^2}{\left[\frac{1}{10}\right]^2\left[\frac{O_2}{10}\right]} = 100;$$

$\therefore [O_2] = 0.1$ mole

$$\text{(ii)}\quad \frac{\left[\frac{2}{10}\right]^2}{\left[\frac{1}{10}\right]^2\left[\frac{O_2}{10}\right]} = 100;$$

$[O_2] = 0.4$ mole

10. 1 mole of N_2 is mixed with 3 moles of H_2 in a 4 litre container. If 0.25% N_2 is converted into NH_3 according to the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$. Calculate K_c. What will be the value of K'_c for the given reaction.

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$$

Sol.

N_2	+	$3H_2$	$\rightleftharpoons$	$2NH_3$	
1		3		0	Initial moles
$1-0.0025$		$3-0.0075$		0.005	Moles at-equilibrium
$\frac{(0.9975)}{4}$		$\frac{(2.9975)}{4}$		$\frac{(0.005)}{4}$	Molar conc. at eqb.

$$K_c=\frac{[NH_3]^2}{[N_2][H_2]^3}=\frac{[0.00125]^2}{[0.2494][0.748]^3}=1.49\times10^{-5}$$

For $\frac{1}{2}N_2+\frac{3}{2}H_2 \rightleftharpoons NH_3$

$$K'_c=\frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}=\sqrt{K_c}=\sqrt{1.49\times10^{-5}}=3.84\times10^{-3}$$

11. At certain temperature the K_c is 16 for the reaction

$$SO_2+NO_2 \rightleftharpoons SO_3+NO$$

If we take one mole each of the four gases in one litre container, what would be equilibrium concentrations of NO and NO_2

Sol.

SO_2 +	NO_2 $\rightleftharpoons$	SO_3	+	NO	
1	1	1		1	Initial moles
$1-x$	$1-x$	$1+x$		$1+x$	Molar conc. at equilibrium

$$K_c=\frac{[SO_3][NO]}{[SO_2][NO_2]}=16 \quad ;\frac{(1+x)(1+x)}{(1-x)(1-x)}=16$$

$$x=\frac{3}{5}=0.6$$

$\therefore$ Concentration of NO $=1+x=1+0.6=1.6$ mole

Concentration of NO_2 $=1-x=1-0.6=0.4$ mole.

12. K_c for $PCl_5 \rightleftharpoons PCl_3+Cl_2$ is 0.04 at 25°C. How many moles of PCl_5 must be added to a 3 litre flask to obtain a Cl_2 of concentration 0.15 M.

Sol. At equil. No. of mole of Cl_2 in 3L $=0.15\times3=0.45$

PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2	
x		0		0	Initial moles
$x-0.45$		0.45		0.45	Moles at eqb.
$\frac{(x-0.45)}{3}$		$\frac{(0.45)}{3}$		$\frac{(0.45)}{3}$	Molar conc. at eqb.

$$K_c=\frac{[PCl_3][Cl_2]}{[PCl_5]}=\frac{(0.15)(0.15)}{\frac{(x-0.45)}{3}}$$

$\therefore x=2.1$ mole

13. The value of K_c is 0.50 for the reaction

$$N_2+3H_2 \rightleftharpoons 2NH_3$$

at 400°C. Calculate the value of K_p for the given reaction at the same temperature (R = 0.0821 atm litre/ deg. mol)

Sol. $K_p=K_c(RT)^{\Delta n}=0.50(0.0821\times673)^{-2}=1.64\times10^{-4}$

14. Prove that the pressure necessary to obtain 50% dissociation of PCl_5 at 250°C is numerically three times of K_p

Sol.

PCl_5	$\rightleftharpoons$ PCl_3	+ Cl_2	
1–0.5	0.5	0.5	Moles at equilibrium

Total moles at equilibrium $=1-0.5+0.5+0.5=1.5$

$$Kp=\frac{p_{PCl_3}\times p_{Cl_2}}{p_{PCl_5}}=\frac{\frac{0.5}{1.5}p\times\frac{0.5}{1.5}p}{\frac{0.5}{1.5}p} \quad \text{(where p is total pressure)}$$

$$K_p=\frac{1}{3}p \quad \text{or} \quad p=3K_p$$

15. An equilibrium mixture at 300 K contains N_2O_4 and NO_2 at 0.28 and 1.1 atm pressure respectively. If the volume of the container is doubled, calculate the new equilibrium pressure of the two gases

Sol.

N_2O_4	$\rightleftharpoons$	$2NO_2$	
0.28 atm		1.1 atm	at equilibrium

$$\therefore \quad Kp=\frac{(1.1)^2}{0.28}=4.32$$

when the volume of the container is doubled, the pressure of N_2O_4 and NO_2 shall be reduced to half

N_2O_4	$\rightleftharpoons$ $2NO_2$	
0.14	0.55	
$(0.14-x)$ atm	$(0.55+2x)$ atm	At new equilibrium

$$K_p=\frac{(0.55+2x)^2}{0.14-x}=4.32$$

$\therefore$ x = 0.045

Since temperature remains the same K_p will not change

$$\therefore.\ p_{N_2O_4}=0.14-0.045=0.095\text{ atm}$$

$$\text{and } p_{NO_2}=0.55+2\times0.045=0.64\text{ atm}$$

16. The value of K_p at 298 K for the reaction

$$1/2\,N_2+3/2\,H_2 \rightleftharpoons NH_3$$

is found to be 826.0, partial pressures being measured in atmospheric units. Calculate $\Delta G°$ at 298K

Sol. $\Delta G°=-2.303\ RT\log K_p$

$$=-2.303\times1.98\times298\ \log826=-3980 \text{ calories}$$

17. If 50% of CO_2 converts to CO at the following equilibrium

$$C\,(s)+CO_2\,(g) \rightleftharpoons 2CO\,(g)$$

and the equilibrium pressure is 12 atm calculate K_p.

Sol. $C(s) + CO_2(g) \rightleftharpoons 2\,CO(g)$

Initial mole	1	0
mole at eqb.	1–0.5	2×0.5 total mole = 1.5
	$\frac{0.5}{1.5}p$	$\frac{1}{1.5}p$
partial pressure	$=\frac{0.5}{1.5}\times12$ atm	$=\frac{1}{1.5}\times12$ atm
	= 4 atm	= 8 atm

$$\therefore K_p = \frac{p_{CO}^2}{p_{CO_2}} = \frac{(8)^2}{4} = 16 \text{ atm}$$

18. The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm and 348K is 1.84 g/c. Calculate K_c for the equilibrium

$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$

Sol. $N_2O_4 \rightleftharpoons 2\,NO_2$

$1–x \quad 2x$

$$\text{Molecular wt of mixture } = \frac{92(1-x)+46\times2x}{1+x} = \frac{92}{1+x}$$

$$\text{Further } P = \frac{dRT}{M}$$

$$1 = \frac{1.84\times0.0821\times348}{\frac{92}{(1+x)}}$$

$\therefore \quad x = 0.75$

$$K_c = \frac{(2x)^2}{1-x} = \frac{4\times(0.75)^2}{1-0.75} = 9.0$$

19. Calculate K_p for the following reaction at 25°

$2N_2O\,(g) \rightleftharpoons 2N_2\,(g) + O_2\,(g)$

$\Delta G_f^\circ(N_2O) = 104.2 \text{ kJ/mole}, \ \Delta G_f^\circ(N_2) = 0$ and

$\Delta G_f^\circ(O_2) = 0\cdot$

Sol. $\Delta G^\circ = 2\times\Delta G_f^\circ(N_2) + \Delta G_f^\circ(O_2) - 2\times\Delta G_f^\circ(N_2O)$

$= (2\times0+0) - 2\times104.2 \ = -2.084\times10^5 \text{ J/mol}$

For gas phase reaction ΔG° is related to K_p as follows

$$\Delta G^\circ = -2.303 \ RT\log K_p$$

$$-2.084\times10^5 = -2.303\times8.314\times298\log K_p$$

$$\therefore K_p = 3.3\times10^{36}$$

Exercise-1 | NCERT Based Questions

Very Short/Short Answer Questions

1. In a reaction a + b $\rightleftharpoons$ c + d the change in enthalpy is –10 kcal. If heat is added to the system in which direction the reaction would proceed?

2. What is meant by the statement 'Equilibrium is dynamic in nature'?

3. $A + B \rightleftharpoons AB;\ K = 1 \times 10^2$

$E + F \rightleftharpoons EF;\ \ K = 1 \times 10^{-3}$

Out of AB and EF, which one is more stable AB or EF ?

4. Which will have CO_2 to more extent, hot cold drink bottle or chilled cold drink bottle, why ?

5. Write the expression for equilibrium constant K_p, for the reaction.

$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

6. In a reaction a + b $\rightleftharpoons$ c + d will addition of c to the system change the value of K?

7. The equilibrium constant for a gas phase reaction is

$$K_c = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2}$$

Write the balanced chemical equation corres- ponding to this expression.

8. In a gaseous reaction a + b $\rightleftharpoons$ c + 2d, 3 mol of inert gas is introduced into the vessel at constant pressure. What will be its effect on equilibrium?

9. For the reaction 2a $\rightleftharpoons$ c + d , the equilibrium constant is 1.0×10^{-3} . At equilibrium, the concentrations observed were $[c] = 1.2 \times 10^{-3}$ M, $[d] = 3.8 \times 10^{-6}$ M.
What was [a] at equilibrium?

10. On the reaction $2NH_3\ (g) \rightleftharpoons N_2\ (g)\ +\ 3H_2(g)$ $\Delta H = +\ 93.6$ kJ. Tell us what would be effect of
(a) temperature
(b) pressure

11. The equilibrium constant for the following reaction is 1.6×10^5 at 1024 K

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

Long Answer Questions

12. (i) Reaction between nitrogen and oxygen takes place as following:

$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$

If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a reaction vessel of volume 10L and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$. Determine the composition of the reaction mixture.

(ii) Bromine monochloride, BrCl, decomposes into bromine and chlorine and reaches the equilibrium

$$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$$

for which $K_c = 32$ at 500 K. If initially pure BrCl is present at a concentration of 3.30×10^{-3} mol L^{-1}; what is its molar concentration in the mixture at equilibrium?

13. **(i)** How much of 0.3 M ammonium hydroxide should be mixed with 30 mL of 0.2 M solution of ammonium chloride to give buffer solution of pH 8.65 and 10?

$[pK_b = 4.75]$

(ii) How much volume of 0.1 M HAc should be added to 50 mL of 0.2 M NaAc solution if we want to prepare a buffer solution of pH 4.91. $(pK_a = 4.76)$

Multiple Choice Questions

14. Which of the following is not a general characteristic of equilibria involving physical processes ?
(a) Equilibrium is possible only in a closed system at a given temperature.
(b) All measurable properties of the system remain constant.
(c) All the physical processes stop at equilibrium.
(d) The opposing processes occur at the same rate and there is dynamic but stable condition.

15. A reaction is A + B $\rightleftharpoons$ C + D. Initially we start with equal concentrations of A and B. At equilibrium we find that the moles of C is two times of A. What is the equilibrium constant of the reaction?

(a) $\frac{1}{4}$ (b) $\frac{1}{2}$
(c) 4 (d) 2

16. In the two gaseous reactions (I) and (II), at 25°C

(I) $NO\,(g) + {}^1\!/_2\,O_2\,(g) \rightleftharpoons NO_2\,(g),\ K_1$

(II) $2NO_2\,(g) \rightleftharpoons 2NO\,(g) + O_2\,(g),\ K_2$

the equilibrium constants K_1 and K_2 are related as

(a) $K_2 = \frac{1}{K_1}$ (b) $K_2 = \frac{K_1}{2}$

(c) $K_2 = \frac{1}{K_1^2}$ (d) $K_2 = K_1^2$

17. For the reversible reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500°C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_C, with concentration in mole litre^{-1}, is

(a) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$ (b) $\dfrac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$

(c) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{2}}$ (d) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$

18. For the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the partial pressures of CO_2 and CO are 2.0 and 4.0 atm respectively at equilibrium. The K_p for the reaction is.

(a) 0.5 (b) 4.0
(c) 8.0 (d) 32.0

19. The reaction quotient (Q) for the reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

is given by $Q = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$. The reaction will proceed from right to left if

(a) $Q < K_c$ (b) $Q > K_c$
(c) $Q = 0$ (d) $Q = K_c$

where K_c is the equilibrium constant.

20. ΔG° for the reaction $X + Y \rightleftharpoons Z$ is –ve 4.606 kcal. The equilibrium constant for the reaction at 227°C is

(a) 100 (b) 10
(c) 2 (d) 0.01

21. On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le Chatelier's principle. Consider the reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature?

(a) K will remain same
(b) K will decrease
(c) K will increase
(d) K will increase initially and decrease when pressure is very high

22. In which of the following reactions, the equilibrium remains unaffected on addition of small amount of argon at constant volume?

(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(d) The equilibrium will remain unaffected in all the three cases.

23. Which of the following statements is incorrect?

(a) In equilibrium mixture of ice and water kept in perfectly insulated flask mass of ice and water does not change with time.
(b) The intensity of red colour increases when oxalic acid is added to a solution containing iron (III) nitrate and potassium thiocyanate.
(c) On addition of catalyst the equilibrium constant value is not affected.
(d) Equilibrium constant for a reaction with negative Δ*H* value decreases as the temperature increases.

Exercise-2 | CONCEPTUAL MCQs

1. Which is a reversible reaction?

(a) $H_2 + I_2 \longrightarrow 2HI$
(b) $H_2SO_4 + Ba(OH)_2 \longrightarrow BaSO_4 \downarrow + 2H_2O$
(c) $NaCl + AgNO_3 \longrightarrow NaNO_3 + AgCl \downarrow$
(d) $2KClO_3 \longrightarrow 2KCl + 3O_2 \uparrow$

2. The standard state Gibb's free energy change for the isomerisation reaction cis-2-pentene $\rightleftharpoons$ trans-2-pentene is –3.67 kJ mol^{-1} at 400 K. If more trans-2-pentene is added to the reaction vessel

(a) more cis-2-pentene is formed
(b) equilibrium shifts in the forward direction
(c) equilibrium remains unaltered
(d) more trans-2-pentene is produced

3. A reaction attains equilibrium when the free energy change accompanying the reaction is

(a) positive and large
(b) zero
(c) negative and large
(d) negative and small

4. The equilibrium constant for the reversible reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is K and for the reaction

$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$, the equilibrium constant is K'.

K and K' will be related as

(a) $K = K'$ (b) $K' = \sqrt{K}$
(c) $K = \sqrt{K'}$ (d) $K \times K' = 1$

5. If K_1 and K_2 are respective equilibrium constants for the two reactions

$XeF_6(g) + H_2O(g) \rightleftharpoons XeOF_4(g) + 2HF(g)$

$XeO_4(g) + XeF_6(g) \rightleftharpoons XeOF_4(g) + XeO_3F_2(g)$

the equilibrium constant for the reaction

$XeO_4(g) + 2HF(g) \rightleftharpoons XeO_3F_2(g) + H_2O(g)$

will be

(a) $\frac{K_1}{K_2^2}$ (b) $K_1.K_2$

(c) $\frac{K_1}{K_2}$ (d) $\frac{K_2}{K_1}$

6. A cylinder fitted with a movable piston contains liquid water in equilibrium with water vapour at 25°C. Which operation result in a decrease in the equilibrium vapour pressure

(a) Moving the piston downward a short distance

(b) Removing a small amount of vapour

(c) Removing a small amount of the liquid water

(d) Dissolving salt in the water

7. The volume of the reaction vessel containing an equilibrium mixture in the reaction

$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

is increased when the equilibrium is re-established

(a) The amount of SO_2 (g) will decrease

(b) The amount of SO_2Cl_2 (g) will increase

(c) The amount of Cl_2 (g) will increase

(d) The amount of Cl_2 (g) will remain unchanged

8. In gaseous equilibrium the correct relation between K_c and K_p is

(a) $K_c = K_p(RT)^{\Delta n}$ (b) $K_p = K_c(RT)^{\Delta n}$

(c) $\frac{K_c}{RT} = (K_p)^{\Delta n}$ (d) $\frac{K_p}{RT} = (K_c)^{\Delta n}$

9. In which of the following reaction $K_p > K_c$

(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (b) $H_2 + I_2 \rightleftharpoons 2HI$

(c) $PCl_3 + Cl_2 \rightleftharpoons PCl_5$ (d) $2SO_3 \rightleftharpoons O_2 + 2SO_2$

10. For reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, the value of K_c at 250°C is 26 mol^{-1} $litre^1$. The value of K_p at this temperature will be

(a) 0.61 atm^{-1} (b) 0.57 atm^{-1}

(c) 0.83 atm^{-1} (d) 0.46 atm^{-1}

11. The equilibrium constant for the reaction,

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

is 4×10^{-4} at 2000 K.

In presence of a catalyst, equilibrium is attained ten times faster. Therefore, the equilibrium constant, in presence of the catalyst, at 2000 K is

(a) 40×10^{-4}

(b) 4×10^{-4}

(c) 4×10^{-3}

(d) difficult to compute without more data

12. For a chemical reaction $2A + B \rightleftharpoons C$, the thermodynamic equilibrium constant K_p is

(a) in atm^{-2} (b) in atm^{-3}

(c) in atm^{-1} (d) dimensionless

13. When two reactants, A and B are mixed to give products C and D, the reaction quotient Q, at the initial stage of the reaction

(a) is zero (b) decreases with time

(c) is independent of time (d) increases with time

14. In the equilibrium reaction involving the dissociation of $CaCO_3$

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

the equilibrium constant is given by

(a) $\frac{p_{CaO} \times p_{CO_2}}{p_{CaCO_3}}$ (b) $C_{CaO} \times \frac{p_{CO_2}}{C_{CaCO_3}}$

(c) $\frac{p_{CaO}}{p_{CaCO_3}}$ (d) p_{CO_2}

15. Steam reacts with iron at high temperature to give hydrogen gas and Fe_3O_4 (s). The correct expression for the equilibrium constant is

(a) $\frac{P_{H_2}^2}{P_{H_2O}^2}$ (b) $\frac{(P_{H_2})^4}{(P_{H_2O})^4}$

(c) $\frac{(P_{H_2})^4[Fe_3O_4]}{(P_{H_2O})^4[Fe]}$ (d) $\frac{[Fe_3O_4]}{[Fe]}$

16. In lime kiln, the reversible reaction

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

proceeds to completion because

(a) of high temperature (b) CO_2 escaped out

(c) CaO is removed (d) of low temperature

17. If 1.0 mole of I_2 is introduced into 1.0 litre flask at 1000 K, at quilibrium ($K_c = 10^{-6}$), which one is correct

(a) $[I_2(g)] > [I^-(g)]$ (b) $[I_2(g)] < [I^-(g)]$

(c) $[I_2(g)] = [I^-(g)]$ (d) $[I_2(g)] = \frac{1}{2}[I^-(g)]$

18. At equilibrium, if $K_p = 1$, then

(a) $\Delta G° = 0$ (b) $\Delta G° > 1$

(c) $\Delta G° < 1$ (d) None of these

19. Van't Hoff's equation giving the effect of temperature on chemical equilibrium is represented as

(a) $\frac{d \ln F}{dT} = \frac{\Delta H}{RT^2}$ (b) $\frac{d \ln K_p}{dT} = \frac{\Delta HT^2}{R}$

(c) $\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$ (d) $\frac{d \ln K_p}{dT} = \frac{RT^2}{\Delta H}$

20. Solubility of a substance which dissolves with a decrease in volume and absorption of heat will be favoured by

(a) high P and high T (b) low P and low T

(c) high P and low T (d) low P and high T

21. In what manner will increase of pressure affect the following equation?

$C\,(s) + H_2O\,(g) \rightleftharpoons CO\,(g) + H_2\,(g)$

(a) Shift in the forward direction

(b) Shift in the reverse direction

(c) Increase in the yield of hydrogen

(d) No effect

22. In a reaction, $A + 2B \rightleftharpoons 2C$, 2.0 mole of 'A', 3.0 mole of 'B' and 2.0 mole of 'C' are placed in a 2.0 L flask and the equilibrium concentration of 'C' is 0.5 mole/L. The equilibrium constant (K) for the reaction is

(a) 0.073 (b) 0.147

(c) 0.05 (d) 0.026

23. 4.5 moles each of hydrogen and iodine were heated in a sealed ten litre vessel. At equilibrium 3 moles of HI were found. The equilibrium constant of

$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$ is

(a) 1 (b) 10

(c) 5 (d) 0.33

24. A reaction is $A + B \rightleftharpoons C + D$. Initially we start with equal concentrations of A and B. At equilibrium we find that the moles of C is two times of A. What is the equilibrium constant of the reaction?

(a) $\frac{1}{4}$ (b) $\frac{1}{2}$

(c) 4 (d) 2

25. In which of the following, the forward reaction is favoured by use of high pressure?

(a) $H_2 + I_2 \rightleftharpoons 2HI$

(b) $N_2 + O_2 \rightleftharpoons 2NO$

(c) $2NH_3 \rightleftharpoons N_2 + 3H_2$

(d) $2SO_2 + O_2 \rightleftharpoons 2SO_3$

26. In a reaction $A + B \rightleftharpoons C + D$, the initial concentrations, of A and B were 0.9 mol. dm^{-3} each. At equilibrium the concentration of D was found to be 0.6 mol dm^{-3}. What is the value of equilibrium constant for the reaction

(a) 8 (b) 4 (c) 9 (d) 3

27. On the basis of Le-Chatelier's principle, predict which of the following conditions would be unfavourable for the formation of SO_3? Given that

$2SO_2 + O_2 \rightleftharpoons 2SO_3;\ \Delta H = -42$ kcal

(a) Low pressure and low temperature

(b) High pressure and low temperature

(c) High temperature and low pressure

(d) High concentration of SO_2

28. If the equilibrium constant for the reaction

$2AB \rightleftharpoons A_2 + B_2$

is 49, what is the value of equilibrium constant for

$AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$?

(a) 49 (b) 2401

(c) 7 (d) 0.02

29. The reaction, $SO_2 + Cl_2 \longrightarrow SO_2Cl_2$ is exothermic and reversible. A mixture of SO_2 (g), Cl_2 (g) and SO_2Cl_2 (l) is at equilibrium in a closed container. Now a certain quantity of extra SO_2 is introduced into the container, the volume remaining the same. Which of the following is/are true?

(a) The pressure inside the container will not change

(b) The temperature will not change

(c) The temperature will increase

(d) The temperature will decrease

30. The rate of forward reaction is two times that of the reverse reaction at a given temperature and identical concentration. $K_{\text{equilibrium}}$ is

(a) 0.5 (b) 1.5

(c) 2.5 (d) 2.0

31. 1 mole of hydrogen and 2 moles of iodine are taken initially in a 2 litre vessel. The number of moles of hydrogen at equilibrium is 0.2. Then the number of moles of iodine and hydrogen iodide at equilibrium are

(a) 1.2, 1.6 (b) 1.8, 1.0

(c) 0.4, 2.4 (d) 0.8, 2.0

32. For the reaction $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$ the forward reaction at constant temperature is favoured by

(a) introducing an inert gas at constant volume

(b) introducing PCl_3 (g) at constant volume

(c) introducing PCl_5 (g) at constant volume

(d) introducing Cl_2 (g) at constant volume

33. For the chemical reaction :

$3X\,(g) + Y\,(g) \rightleftharpoons X_3Y\,(g)$

the amount of X_3Y at equilibrium is affected by

(a) temperature and pressure

(b) pressure only

(c) temperature only

(d) temperature, pressure and catalyst

34. When 3 mole of reactant A and one mole of the reactant B are mixed in a vessel of volume 1 litre, the following reaction takes place

$A\,(g) + B\,(g) \rightleftharpoons 2C\,(g)$

If 1.5 mole of C is formed at equilibrium, the equilibrium constant (K_c) of the reaction is

(a) 0.12 (b) 0.50 (c) 0.25 (d) 4.00

35. K_c for the reaction

$N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$

at 300 K is 4.0×10^{-6}. K_p for the above reaction will be ($R = 2$ cal $mol^{-1}\,K^{-1}$)

(a) 2.4×10^{-3} (b) 4×10^{-6}

(c) $4 \times 10^{-6}\,(RT)^2$ (d) 16×10^{-12}

36. Which of the following equilibria will shift to right side on increasing the temperature?

(a) $CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)$

(b) $2SO_2(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$

(c) $H_2O\,(g) \rightleftharpoons H_2\,(g) + \frac{1}{2}O_2\,(g)$

(d) $4HCl\,(g) + O_2\,(g) \rightleftharpoons 2H_2O\,(g) + 2Cl_2\,(g)$

37. 1 mole of N_2 and 2 moles of H_2 are allowed to react in a 1 dm^3 vessel. At equilibrium 0.8 mole of NH_3 is formed. The concentration of H_2 in the vessel is

(a) 0.6 mole (b) 0.8 mole

(c) 0.2 mole (d) 0.4 mole

38. The equilibrium

$SO_2Cl_2\,(g) \rightleftharpoons SO_2\,(g) + Cl_2\,(g)$

is attained at 25°C in a closed container and an inert gas, helium is introduced. Which of the following statement is correct?

(a) More chlorine is formed

(b) Concentration of SO_2 is reduced

(c) More SO_2Cl_2 is formed

(d) Concentration of SO_2Cl_2, SO_2 and Cl_2 do not change

39. For which reaction high pressure and high temperature is helpful in obtaining a high equilibrium yield

(a) $2NF_3(g) \rightleftharpoons N_2(g) + 3F_2(g) - 54.40$ kcal

(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22.08$ kcal

(c) $Cl_2(g) + 2O_2(g) \rightleftharpoons 2ClO_2(g) - 49.40$ kcal

(d) $2Cl_2O_7\,(g) \rightleftharpoons 2Cl_2\,(g) + 7O_2(g) + 126.8$ kcal

40. For the reversible reaction

$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

at 500°C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c with concentration in mole $litre^{-1}$, is

(a) $1.44 \times 10^{-5} / (0.082 \times 500)^{-2}$

(b) $1.44 \times 10^{-5} / (8.314 \times 773)^{-2}$

(c) $1.44 \times 10^{-5} / (0.082 \times 773)^{2}$

(d) $1.44 \times 10^{-5} / (0.082 \times 773)^{-2}$

41. A 1 M solution of glucose reaches dissociation equilibrium according to the equation given below

$6HCHO \rightleftharpoons C_6H_{12}O_6$

What is the concentration of HCHO at equilibrium if equilibrium constant is 6×10^{22}

(a) 1.6×10^{-8} M (b) 3.2×10^{-6} M

(c) 3.2×10^{-4} M (d) 1.6×10^{-4} M

42. 8 mole of a gas AB_3 are introduced into a 1.0 dm^3 vessel. It dissociates as, $2AB_3\,(g) \rightleftharpoons A_2\,(g) + 3B_2\,(g)$. At equilibrium, 2 mole of A_2 are found to be present. The equilibrium constant of reaction is .... in mol^2L^{-2}

(a) 2 (b) 3

(c) 27 (d) 36

43. $\Delta G°$ for the reaction $X + Y \rightleftharpoons Z$ is –ve 4.606 kcal. The equilibrium constant for the reaction at 227°C is

(a) 100 (b) 10

(c) 2 (d) 0.01

44. The partial pressure of CH_3OH (g), CO (g) and H_2 (g) in equilibrium mixture for the reaction,

$CO\,(g) + 2H_2\,(g) \rightleftharpoons CH_3OH\,(g)$ are 2.0, 1.0 and 0.1 atm respectively at 427°C. The value of K_p for the decomposition of CH_3OH to CO and H_2 is

(a) 10^2 atm (b) $2 \times 10^2\ atm^{-1}$

(c) 50 atm^2 (d) $5 \times 10^{-3}\ atm^2$

45. Which of the following is not affected by pressure change?

(a) $2NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$

(b) $CO_2\,(g) + H_2O\,(l) \rightleftharpoons CO_2$ solution

(c) $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$

(d) $2O_3\,(g) \rightleftharpoons 3O_2\,(g)$

46. The degree of dissociation of dinitrogen tetroxide $N_2O_4\,(g) \longrightarrow 2NO_2(g)$ at temperature T and total pressure P is α. Which one of the following is the correct expression for the equilibrium constant (K_p) at this temperature?

(a) $\frac{2\alpha}{(1-\alpha^2)}$ (b) $\frac{\alpha^2 P}{1-\alpha}$

(c) $\frac{4\alpha^2}{(1-\alpha^2)}$ (d) $\frac{4\alpha^2 P}{(1-\alpha^2)}$

47. Calculate the degree of dissociation of PCl_5, the density at 230°C is 70

(a) 97.8% (b) 48.9%

(c) 4.89% (d) 24.45%

48. When heated to 100°C the V.D. of N_2O_4 becomes 24.5. The degree of dissociation of N_2O_4 at this temp. will be

(a) 80% (b) 87.74%

(c) 40.34% (d) 60%

49. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_c is

(a) $\Delta G = RT \ln K_c$ (b) $-\Delta G = RT \ln K_c$

(c) $\Delta G° = RT \ln K_c$ (d) $-\Delta G° = RT \ln K_c$

50. The reaction quotient (Q) for the reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

is given by $Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$. The reaction will proceed from right to left if

(a) $Q < K_c$ (b) $Q > K_c$
(c) $Q = 0$ (d) $Q = K_c$

where K_c is the equilibrium constant.

51. In Haber process 30 litres of dihydrogen and 30 litres of dinitrogen were taken for reaction which yielded only 50% of the expected product. What will be the composition of gaseous mixture under the aforesaid conditions in the end?

(a) 10 litres of ammonia, 25 litres nitrogen, 15 litres hydrogen
(b) 20 litres ammonia, 10 litres nitrogen, 30 litres hydrogen
(c) 20 litres ammonia, 25 litres nitrogen, 15 litres hydrogen
(d) 20 litres ammonia, 20 litres nitrogen, 20 litres hydrogen

Exercise-3 | PAST COMPETITION MCQs

1. The following equilibrium constants are given: **[CBSE-PMT 2003, 2007]**

$N_2 + 3H_2 \rightleftharpoons 2NH_3; K_1$

$N_2 + O_2 \rightleftharpoons 2NO; K_2$

$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O; K_2$

The equilibrium constant for the oxidation of NH_3 by oxygen to give NO is

(a) $\frac{K_2K_3^2}{K_1}$ (b) $\frac{K_2^2K_3}{K_1}$

(b) $\frac{K_1K_2}{K_3}$ (d) $\frac{K_2K_3^3}{K_1}$

2. The dissociation equilibrium of a gas AB_2 can be represented as : **[CBSE-PMT 2008]**

$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$

The degree of dissociation is 'x' and is small compared to 1. The expression relating the degree of dissociation (x) with equilibrium constant K_p and total pressure P is :

(a) $(2K_p/P)$ (b) $(2K_p/P)^{1/3}$
(c) $(2K_p/P)^{1/2}$ (d) (K_p/P)

3. The values of Kp_1 and Kp_2 for the reactions

$X \rightleftharpoons Y + Z$ ...(1) **[CBSE-PMT 2008]**

and $A \rightleftharpoons 2B$ ...(2)

are in the ratio of 9 : 1. If degree of dissociation of X and A be equal, then total pressure at equilibrium (1) and (2) are in the ratio :

(a) 3 : 1 (b) 1 : 9 (c) 36 : 1 (d) 1 : 1

4. The value of equilibrium constant of the reaction

$HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2$ is 8.0 **[CBSE-PMT 2008]**

The equilibrium constant of the reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ will be:

(a) $\frac{1}{16}$ (b) $\frac{1}{64}$ (c) 16 (d) $\frac{1}{8}$

5. In which of the following equilibrium K_c and K_p are not equal?

(a) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$ **[CBSE-PMT 2010]**

(b) $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

(c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(d) $2C(s) + O_2(g) \rightleftharpoons 2CO_2(g)$

6. The reaction $2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$ is began with the concentrations of A and B both at an initial value of 1.00 M. When equilibrium is reached, the concentration of D is measured and found to be 0.25 M. The value for the equilibrium constant for this reaction is given by the expression **[CBSE-PMT 2010]**

(a) $[(0.75)^3(0.25)] \div [(0.75)^2(0.25)]$
(b) $[(0.75)^3(0.25)] \div [(1.00)^2(1.00)]$
(c) $[(0.75)^3(0.25)] \div [(0.50)^2(0.75)]$
(d) $[(0.75)^3(0.25)] \div [(0.50)^2(0.25)]$

7. Given that the equilibrium constant for the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ has a value of 278 at a particular temperature. What is the value of the equilibrium constant for the following reaction at the same temperature ? **[CBSE-PMT 2012M]**

$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$

(a) 1.8×10^{-3} (b) 3.6×10^{-3} (c) 6.0×10^{-2} (d) 1.3×10^{-5}

8. Given the reaction between 2 gases represented by A_2 and B_2 to give the compound $AB(g)$. **[CBSE-PMT 2012M]**

$A_2(g) + B_2(g) \rightleftharpoons 2\,AB(g)$.

At equilibrium, the concentration

of $A_2 = 3.0 \times 10^{-3}$ M

of $B_2 = 4.2 \times 10^{-3}$ M

of $AB = 2.8 \times 10^{-3}$ M

If the reaction takes place in a sealed vessel at 527°C, then the value of K_c will be :

(a) 2.0 (b) 1.9 (c) 0.62 (d) 4.5

9. Change in volume of the system does not alter the number of moles in which of the following equilibria? **[AIEEE 2002]**

(a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(d) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$.

10. In which of the following reactions, increase in the volume at constant temperature does not affect the number of moles at equilibrium. **[AIEEE 2002]**

(a) $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

(b) $C(s) + (1/2)O_2(g) \rightarrow CO(g)$

(c) $H_2(g) + O_2(g) \rightarrow H_2O_2(g)$

(d) None of these.

11. For the reaction **[AIEEE 2002]**

$CO(g) + (1/2)\,O_2(g) \rightleftharpoons CO_2(g)$, K_p/K_c is

(a) RT (b) $(RT)^{-1}$

(c) $(RT)^{-1/2}$ (d) $(RT)^{1/2}$

12. For the reaction equilibrium

$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$

the concentrations of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol L^{-1} respectively. The value of K_c for the reaction is **[AIEEE 2003]**

(a) 3×10^{-1} mol L^{-1} (b) 3×10^{-3} mol L^{-1}

(c) 3×10^{3} mol L^{-1} (d) 3.3×10^{2} mol L^{-1}

13. Consider the reaction equilibrium

$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g);\ \Delta H^\circ = -198$ kJ

On the basis of Le Chatelier's principle, the condition favourable for the forward reaction is **[AIEEE 2003]**

(a) increasing temperature as well as pressure

(b) lowering the temperature and increasing the pressure

(c) any value of temperature and pressure

(d) lowering of temperature as well as pressure

14. What is the equilibrium expression for the reaction $P_{4(s)} + 5O_{2(g)} \rightleftharpoons P_4O_{10(s)}$? **[AIEEE 2004]**

(a) $K_c = [O_2]^5$ (b) $K_c = [P_4O_{10}]/5[P_4][O_2]$

(c) $K_c = [P_4O_{10}]/[P_4][O_2]^5$ (d) $K_c = 1/[O_2]^5$

15. For the reaction, $CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$ the K_p/K_c is equal to **[AIEEE 2004]**

(a) $\sqrt{RT}$ (b) RT

(c) $1/RT$ (d) 1.0

16. In a cell that utilises the reaction

$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$ addition of H_2SO_4 to cathode compartment, will **[AIEEE 2004]**

(a) increase the E and shift equilibrium to the right

(b) lower the E and shift equilibrium to the right

(c) lower the E and shift equlibrium to the left

(d) increase the E and shift equilibrium to the left

17. The exothermic formation of CIF_3 is represented by the equation :

$CI_{2(g)} + 3F_{2(g)} \rightleftharpoons 2ClF_{3(g)}\ ;\ \Delta H = -329$ kJ

Which of the following will increase the quantity of CIF_3 in an equilibrium mixture of CI_2, F_2 and CIF_3 ? **[AIEEE 2005]**

(a) Adding F_2

(b) Increasing the volume of the container

(c) Removing Cl_2

(d) Increasing the temperature

18. For the reaction **[AIEEE 2005]**

$2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$,

($K_c = 1.8 \times 10^{-6}$ at 184°C) (R = 0.0831 kJ/(mol. K))

When K_p and K_c are compared at 184°C, it is found that

(a) Whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure

(b) $K_p = K_c$

(c) K_p is less than K_c

(d) K_p is greater than K_c

19. An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm? The equilibrium constant for NH_4HS decomposition at this temperature is

(a) 0.11 (b) 0.17 **[AIEEE 2005]**

(c) 0.18 (d) 0.30

20. The equilibrium constant for the reaction

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$$

is $K_c = 4.9 \times 10^{-2}$. The value of K_c for the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

will be **[AIEEE 2006]**

(a) 9.8×10^{-2} (b) 4.9×10^{-2}

(c) 416 (c) 2.40×10^{-3}

21. The equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressures at these equilibria is **[AIEEE 2008]**

(a) 1 : 1 (b) 1:36
(c) 1 : 3 (d) 1 : 9

22. For the following three reactions a, b and c, equilibrium constants are given: **[AIEEE 2008]**

(i) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g); K_1$

(ii) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g); K_2$

(iii) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g); K_3$

(a) $K_1\sqrt{K_2} = K_3$ (b) $K_2K_3 = K_1$
(c) $K_3 = K_1 K_2$ (d) $K_3.K_2^3 = K_1^2$

23. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is : **[AIEEE 2011]**

(a) 1.8 atm (b) 3 atm (c) 0.3 atm (d) 0.18 atm

24. The equilibrium constant (K_c) for the reaction $N_2(g) + O_2(g) \rightarrow 2NO(g)$ at temperature T is 4×10^{-4}. The value of K_c for the reaction **[AIEEE 2012]**

$NO(g) \rightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is:

(a) 0.02 (b) 2.5×10^2 (c) 4×10^{-4} (d) 50.0

Exercise-4 | Applied MCQs

1. The decomposition of N_2O_4 to NO_2 is carried out at 280 K in chloroform. When equilibrium has been established, 0.2 mol of N_2O_4 and 2×10^{-3} mol of NO_2 are present in a 2*l* solution. The equilibrium constant for the reaction, $N_2O_4 \rightleftharpoons 2NO_2$ is

(a) 1×10^{-2} (b) 2×10^{-3}
(c) 1×10^{-5} (d) 2×10^{-5}

2. In an equilibrium reaction for which $\Delta G° = 0$, the equilibrium constant, K , should be equal to

(a) 0 (b) 1
(c) 2 (d) 10

3. The pressure change due to which equilibrium is not affected is

(a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(c) $2O_3(g) \rightleftharpoons 3O_2(g)$

(d) $2NO_2(g) \rightleftharpoons N_2O_4(g)$

4. A reversible chemical reaction having two reactants in equilibrium. If the concentration of the reactants are doubled then the equilibrium constant will

(a) be doubled (b) be halved
(c) become one-fourth (d) remain same

5. 3.2 moles of hydrogen iodide were heated in a sealed bulb at 444°C till the equilibrium state was reached. Its degree of dissociation at this temperature was found to be 22% The number of moles of hydrogen iodide present at equilibrium are

(a) 2.496 (b) 1.87
(c) 2 (d) 4

6. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 721 K, the value of equilibrium constant is 50, when equilibrium concentration of both is 5M. Value of K_p under the same conditions will be

(a) 0.02 (b) 0.2
(c) 50 (d) 50 RT

7. For which one of the following systems at equilibrium, at constant temperature will the doubling of the volume cause a shift to the right?

(a) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

(b) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$

(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(d) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

8. For the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the partial pressures of CO_2 and CO are 2.0 and 4.0 atm respectively at equilibrium. The K_p for the reaction is.

(a) 0.5 (b) 4.0
(c) 8.0 (d) 32.0

9. In a chemical reaction calculate rate constant of backward reaction when the rate constant of forward reaction is 20 and the equilibrium constant is 50

(a) (0.2) (b) (0.1)
(c) (0.4) (d) None of these

10. The rate constant is given by the equation $K = PZe^{-E/RT}$. Which factor should register a decrease for the reaction to proceed more rapidly?

(a) T (b) Z
(c) E (d) P

11. For the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at a given temperature the equilibrium amount of $CO_2(g)$ can be increased by

(a) adding a suitable catalyst
(b) adding an inert gas
(c) decreasing the volume of the container
(d) increasing the amount of CO(g).

12. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_p = (4x^2P)/(1-x^2)$, where P = pressure, x = extent of decomposition. Which one of the following statements is true?

(a) K_p increases with increase of P

(b) K_p increases with increase of x

(c) K_p increases with decrease of x

(d) K_p remains constant with change in P and x

13. Consider the following equilibrium in a closed container $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α)?

(a) K_p does not changes, but α changes

(b) K_p changes, but α does not change

(c) both K_p and α change

(d) neither K_p nor α changes

14. Which of the following is true at chemical equilibrium?

(a) $(\Delta G)_{T,P}$ is minimum and $(\Delta S)_{U,V}$ is also minimum

(b) $(\Delta G)_{T,V}$ is minimum and $(\Delta S)_{U,V}$ is maximum

(c) $(\Delta G)_{T,V}$ is maximum and $(\Delta S)_{U,V}$ is zero

(d) $(\Delta G)_{T,P}$ is zero and $(\Delta S)_{U,V}$ is also zero

15. For the reaction $A(g) \rightleftharpoons B(g) + C(g)$,

(a) $K_p = \alpha^3 p$

(b) $K_p = \alpha^2(K_p + p + 1)$

(c) $K_p = \alpha^2(K_p + p)$

(d) $K_p = \alpha^2\left(\dfrac{K_p + p}{p}\right)$

16. In the van't Hoff equation

$$\frac{d\ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

(a) when $\dfrac{d\ln K}{dT} < 0$, the reaction is exothermic

(b) when $\dfrac{d\ln K}{dT} < 0$, the reaction is endothermic

(c) the slope of the graph is positive throughout

(d) the slope of graph increases and then decreases

17. Consider the expression $\Delta G = -RT\ln K_p + RT\ln Q_p$ and indicate the correct statement at equilibrium

(a) $\Delta G = 0, Q_p > K_p$ the equilibrium reaction will shift from left to right

(b) $\Delta G = 0, Q_p = K_p$ the equilibrium reaction will shift from left to right

(c) $\Delta G = \infty, Q_p < K_p$ the equilibrium reaction will shift from right to left

(d) $\Delta G < 0, Q_p > K_p$ the equilibrium reaction will shift from right to left

where Q_p and K_p term refer to reaction quotient and equilibrium constant at constant pressure respectively.

18. By which of the following reactions, the equilibrium constant is related to tempearture?

(a) $\ln K_2 - \ln K_1 = \dfrac{\Delta H^\circ}{R}\displaystyle\int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$

(b) $\ln K_2 - \ln K_1 = -\dfrac{\Delta H^\circ}{R}\displaystyle\int_{1/T_1}^{1/T_2} d\left(\frac{1}{T^2}\right)$

(c) $\ln K_2 - \ln K_1 = -\dfrac{\Delta H^\circ}{R}\displaystyle\int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$

(d) $\ln K_2 - \ln K_1 = -\dfrac{\Delta H^\circ}{R}\displaystyle\int_{1/T_2}^{1/T_1} d\left(\frac{1}{T}\right)$

19. Which of the following expressions is incorrect?

(a) $\left(\dfrac{\partial \ln K_p}{\partial p}\right)_T = 0$

(b) $\left(\dfrac{\partial \ln K_c}{\partial p}\right)_T = 0$

(c) $\left(\dfrac{\partial \ln K_x}{\partial p}\right)_T = \dfrac{-\Delta n}{(p/p^\circ)}$

(d) All of these

20. K_c for $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 0.04 at 250°C. How many moles of PCl_5 must be added to a 3 L flask to obtain a Cl_2 concentration of 0.15 M

(a) 4.2 moles

(b) 2.1 moles

(c) 5.5 moles

(d) 6.3 moles

21. If $CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4.3H_2O(s) + 2H_2O(g)$ $K_p = 1.086 \times 10^{-4}\,\text{atm}^2$ at 25° C. The eflorecent nature of $CuSO_4.5H_2O$ can be noticed when the vapour pressure of H_2O in atmosphere is

(a) >9.72 mm

(b) <7.92 mm

(c) <7.92 mm

(d) <11.92 mm

22. In a closed system, $A(s) \rightleftharpoons 2B(g) + 3C(g)$, if partial pressure of C is doubled, then partial pressure of B will be

(a) $2\sqrt{2}$ times the original value

(b) $\dfrac{1}{2}$ times the original value

(c) 2 times the original value

(d) $\dfrac{1}{2\sqrt{2}}$ times the original value

23. For the reactions

$A \rightleftharpoons B$ $K_c = 2$

$B \rightleftharpoons C$ $K_c = 4$

$C \rightleftharpoons D$ $K_c = 6$

K_c for the reaction $A \rightleftharpoons D$ is

(a) $2 \times 4 \times 6$

(b) $\dfrac{2 \times 4}{6}$

(c) $2 + 4 + 6$

(d) $\dfrac{4 \times 6}{2}$

24. 1 mol of N_2 and 3 mol of H_2 are placed in a closed container at a pressure of 4 atm. The pressure falls to 3 atm at the same temperature when the following equilibrium is attained

$N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g)$.

The K_p for the dissociation of NH_3 is

(a) $\dfrac{3\times3}{0.5\times(1.5)^3}\text{atm}^{-2}$ (b) $0.5\times(1.5)^3\text{atm}^2$

(c) $\dfrac{0.5\times(1.5)^3}{3\times3}\text{atm}^2$ (d) $\dfrac{(1.5)^3}{0.5}\text{atm}^{-2}$

25. The reactions

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ and

$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

are simultaneously in equilibrium in a vessel at constant volume. If some CO is introduced into the vessel then at the new equilibrium

(a) Cl_2 is greater

(b) PCl_5 is less

(c) PCl_3 remain unchanged

(d) PCl_5 is greater

26. For the complexation reaction

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$

The rates of forward and reverse reactions are given by

$\text{rate (f)} = 1.0\times10^6\,L^2mol^{-2}S^{-1}\quad[Ag^+][NH_3]^2$

$\text{rate (r)} = 2.0\times10^{-2}\,L^2mol^{-2}S^{-1}\quad[Ag(NH_3)_2]^+$

The instability constant of the complex is

(a) 2.0×10^{-8} (b) 5.0×10^{9}

(c) 2.0×10^{-4} (d) 2.0×10^{4}

27. The equilibrium constant for a reaction is 1×10^{20} at 300 K. The standard free energy change for the reaction is

(a) +115 KJ (b) +166 KJ

(c) –115 KJ (d) –166 KJ

28. At temperature T K, PCl_5 is 50% dissociated at an equilibrium pressure of 4 atm. At what pressure it would dissociate to 80% at the same temperature

(a) 0.75 atm (b) 0.50 atm

(c) 0.60 atm (d) 2.50 atm

29. For the equilibrium reaction

$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$

If $P_{Br_2} = \dfrac{P}{9}$, where P is total pressure at equilibrium. The ratio $\dfrac{K_p}{P}$ is equal to

(a) $\dfrac{1}{3}$ (b) $\dfrac{1}{81}$

(c) $\dfrac{1}{9}$ (d) $\dfrac{1}{27}$

30. Equilibrium constant for the reaction

$NH_4OH(aq) + H^+(aq) \rightleftharpoons NH_4^+(aq) + H_2O(\ell)$

is 1.8×10^9. Hence equilibrium constant for ionisation

$NH_3 + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ is

(a) 1.80×10^{-9} (b) 1.80×10^{5}

(c) 1.80×10^{-5} (d) 5.55×10^{-10}

31. The degree of dissociation of $PCl_5(\alpha)$ obeying the equilibrium $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is related to the equilibrium pressure by

(a) $\alpha \propto \dfrac{1}{P^4}$ (b) $\alpha \propto \dfrac{1}{\sqrt{P}}$

(c) $\alpha \propto \dfrac{1}{P^2}$ (d) $\alpha \propto P$

32. In the following hypothetical reaction

$A + 3B \rightleftharpoons 2C + D$

initial moles of A are twice that of B. If at equilibrium moles of B and C are equal. Percentage of B reacted is

(a) 60% (b) 40%

(c) 10% (d) 20%

33. I^- ions react with iodine in aqueous solution to form I_3^- ion as

$I^-(aq) + I_2(aq) \rightleftharpoons I_3^-(aq)$.

When L of solution containing 1 mol of KI and 0.25 mol of I_2 was reacted with excess of $AgNO_3$, 0.80 mol of yellow ppt. was obtained. The stability constant of I_3^- ion is

(a) 0.20 (b) 5.0

(c) 20.0 (d) 0.05

34. A reaction $A + 2B \rightleftharpoons 2C + D$ was studied using the initial concentrations of B which was 1.5 times that of A. At the quilibrium, concentration of A and C were found to be equal. Then K_c for the equilibrium is

(a) 8 (b) 4

(c) 6 (d) 0.32

35. 1.0 mol of $AB_5(g)$ is placed in a closed container under one atmosphere and at 300K. It is heated to 600K, when 20% by mass of it dissociates as

$$AB_5(g) \longrightarrow AB(g) + 2B_2(g).$$

The resultant pressure is

(a) 1.2 atm (b) 2.4 atm
(c) 1.4 atm (d) 2.8 atm

36. The pressure necessary to obtain 50% dissociation of PCl_5 at 250°C is numerically equal to

(a) three times of K_p (b) 6 times of K_p
(c) 2.5 times of K_p (d) 8 times of K_p

37. The activation energies for the forward and reverse reactions in the system $A \rightleftharpoons B$ are 10.303 and 8.000 kcal respectively at 500 K. Assuming that pre exponential factor to be same for both the forward and the reverse steps and $R = 2$ cal K^{-1} mol^{-1}. Calculate the K_c of the reaction

(a) 1.00 (b) 10.0
(c) 0.1 (d) 100

38. 28g N_2 and 6.0 g of H_2 are heated over catalyst in a closed one litre flask of 450°C. The entire equilibrium mixture required 500 ml of 1.0 M H_2SO_4 for neutralisation. The value of K_c for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \text{ is}$$

(a) 0.06 $mol^{-2}L^2$ (b) 0.59 $mol^{-2}L^2$
(c) 1.69 mol^2L^{-2} (d) 0.03 mol^2L^{-2}

39. 2 mol of SO_2 and 1 mol of O_2 are heated in a closed vessel to reach the equilibrium

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3$$

The equilibrium mixture exerted a presure of 5 atm and required 1/3 mol of $K_2Cr_2O_7$ in acidic medium. K_p for the reaction is

(a) 1.0 (b) 2.0
(c) 0.5 (d) 4.0

40. A gaseous compound of molecular mass 82.1 dissociates on heating to 400 K as

$$X_2Y_4(g) \rightleftharpoons X_2(g) + 2Y_2(g)$$

The density of the equilibrium mixture at a pressure of 1 atm and temperature of 400K is $2.0 gL^{-1}$. The percentage dissociation of the compound is

(a) 12.5% (b) 48.5%
(c) 90.1% (d) 25.0%

41. When the reactants A and B are mixed to give products C and D, the reaction quotient Q at the initial stage of reaction is

(a) zero (b) independent of time
(c) increases with time (d) decreases with time

42. The eqilibrium constant for the reaction

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

is 4.3 at 250° C and 1.8 at 275° C. The reaction is

(a) exothermic (b) endothermic
(c) Both (a) and (b) (d) Neither (a) nor (b)

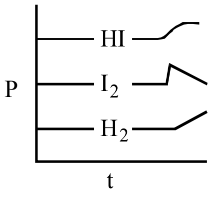
43. The element Bi melts at 271°C and has density of 9.73 g/ml as a solid and 10.05 g/ml as a liquid at this temperature. For the equilibrium $Bi(s) \rightleftharpoons Bi(\ell)$, the melting point is favoured in this endothermic reaction either by

(a) increasing temperature, decreasing pressure
(b) decreasing temperature, decreasing pressure
(c) increasing temperature, increasing pressure
(d) there is no effect of pressure on melting point

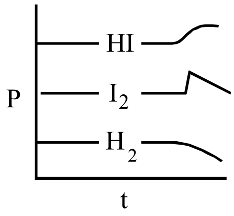
44. Consider the gaseous equilibrium of

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

In the following graphs the three gases are at equilibrium in a container. At some time t, extra I_2 is added. Which of the following sets will respond to this situation ?



A



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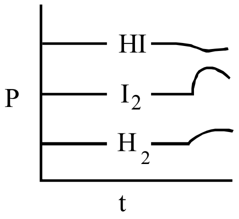
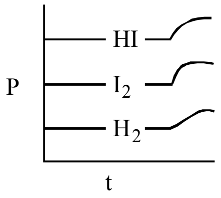
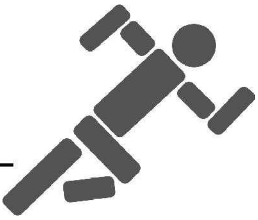


C



D

(a) A (b) B
(c) C (d) D



Hints & Solutions

EXERCISE 1

1. In the backward direction.

3. AB is more stable. Higher the value of K more will be the stability of product formed.

4. Solubility of gases in liquid increases with decrease in temperature.

5. $K_p = \dfrac{\left(p_{H_2}\right)^4}{\left(p_{H_2O}\right)^4}$ [Fe and Fe_3O_4 are solids]

6. No, K remains constant.

7. $CH_4(g) + 2H_2S(g) \rightarrow 4H_2(g) + CS_2(g)$

9. 4.56×10^{-6} mol²/*l*²

10. (a) Increase in temperature would favour the forward reaction while decrease in temperature would favour the backward reaction.

(b) Increase in pressure favours the reaction towards less number of moles of gaseous species.

11. $p_{H_2} = p_{Br_2} = 2.5 \times 10^{-2}$ bar

$p_{HBr} = 10.0 - 5.0 \times 10^{-2}$

≈ 10.0 bar

14. (c) **15.** (c) **16.** (c) **17.** (d) **18.** (c)

19. (b) **20.** (a) **21.** (a) **22.** (d) **23.** (b)

EXERCISE 2

1. (a) The product is separated as solid or escapes as gas in an irreversible reaction.

2. (a) Le Chatelier's principle, equilibrium shifted in the backward direction.

3. (b) $\Delta G = 0$ at equilibrium.

4. (b) $K' = \sqrt{K}$

5. (d) Reaction (II) and reverse of reaction (I) gives the desired reaction hence $K = K_2 \times \dfrac{1}{K_1} = \dfrac{K_2}{K_1}$.

6. (d) Dissolution of salt lowers the V.P. It is also effected by temperature.

7. (c) It will decrease the concentration. The equilibrium will shift in the direction where more moles are formed to keep K_c constant.

8. (b) Relation is $K_p = K_c\,(RT)^{\Delta n}$

9. (d) $\Delta n = 3 - 2 = 1$; $K_p = K_c\,(RT)$ hence $K_p > K_c$

10. (a) $\because \Delta n = -1 \therefore K_p = 26 \times (0.0821 \times 523)^{-1} = 0.61\ \text{atm}^{-1}$

11. (b) K_c is not influenced by presence of a catalyst.

12. (a) Unit of $K_p = (\text{Atm})^{\Delta n} = (\text{Atm})^{-2}$

(Δn = moles of products – moles of reactants)

13. (d) Q increases with the formation of products

$$Q = \frac{[\text{Conc. of Products}]}{[\text{Conc. of Reactants}]}$$

14. (d) $K_p = p_{CO_2}$ others are solids. The concentration terms for solids and liquids are taken as unity.

15. (b) $3Fe(s) + 4H_2O\,(\text{steam}) \rightleftharpoons Fe_3O_4\,(s) + 4\,H_2\,(g)$

$K_p = \dfrac{(p_{H_2})^4}{(p_{H_2O})^4}$ only gaseous products and reactants.

16. (b) Forward reaction is favoured by removal of products.

17. (a) $I_2 \rightleftharpoons 2I^-$

$1 - x \qquad 2x$

$$K_c = \frac{(2x)^2}{(1-x)} = 10^{-6}$$

Soln. shows that $(1 - x) > 2x \therefore \left[I_2(g)\right] > \left[I^-(g)\right]$

18. (a) $\Delta G° = -2.303\,RT \log K_p$ when $K_p = 1, \Delta G° = 0$ since $\log 1 = 0$

19. (c) Van't Hoff's Isochore $\dfrac{d \ln K_p}{dt} = \dfrac{\Delta H}{RT^2}$. Relation between T and K_c.

20. (a) See Le Chatelier's principle.

21. (b) Reverse reaction, Le Chatelier's principle $\Delta n = 2 - 1 = 1$.

22. (c)

	A	+ 2B	⇌ 2C
Initial moles in 2 litres	2	3	2
At Equilibrium moles in 2 litres	2.5	4	1
Molar conc. moles in 2 litres	1.25	2	0.5

$$K_c = \frac{(0.5)^2}{(1.25)(2)^2} = 0.05$$

23. (a)

	H_2	+ I_2	⇌ 2HI
Initial moles	4.5	4.5	0
Moles at eqm.	3	3	3

$K = \dfrac{(3)^2}{3 \times 3} = 1$. Note : when there is no change in the number of moles, $\Delta n = 0$ the volume or capacity of vessel can be ignored.

24. (c) $$A + B \rightleftharpoons C + D$$

At eqb. $x \quad x \qquad 2x \quad 2x$

$$K_c = \frac{2x.2x}{x.x} = 4$$

25. (d) See Le Chatelier's principle.

26. (b) $$A + B \rightleftharpoons C + D$$

Initial $0.9 \quad 0.9 \qquad 0 \quad 0$

At eqm. $0.3 \quad 0.3 \qquad 0.6 \quad 0.6$

$$K_c = \frac{0.6\times0.6}{0.3\times0.3} = 4$$

27. (c) Le Chatelier's principle since reaction is exothermic hence low temperature will favour forward reaction also volume is decreased by applying high pressure.

28. (c) Reaction (II) is $\frac{1}{2}$ of (I). $\therefore K = \sqrt{K} = \sqrt{49} = 7$.

29. (c) By addition of SO_2 equilibrium will shift to RHS which is exothermic. Hence temperature will increase.

30. (d) $K_{eqb} = \frac{K_f}{K_b} = \frac{2}{1} = 2$

31. (a) $$H_2 + I_2 \rightleftharpoons 2HI$$

Initial $1 \qquad 2 \qquad 0$

At eqb. $0.2 \quad 2 - 0.8 = 1.2 \quad 2 \times 0.8 = 1.6$

32. (c) Le Chatelier's principle.

33. (a) Temperature and pressure (Le Chatelier's principle) $\Delta n \neq 0$.

34. (d) $$A + B \rightleftharpoons 2C$$

Initial moles $3 \qquad 1 \qquad 0$

At eqb. $3 - 0.75 \quad 1 - 0.75 \quad 1.5$

$$K_c = \frac{(1.5)^2}{(2.25)(0.25)} = 4$$

35. (b) $K_p = K_c\,(RT)^{\Delta n}$ since $\Delta n = 0$, $K_p = K_c$.

36. (c) Reaction (c) is endothermic. Electrolysis or decomposition of H_2O is endothermic in nature.

37. (b) $$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Initial mole $1 \qquad 2 \qquad 0$

Moles at eqb. $1 - 0.4 = 0.6 \quad 2 - 3 \times 0.4 = 0.8 \quad 0.8$

38. (d) No change in concentration at constant volume only pressure is increased when some inert gas is introduced.

39. (c) Follow Le Chatelier's principle.

40. (d) $K_p = K_c\,(RT)^{\Delta n}$; $K_c = \frac{1.44\times10^{-5}}{(0.082\times773)^{-2}}$

41. (d) $$C_6H_{12}O_6 \rightleftharpoons 6HCHO$$

Initial 1 M

At eqb. $1 - x \qquad 6x$

$K_c = \frac{[6x]^6}{1-x}$ for reverse reaction $\frac{1-x}{(6x)^6} = 6\times10^{22}$;

On solving $6x = 1.6 \times 10^{-4}$ M.

42. (c) $$2AB_3 \rightleftharpoons A_2\,(g) + 3B_2\,(g)$$

Initial moles $8 \qquad 0 \qquad 0$

Moles at eqb. $8 - x \qquad x/2 \qquad 3x/2$

given $x/2 = 2 \;\therefore x = 4$ $\quad K_c = \frac{[B_2]^3[A_2]}{[AB_3]^2} = \frac{(6)^3\times2}{(4)^2} = 27$

43. (a) $\Delta G^\circ = -2.303\,RT\log K$

$-4.606 \times 10^3 = -2.303 \times 2 \times 500 \log K_c$

$\therefore K_c = 100$.

44. (d) $K_p = \frac{p_{CH_3OH}}{p_{CO}\times p_{H_2}} = \frac{2}{1\times(0.1)^2} = 200$;

For reverse reaction $\frac{1}{K_p} = \frac{1}{200} = 5\times10^{-3}\,\text{atm}^2$

45. (c) No effect of pressure when $\Delta n = 0$.

46. (d) $$N_2O_4 \rightleftharpoons 2NO_2$$

$1 - \alpha \qquad 2\alpha$

Total moles at eqb $= 1 - \alpha + 2\alpha = 1 + \alpha$

$$K_c = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{\left(\frac{2\alpha}{1+\alpha}.P\right)^2}{\frac{1-\alpha}{1+\alpha}.P} = \frac{4\alpha^2P}{1-\alpha^2}$$

47. (b) Degree of dissociation

$$\alpha = \frac{D-d}{d(n-1)} = \frac{104.25-70}{70(2-1)} = 48.9\% \qquad \left(D = \frac{M}{2}\right)$$

48. (b) $\alpha = \frac{46-24.5}{24.5(2-1)} = 87.74\%$

49. (d) Relation $\Delta G^\circ = -RT\ln K_c$ or $-\Delta G^\circ = RT\ln K_c$

50. (b) $Q > K_c$ will make the reaction to proceed from right to left.

51. (a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

30	30		taken
10	30	20	If yield were 100%
5	15	10	Since yield is 50%
25	15	10	On completion of reaction reactants, the left and products formed.

EXERCISE 3

1. **(d)** Given,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3;\quad K_1 \qquad ....(i)$$

$$N_2 + O_2 \rightleftharpoons 2NO;\quad K_2 \qquad ....(ii)$$

$$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O;\quad K_3 \qquad ....(iii)$$

We have to calculate

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O;\ K = ?$$

or $2NH_3 + \frac{5}{2}O_2 \longrightarrow 2NO + 3H_2O$

For this equation, $K = \dfrac{[NO]^2\,[H_2O]^3}{[NH_3]^2\,[O_2]^{5/2}}$

but $K_1 = \dfrac{[NH_3]^2}{[N_2][H_2]^3},\ K_2 = \dfrac{[NO]^2}{[N_2][O_2]}$

$$\&\ K_3 = \frac{[H_2O]}{[H_2][O_2]^{1/2}} \text{ or } K_3^3 = \frac{[H_2O]^3}{[H_2]^3\,[O_2]^{3/2}}$$

Now operate, $\dfrac{K_2\,.\,K_3^{\,3}}{K_1}$

$$= \frac{[NO]^2}{[N_2][O_2]} \times \frac{[H_2O]^3}{[H_2]^3\,[O_2]^{3/2}} \cdot \frac{[N_2][H_2]^3}{[NH_3]^2}$$

$$= \frac{[NO]^2\,[H_2O]^3}{[NH_3]^2\,[O_2]^{5/2}} = K$$

$$\boxed{\therefore\ K = \frac{K_2\,.\,K_3^{\,3}}{K_1}}$$

2. **(b)** For the reaction

$$\underset{\text{at equi}}{} \quad \underset{2(1-x)}{2AB_2(g)} \rightleftharpoons \underset{2x}{2AB(g)} + \underset{x}{B_2(g)}$$

$$K_c = \frac{[AB]^2\,[B_2]}{[AB_2]^2} \text{ or } K_c = \frac{(2x)^2 \times x}{\{2(1-x)\}^2}$$

$= x^3$ [$(1-x)$ can be neglected in denominator $(1-x) \simeq 1$]

The partial pressure at equilibrium are calculated on the basis of total number of moles at equilibrium.

Total number of moles

$= 2\,(1-x) + 2x + x = (2+x)$

$\therefore\ P_{AB_2} = \dfrac{2(1-x)}{(2+x)} \times P$, where P is the total pressure.

$$P_{AB} = \frac{2x}{(2+x)} \times P,\quad P_{B_2} = \frac{x}{(2+x)} \times P$$

Since x is very small so can be neglected in denominator

Thus, we get

$P_{AB_2} = (1-x) \times P \qquad P_{AB} = x \times P$

$$P_{B_2} = \frac{x}{2} \times P$$

Now, $K_P = \dfrac{(P_{AB})^2\,(P_{B_2})}{(P_{AB_2})^2}$

$$= \frac{(x)^2 \times P^2.P \times \frac{x}{2}}{(1-x)^2 \times P^2}$$

$$= \frac{x^3.P^3}{2 \times 1 \times P^2} \qquad [\because\ 1 - x \simeq 1\,]$$

$$= \frac{x^3.P}{2} \text{ or } x^3 = \frac{2.K_p}{P} \text{ or } x = \left(\frac{2K_p}{P}\right)^{\frac{1}{3}}$$

3. **(c)** Given reactions are

$X \rightleftharpoons Y + Z \qquad .....(i)$

and $A \rightleftharpoons 2B \qquad ......(ii)$

Let the total pressure for reaction (i) and (ii) be P_1 and P_2 respectively, then

$\dfrac{K_{P_1}}{KP_2} = \dfrac{9}{1} \qquad$ (given)

After dissociation,

$$\begin{array}{lccc} & X & \rightleftharpoons & Y + Z \\ \text{At equilibrium} & (1-\alpha) & \alpha & \alpha \end{array}$$

[Let 1 mole of X dissociate with α as degree of dissociation]

Total number of moles $= 1 - \alpha + \alpha + \alpha$

$= (1+\alpha)$

Thus $P_X = \left(\dfrac{1-\alpha}{1+\alpha}\right).\,P_1\,;\ P_Y = \left(\dfrac{\alpha}{1+\alpha}\right)P_1;$

$$P_Z = \left(\frac{\alpha}{1+\alpha}\right).P_1$$

$$\therefore\ K_{P_1} = \left(\frac{\alpha}{1+\alpha}\right).P_1 \times \frac{\alpha}{(1+\alpha)}.$$

$$P_1 / \left(\frac{1-\alpha}{1+\alpha}\right).P_1 \ ....\ (i)$$

$$\begin{array}{lccc} \text{Similarly for} & A & \rightleftharpoons & 2B \\ \text{At equilibrium} & (1-\alpha) & & 2\alpha \end{array}$$

We have,

$$K_{P_2} = \left(\frac{2\alpha P_2}{1+\alpha}\right)^2 / \left(\frac{1-\alpha}{1+\alpha}\right)P_2 \ ....(ii)$$

Dividing (i) by (ii), we get

$$\frac{K_{P_1}}{K_{P_2}} = \frac{\alpha^2.P_1}{4\alpha^2.P_2} \text{ or } \frac{K_{P_1}}{K_{P_2}} = \frac{1}{4}.\frac{P_1}{P_2}$$

or $9 = \frac{1}{4}\cdot\frac{P_1}{P_2}$ $\left[\therefore \frac{K_{P_1}}{K_{P_2}} = \frac{9}{1}\right]$

or $\frac{P_1}{P_2} = \frac{36}{1}$ or $P_1 : P_2 = 36 : 1$

i.e. option (c) is correct answer.

4. **(b)** Given : Equilibrium constant (K_1) for the reaction

$$HI(g) \xrightleftharpoons{K_1} \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g);\ K_1 = 8; \qquad ....(i)$$

To find equilibrium constant for the following reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g);\ K_2 = ?$ .....(ii)

For this multiply (i) by 2, we get

$2HI(g) \rightleftharpoons H_2(g) + I_2(g);$

$K_1 = 8^2 = 64.$ .....(iii)

[*Note*: When the equation for an equilibrium is multiplied by a factor, the equilibrium constant must be raised to the power equal to the factor]

Now reverse equation (iii), we get

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g); K = \frac{1}{64}$ .....(iv)

[Note: For a reversible reaction, the equilibrium constant of the backward reaction is inverse of the equilibrium constant for the forward reaction.]

Equation (iv) is the same as the required equation (ii), thus K_2 for equation (ii) is $\frac{1}{64}$ i.e. option (b) is correct.

5. **(d)** $2C(s) + O_2(g) \rightleftharpoons 2CO_2(g)$

$\Delta n = 2 - 1 = +1$

$\therefore$ K_c and K_p are not equal.

6. **(c)**

	$2A(g)$ +	$B(g) \rightleftharpoons$	$3C(g)$ +	$D(g)$	
Mole ratio	2	1	3	1	
Molar concentration	1	1	0	0	at t = 0
Equilibrium molar concentration	1 − 0.5 = 0.50	1 − 0.25 = 0.75	0.75	0.25	

7. **(c)** $2SO_2 + O_2 \rightleftharpoons 2SO_3$ $K = 278$ (given)

$SO_3 \rightleftharpoons SO_2 + \frac{1}{2}O_2$ $K' = \left(\sqrt{\frac{1}{K}}\right)$

$= \sqrt{\frac{1}{278}} = \sqrt{35.97 \times 10^{-4}} = 6 \times 10^{-2}$

8. **(c)** $A_2 + B_2 \rightleftharpoons 2AB$ $K_c = \frac{[AB]^2}{[A_2][B_2]}$

$K_c = \frac{(2.8 \times 10^{-3})^2}{3 \times 10^{-3} \times 4.2 \times 10^{-3}}$

$= \frac{(2.8)^2}{3 \times 4.2} = 0.62$

9. **(a)** In this reaction the ratio of number of moles of reactants to products is same i.e. 2 : 2, hence change in volume will not alter the number of moles.

10. **(d)** In (a), (b) and (c) no. of mole of products is not equal to no. of mole of reactants.

11. **(d)** $K_p = K_c(RT)^{\Delta n};\ \Delta n = 1 - \left(1 + \frac{1}{2}\right) = 1 - \frac{3}{2} = -\frac{1}{2}.$

$\therefore \frac{K_p}{K_c} = (RT)^{-1/2}$

12. **(b)** $K_C = \frac{[NO_2]^2}{[N_2O_4]} = \frac{[1.2 \times 10^{-2}]^2}{[4.8 \times 10^{-2}]} = 3 \times 10^{-3}$ mol/L

13. **(b)** Due to exothermicity of reaction low or optimum temperature will be required. Since 3 moles are changing to 2 moles.

$\therefore$ High pressure will be required.

14. **(d)** For $P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$

$K_c = \frac{1}{(O_2)^5}$. The solids have concentration unity

15. **(c)** $K_p = K_c(RT)^{\Delta n};\ \Delta n = 1 - 2 = 1$ $\therefore \frac{K_p}{K_c} = \frac{1}{RT}$

16. **(a)** $Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$

$E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}][H_2]}{[H^+]^2}$

Addition of H_2SO_4 will increase $[H^+]$ and E_{cell} will also increase and the equilibrium will shift towards RHS

17. **(a)** The reaction given is an exothermic reaction thus according to Le chatalier's principle lowering of temperature, addition of F_2 and Cl_2 favour the forward direction and hence the production of ClF_3.

18. **(d)** For the reaction:- $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

Given $K_c = 1.8 \times 10^{-6}$ at 184 °C

R = 0.00831 kJ/mol. K

$K_p = K_c(RT)^{\Delta n_g}$

$\Delta n_g = 3 - 2 = 1$

$K_p = 1.8 \times 10^{-6} \times 0.00831 \times 457$

$= 6.836 \times 10^{-6}$

Hence it is clear that $K_p > K_c$

19. **(a)**

	$NH_4HS_{(s)} \rightleftharpoons$	$NH_{3(g)}$	+ $H_2S_{(g)}$
	start	0.5 atm	0 atm
	At equib.	0.5 + x atm	x atm.

Then $0.5 + x + x = 2x + 0.5 = 0.84$ (given)

$\Rightarrow x = 0.17$ atm.

$p_{NH_3} = 0.5 + 0.17 = 0.67$ atm; $p_{H_2S} = 0.17$ atm

$K = p_{NH_3} \times p_{H_2S} = 0.67 \times 0.17\ atm^2 = 0.1139 = 0.11$

20. **(c)** $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$

$$K_C = \frac{[SO_2][O_2]^{1/2}}{[SO_3]} = 4.9 \times 10^{-2};$$

On taking the square of the above reaction

$$\frac{[SO_2]^2[O_2]}{[SO_3]^2} = 24.01 \times 10^{-4}$$

Now K'_C for $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3$

$$= \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = \frac{1}{24.01 \times 10^{-4}} = 416$$

21. **(b)** Let the initial moles of X be ‘a’ and that of Z be ‘b’ then for the given reactions, we have

	X	$\rightleftharpoons$ $2Y$
Initial	a moles	0
At equi (moles)	$a(1-\alpha)$	$2a\alpha$

Total no. of moles $= a(1-\alpha) + 2a\alpha$

$= a - a\alpha + 2a\alpha$

$= a(1+\alpha)$

Now, $$K_{P_1} = \frac{(n_y)^2}{n_x} \times \left(\frac{P_{T_1}}{\Sigma n}\right)^{\Delta n}$$

or, $$K_{P_1} = \frac{(2a\alpha)^2.P_{T_1}}{[a(1-\alpha)][a(1+\alpha)]}$$

	Z	$\rightleftharpoons$ P	$+$ Q
Initial	b moles	0	0
At equi (moles)	$b(1-\alpha)$	$b\alpha$	$b\alpha$

Total no . of moles $= b(1-\alpha) + b\alpha + b\alpha$

$= b - b\alpha + b\alpha + b\alpha$

$= b(1+\alpha)$

Now $$K_{P_2} = \frac{n_Q \times n_P}{n_2} \times \left[\frac{P_{T_2}}{\Sigma_n}\right]^{\Delta_n}$$

or $$K_{P_2} = \frac{(b\alpha)(b\alpha).P_{T_2}}{[b(1-\alpha)][b(1+\alpha)]}$$

or $$\frac{K_{P_1}}{K_{P_2}} = \frac{4\alpha^2.P_{T_1}}{(1-\alpha^2)} \times \frac{(1-\alpha)^2}{P_{T_2}.\alpha^2} = \frac{4P_{T_1}}{P_{T_2}}$$

or $$\frac{P_{T_1}}{P_{T_2}} = \frac{1}{9} \qquad \left[\because \frac{K_{P_1}}{K_{P_2}} = \frac{1}{9} \text{ given}\right]$$

or $$\frac{P_{T_1}}{P_{T_2}} = \frac{1}{36} \text{ or } 1:36$$

i.e., (b) is the correct answer.

22. **(c)** Reaction (c) can be obtained by adding reactions (a) and (b) therefore $K_3 = K_1 . K_2$
Hence (c) is the correct answer.

23. **(a)**

	$CO_2 + C_{(graphite)}$	$\rightleftharpoons$ $2CO$
$P_{initial}$	0.5atm	0
P_{final}	$(0.5-x)$atm	$2x$ atm

Total P at equilibrium $= 0.5 - x + 2x = 0.5 + x$ atm

$0.8 = 0.5 + x$

$\therefore \quad x = 0.8 - 0.5 = 0.3$ atm

Now $K_p = (P_{CO})^2 / P_{CO_2}$

$$= \frac{(2 \times 0.3)^2}{(0.5-0.3)} = \frac{(0.6)^2}{(0.2)} = 1.8 \text{ atm}$$

24. **(d)** For the reaction

$N_2 + O_2 \longrightarrow 2NO \quad K = 4 \times 10^{-4}$

Hence for the reaction

$$NO \longrightarrow \frac{1}{2}N_2 + \frac{1}{2}O_2 \quad K' = \frac{1}{\sqrt{K}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = 50$$

EXERCISE 4

1. **(c)** $N_2O_4 \rightleftharpoons 2NO_2$

0.2/2 $\quad 2 \times 10^{-3}/2$ Concentration at equilibrium

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{10^{-3} \times 10^{-3}}{0.1} = 1 \times 10^{-5}$$

2. **(b)** $\Delta G^\circ = -RT \ln K_c$ for $\Delta G^\circ = 0$, $K_c = 1$; since $\ln 1 = 0$

3. **(a)** When moles of gaseous reactants and the products are the same on both sides, their is no effect of pressure

4. **(d)** The equilibrium constant does not vary with any factor other than temperature

5. **(a)** $2HI \rightleftharpoons H_2 + I_2$. It is 22% decomposed, $\therefore \frac{3.20 \times 22}{100} = 0.704$

(3.2–0.704) is equal to HI present at equilibrium which is =2.496

6. **(c)** $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$K_p = K_c(RT)^{\Delta n}$; $\Delta n = 2 - 2 = 0$; $\therefore K_p = K_c$

7. **(d)** When volume is increased the conc. decreases & the equilibrium shifts in the direction where more moles are formed.

8. **(c)** $K_p = \frac{P_{CO}^2}{P_{CO_2}}; K_p = \frac{4 \times 4}{2} = 8$; C(s) = 1; The concentration of solids and liquids are taken as unity

9. **(c)** $K_c = \frac{K_f}{K_b}; K_b = \frac{20}{50}; K_b = 0.4$

10. **(c)** The lower the energy of activation, the more is the rate of reaction

11. **(d)**

12. **(d)** With change of pressure, x will change in such a way that K_p remains constant.

13. **(a)** For the equilibria : $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$K_P = K_C \times (RT)^{\Delta n}$ Since temperature is constant so K_C or K_P will remain constant. Further since volume is halved, the pressure will be doubled so α will decrease so as to maintain the constancy of K_C or K_P.

14. **(d)** The condition for the equilibrium is

$(\Delta G)_{T,P} = 0$ and $(\Delta S)_{U,V} = 0$

15. **(c)** $K_p = \frac{\alpha^2 p}{(1-\alpha^2)}$

or $K_p(1-\alpha^2) = \alpha^2 p$

$\therefore K_p = \alpha^2(K_p + p)$

16. **(a)** In Van't Hoff equation $\frac{d\ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$ when $\frac{d\ln K}{dT} < 0$ we will get negative value for ΔH°, the reaction will be exothermic in nature.

17. **(b)** Van't Hoff reaction isotherm is $\Delta G = \Delta G^\circ + RT \ln Qp$
When the reaction is in a state of equilibrium $\Delta G = 0$
Then $\Delta G^\circ = -RT \ln Q_p = -RT \ln K_p$

18. **(c)** Van't Hoff isochore is $\frac{\ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$

integrating $\ln K_2 - \ln K_1 = -\frac{\Delta H^\circ}{R}\int_{T_1}^{T_2} d(1/T)$

19. **(d)** K_p and K_C are independent of pressure. K_x is related to pressure.

20. **(b)** At equilibrium the moles of Cl_2 must be $= 0.15 \times 3 = 0.45$

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$\frac{x-0.45}{3}$ $\frac{0.45}{3}$ $\frac{0.45}{3}$ Eqb. Conc.

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$\therefore 0.04 = \frac{0.15 \times 0.15}{(x-0.45)/3}$ $\therefore x = 2.1$ moles

21. **(b)** The efflorescent salts loss water to atmosphere

$K_p = p^2_{H_2O} = 1.086 \times 10^{-4};$

$p_{H_2O} = 1.042 \times 10^{-2}$ atm $= 7.92$ mm

If H_2O pressure at 25°C is less than 7.92 mm.
The reaction

$$CuSO_4.5H_2O(s) \longrightarrow CuSO_4.3H_2O(s) + H_2O(g)$$

will not proceed in RHS.

22. **(d)** $K_p = p^2_{B_1} \times p^3_{C_1}$

Again, $K_p = p^2_{B_2} \times (2p_{C_1})^3$

$\therefore p^2_{B_1} \times p^3_{C_1} = P^2_{B_2} \times 8p^3_{C_1}$

$\therefore \frac{p^2_{B_1}}{8} = p^2_{B_2}$ or, $\frac{p_{B_1}}{2\sqrt{2}} = p_{B_2}$

23. **(a)** $\frac{[B]}{[A]} = 2, \frac{[C]}{[B]} = 4$ and $\left[\frac{D}{C}\right] = 6$

Multiply the three equations,

$2 \times 4 \times 6 = \frac{[D]}{[A]} = K_c$

24. **(b)** $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$1-x$ $3-3x$ $2x$ at equilibrium

Total moles,
$1 - x + 3 - 3x + 2x = 4 - 2x = 3$ (given)
(Since 4 moles = 4 atm given)
$\therefore x = 0.5$

K_p for dissociation of $NH_3 = \frac{p_{N_2} \times p^3_{H_2}}{p^2_{NH_3}}$

$$= \frac{\left(\frac{1-0.5}{3} \times 3\right) \times \left[\left(\frac{3-3\times0.5}{3}\right) \times 3\right]^3}{\left[\frac{2\times0.5\times3}{3}\right]^2}$$

$= 0.5 \times (1.5)^3$ atm^2

25. **(b)** Introduction of CO will suppress the dissociation of $COCl_2$ and concentration of Cl_2 will decrease. This will favour the dissociation of PCl_5.

26. **(a)** Instability constant

$$= \frac{1}{\text{formation constant}} = \frac{K_{(\text{reverse})}}{K_{(\text{forward})}} = \frac{2.0\times10^{-2}}{1.0\times10^{6}}$$

$= 2.0 \times 10^{-8}$

27. **(c)** $\Delta G^\circ = -2.303\, RT \log K_p$

$= -2.303 \times 8.314 \times 300 \log 10^{20}$

$\Delta G^\circ \approx -115$ KJ

28. **(a)** $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$1-x \qquad x \qquad x$ at pressure P

$1-x_1 \qquad x_1 \qquad x_1$ at pressure P_1

$$K_p = \frac{\frac{x}{1+x}.P \frac{x}{1+x}.P}{\frac{1-x}{1+x}.P} = \frac{x^2p}{(1-x^2)} = \frac{x_1^2P_1}{(1-x_1^2)}$$

Put $x = 0.5, P = 4$ atm, $x_1 = 0.8,\ P_1 = ?$

P_1 will come out be 0.75 atm

29. **(b)** $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$

$\frac{6P}{9} \qquad \frac{2P}{9} \qquad \frac{P}{9}$

Since total pressure is P.

So, $\frac{6P}{9} + \frac{2P}{9} + \frac{P}{9} = P$

$$\therefore K_p = \frac{p_{NO}^2 \times p_{Br_2}}{p_{NOBr}^2} = \frac{\left(\frac{2P}{9}\right)^2 \times \frac{P}{9}}{\left(\frac{6P}{9}\right)^2}$$

$$\therefore \frac{K_p}{P} = \frac{1}{81}$$

30. **(c)** $NH_4OH(aq) + H^+(aq) \rightleftharpoons NH_4^+(aq) + H_2O(\ell)$

$$K_1 = \frac{[\overset{+}{NH_4}]}{[NH_4OH][H^+]} = 1.8 \times 10^9;$$

$NH_4OH\ (aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_2 = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

Multiply this by $[H^+]$ and divide also

$$K_2 = \frac{[NH_4^+][OH^-][H^+]}{[NH_4OH][H^+]} = K_1 \times K_w$$

$$= 1.8 \times 10^9 \times 1.0 \times 10^{-14} = 1.80 \times 10^{-5}$$

31. **(b)** $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$1-\alpha \qquad \alpha \qquad \alpha$

$$\therefore K_p = \frac{\frac{\alpha}{1+\alpha}P \times \frac{\alpha}{1+\alpha}P}{\frac{1-\alpha}{1+\alpha}P} = \frac{\alpha^2P}{1-\alpha^2}$$

or, $K_p = \alpha^2P \qquad \therefore \alpha = \sqrt{\frac{K_p}{P}}$ when $1-\alpha^2 = 1$

32. **(a)** $A + 3B \rightleftharpoons 2C + D$

$2a \qquad a \qquad 0 \qquad 0$

$2a-x \qquad a-3x \qquad 2x \qquad x$

$a-3x = 2x$ (condition given)

$\therefore x = \frac{a}{5}$

The % of B reacted is

$$\frac{3x}{a} \times 100 = \frac{3}{a}.\frac{a}{5} \times 100 = 60\%$$

33. **(b)** $I^-(aq) + Ag^+(aq) \longrightarrow AgI(s)$

0.8 mol at equilibrium.

Thus mole of I^- reacted $= 1.0 - 0.8 = 0.2$

$I^- \ + \ I_2 \rightleftharpoons I_3^-(aq)$

1 mol $\quad 0.25$ mol $\qquad 0$ mol

$1-0.2 \quad 0.25-0.20 \qquad 0.2$

$= 0.8 \qquad = 0.05$

$$\text{Stability constant } K = \frac{I_3^-}{[I^-][I_2]} = \frac{0.2}{0.8 \times 0.05} = 5$$

34. **(d)** $A + 2B \rightleftharpoons 2C + D$

$2 \qquad 3 \qquad 0 \qquad 0$ initial conc.

$2-x \quad 3-2x \qquad 2x \qquad x$ equilibrium conc.

Again $2-x = 2x$

$\therefore\ x = 2/3$

$$K_c = \frac{[2x]^2[x]}{[2-x][3-2x]^2}$$

Put $x = 2/3 \qquad \therefore K_c = 0.32$

35. **(d)** $AB_5(g) \rightleftharpoons AB(g) + 2B_2(g)$

$1-\alpha \qquad \alpha \qquad 2\alpha$

Total moles at equilibrium $= 1 + 2\alpha$

$$= 1 + \frac{20 \times 2}{100} = 1.4$$

$$\frac{p_1}{p_2} = \frac{n_1T_1}{n_2T_2}; \quad \frac{1}{p_2} = \frac{1 \times 300}{1.4 \times 600}$$

$\therefore \qquad p_2 = 2.8$ atm

36. **(a)** $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$1-0.5 \qquad 0.5 \qquad 0.5$ Moles at equilibrium

Total moles = 1.5

$$K_p = \frac{\frac{0.5}{1.5}P \times \frac{0.5}{1.5}P}{\frac{0.5}{1.5}P} = \frac{P}{3} \quad \therefore\ P = 3K_p$$

37. **(c)** $K_f = Ae^{-E_f/RT}$ and $K_r = Ae^{-E_r/RT}$

$$\therefore \frac{K_f}{K_r} = K_c = e^{E_r - E_f/RT}$$

$$\text{or, } \log K_c = \frac{E_r - E_f}{RT \times 2.3010} = \frac{(8.000 - 10.3010) \times 1000}{2.3010 \times 2 \times 500}$$

$\therefore\ K_c = 0.1$

38. **(b)** Moles of $N_2 = \frac{28}{28} = 1$, Moles of $H_2 = \frac{6}{2} = 3$

Moles of H_2SO_4 required $= \frac{500 \times 1}{1000} = 0.5$

Moles of NH_3 neutralised by $H_2SO_4 = 1.0$

$$\left(2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4\right)$$

Hence 1 mol of NH_3 by the reaction between N_2 and H_2.

N_2 +	$3H_2$ $\rightleftharpoons$	$2\,NH_3$	
1	3	0	initial
$1 - 0.5$	$3 - 0.5 \times 3$	1	at equilibrium

$$K_c = \frac{1 \times 1}{0.5 \times (1.5)^3} = 0.592$$

39. **(a)** Eq. wt. of SO_2 = Mol. wt./2 $(SO_2 \longrightarrow SO_3)$

Eq. wt. of $K_2Cr_2O_7$ = Mol. wt./6 $(Cr_2O_7^{2-} \rightarrow 2Cr^{3+})$

$\frac{1}{3}$ mol of $K_2Cr_2O_7 = \frac{6}{3}$

or, 2 geq of $K_2Cr_2O_7$ = 2 geq of SO_2 = 1 mol of SO_2

It means only 1 mole of SO_2 reacted with O_2.

$2\,SO_2$ +	O_2 $\rightleftharpoons$	$2SO_3$	
1 mol	1 mol	0 mol	initial
1 mol	$(1 - 0.5)$ mol	1 mol	at equilibrium

$\therefore$ Total moles at equilibrium $= 1 + 0.5 + 1 = 2.5$

$$K_p = \frac{p^2{}_{SO_3}}{p^2{}_{SO_2} \times p_{O_2}} = \frac{\left(\frac{1}{2.5} \times 5\right)^2}{\left(\frac{1}{2.5} \times 5\right)^2 \times \left(\frac{0.5}{2.5} \times 5\right)} = 1.0$$

40. **(a)** $D = \frac{PM}{RT} = \frac{1 \times 82.1}{0.0821 \times 400} = 2.5\ g\ L^{-1}$

$d = 2.0\ g\ L^{-1}$ (given)

$$\alpha = \frac{D - d}{d(n-1)} = \frac{2.5 - 2}{2(3-1)} = 0.125 = 12.5\%$$

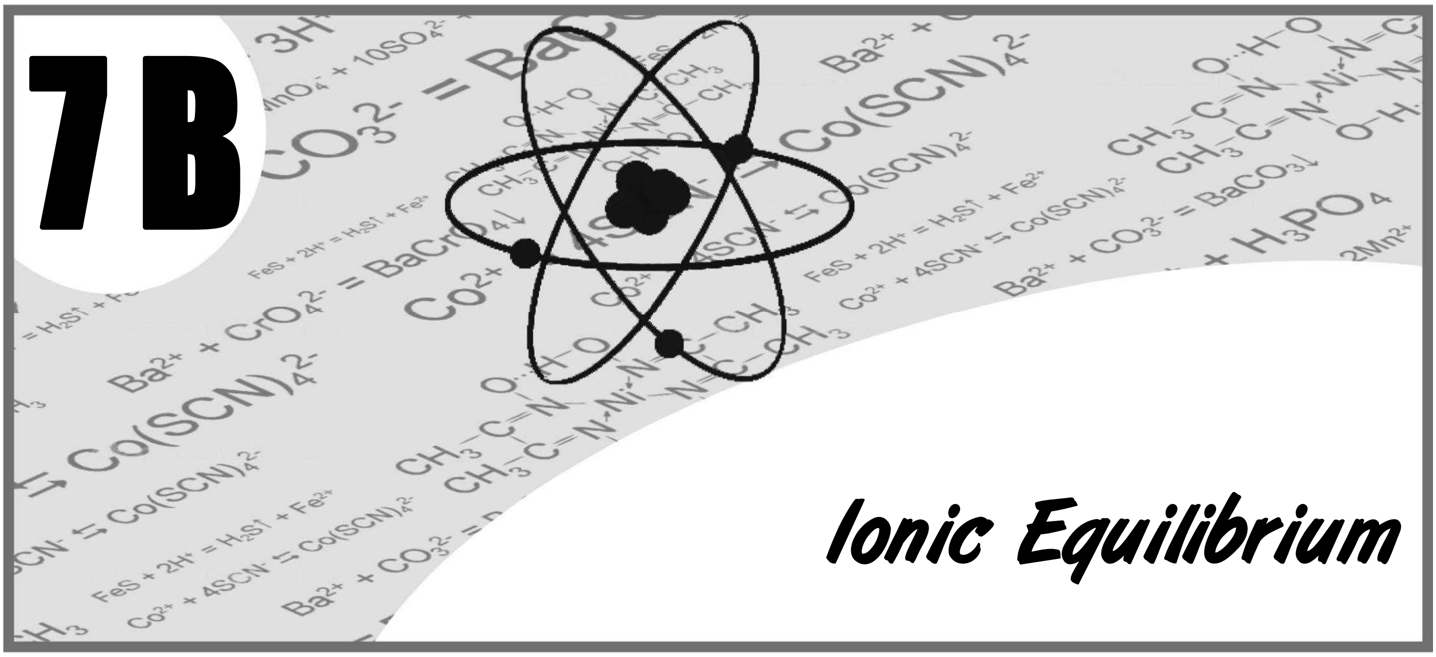
41. **(a)** The reaction quotient Q is $\frac{p_C \times p_D}{p_A \times p_B}$. In the initial stage C and D are not present. So p_C and p_D are zero. Then With the passage of the time p_C and p_D increase and p_A and p_B decrease.

42. **(a)** For exothermic reaction, $K_c \propto \frac{1}{\text{Temperature}}$

43. **(c)** Since the melting is endothermic increasing temperature will favour melting. Since density of solid is less $\left(D = \frac{M}{V}\right)$, the high pressure will reduce V and increase D, hence more melting.

44. **(b)** $K_p = \frac{p_{HI}^2}{p_{H_2} \times p_{I_2}}$

Addition of I_2 will increase p_{I_2}, hence to keep K_p constant, either p_{H_2} should decrease or p_{HI} should increase. Hence the graph (B).



7B

Ionic Equilibrium

ARRHENIUS THEORY OF IONISATION :

On the basis of colligative properties of solutions of salts, acids and bases, Arrhenius proposed the theory of ionisation i.e. spliting of these substances into ions in solution. It is reversible process, effects electrical conductivity, colligative properties like depression in freezing point, elevation in boiling point, lowering of vapour pressure, osmotic pressure.

EVIDENCES IN FAVOUR OF IONISATION :

1. *X-ray diffraction studies*
2. *Ionic reactions*
3. *Heat of neutralisation*
4. *Colour of compounds and their solutions*
5. *Colligative properties*
6. *Conductance of electrolytes in solution*

DEGREE OF IONISATION OR DISSOCIATION (α) :

The fraction of the total number of molecules which is ionised at the equilibrium state is known as degree of ionisation or dissociation.

$$\alpha = \frac{\text{Number of moles ionised}}{\text{Total number of moles}}$$

FACTORS AFFECTING IONISATION OR DISSOCIATION :

1. ***Nature of electrolytes :*** The stronger the electrolyte, the more is the ionisation and vice versa.
2. ***Nature of solvent :*** The more the dielectric constant of solvent, the more is the ionisation.
3. ***Concentration :*** The lesser the concentration, the more is the ionisation.
4. ***Temperature :*** The higher the temperature, the more is the ionisation.
5. ***Solvation :*** The more the solvation, the more is the ionisation.
6. ***Presence of the ions in the solution :*** Ionisation decreases in presence of common ions.

ELECTROLYTE :

A substance which splits into ions in solution is called electrolyte. It can be an acid, base or salt.

(i) ***Strong electrolyte :*** Which dissociates almost completely into ions even in concentrated solution eg. NaOH, KOH, HCl, H_2SO_4, NaCl, $CaCl_2$.

(ii) ***Weak electrolyte :*** Which dissociates to a small extent into ions in solution eg CH_3COOH, NH_4OH etc.

Note : **Salts are always strong electrolytes**.

OSTWALD'S DILUTION LAW :

The degree of ionisation or dissociation (α) of weak electrolytes increases with dilution and law of mass action can be applied to them.

AB	$\rightleftharpoons$	A^+	+	B^-	
C		0		0	initial conc.
C(1-α)		Cα		Cα	equilibrium conc.

Ionisation constant $K = C\alpha^2$

$$\therefore \alpha = \sqrt{\frac{K}{C}} \qquad \alpha \propto \sqrt{\frac{1}{C}}$$

Concentration of A^+ or $B^- = C\alpha$

α approaches unity with dilution.

ACIDS AND BASES :

1. **Arrhenius concept *:*** An acid is a substance that dissociates to give hydrogen ions when dissolved in water eg. HCl, CH_3COOH, H_3PO_4.

   A base is a substance that dissociates to give hydroxyl ions when dissolved in water eg. NaOH, $Ca(OH)_2$.

2. **Lowry and bronsted concept :** An acid is a substance which has a tendency to donate a proton (H^+) to any other substance.

   A base is a substance which has a tendency to accept a proton (H^+) from any other substance.

   $$\text{Acid} \rightleftharpoons H^+ + \text{Base}$$

   Acid and base differing by a proton are known as ***conjugate pair.*** **The weaker the acid, the stronger the base in conjugate pair and vice versa.**

   $$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$
   $$HCl + H_2O \rightleftharpoons H_3\overset{+}{O} + \overset{-}{Cl}$$
   $$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$
   $$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$
   $$\text{Conjugate acid} \rightleftharpoons \text{Conjugate base} + H^+$$

3. **Lewis concept :** An acid is a substance which can accept a pair of electrons from any other substance e.g. BF_3, $AlCl_3$ (incomplete octet), $SnCl_4$, SF_4 (central atom has vacant d-orbital) or cations Fe^{3+}, Cu^{2+} etc.

   A base is a substance capable to donating a pair of electrons to any other substance eg. anions X^-, OH^-, CN^- or neutral molecules having lone pair(s) of electrons on one or more atom $R\ddot{\underset{..}{O}}H$, $\ddot{N}H_3$, $H_2\ddot{\underset{..}{O}}$ etc.

   Lewis acid may be any of the following types of substances

   1. Molecules having an atom with incomplete octet
   2. Simple cations
   3. Molecules with central atom having empty d-orbitals
   4. Molecules with a multiple bond between atoms of different electronegativities

      Strength of some Lewis acids

      $BX_3 > AlCl_3 > FeX_3 > GaX_3 > SbX_5 > InX_3 > SnX_4 > AsX_5 > ZnX_2 > HgX_2$

4. **Extended Lewis concept :** When the central atom is bonded to atoms of different electronegativities by multiple bonds, the substance is known as extended Lewis acid e.g. CO_2, CS_2 etc.

   Extended Lewis base e.g. CO and unsaturated hydrocarbons like alkenes, alkynes etc. are also known as border line Lewis bases.

5. **Hard acids :** Cations of lighter elements, smaller size, higher charge not easily polarisable e.g. light alkali and alkaline metal ions of B, Al, Si, Ti^{4+}, Cr^{3+}, Co^{2+}, Fe^{3+} (lighter transition elements).

   Soft acids : Cations of **heavier elements**, **larger size**, **lower charge** and **easily polarisable** e.g. heavy transition metal ions (second and third row) e.g. Hg^{2+}, Pd^{2+}, Cd^{2+}, Cu^+, Ag^+, Hg^+ etc.

6. **Hard bases :** Species having donor atoms of higher electronegativity and low polarisability e.g. N, O, F, Cl etc. Examples H_2O, NH_3, ROH.

   Soft bases : Species having donor atom of lower electronegativity and higher polarisability e.g. P, As, S, Se etc. Examples R_3P, R_2S, I^-.

7. **Lux-flood concept of acids and bases :** An oxide ion donor is a base and an oxide ion acceptor is an acid.

   $$\underset{\text{base}}{BaO} + \underset{\text{acid}}{SiO_2} \longrightarrow BaSiO_3$$

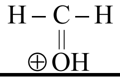
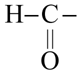
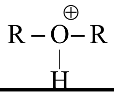
   $$\underset{\text{base}}{MgO} + \underset{\text{acid}}{SO_3} \longrightarrow MgSO_4$$

8. **Ingold concept :** All electrophiles are acids and nucleophiles are bases.

STRENGTH OF ACIDS AND BASES :

The greater the value of K_a or K_b the stronger is the acid or base. the smaller the value of pK_a the sronger is the acid.

pK_a values of some acids (Acid strength)

	Acid	**Base**	**Approximate pK_a**
1.	$HClO_4$	ClO_4^-	–10
2.	HI	I^-	–10
3.	H_2SO_4	HSO_4^-	–9.5
4.	HBr	Br^-	–9
5.	HCl	Cl^-	–7
6.	Ar. SO_3H	$ArSO_3^-$	–6.5
7.	$CH(CN)_3$	$C^-(CN)_3$	–5
8.	 $\underset{\oplus OH}{\overset{}{H-\underset{\Vert}{C}-H}}$	 $\underset{O}{H-\underset{\Vert}{C}-H}$	–4
9.	 $R-\underset{H}{\overset{\oplus}{\underset{\vert}{O}}}-R$	R–O–R	–3.5
10.	H_3O^+	H_2O	–1.74
11.	HNO_3	NO_3^-	–1.4
12.	HSO_4^-	SO_4^{--}	1.99
13.	HF	F^-	3.17
14.	HNO_2	NO_2^-	3.29
15.	$Ar\overset{+}{N}H_3$	$ArNH_2$	3.5
16.	RCOOH	$RCOO^-$	4.5
17.	H_2CO_3	HCO_3^-	6.35
18.	H_2S	HS^-	7.00
19.	NH_4^+	NH_3	9.24
20.	ArOH	ArO^-	8-11
21.	HCO_3^-	CO_3^{--}	10.33
22.	H_2O	OH^-	15.74
23.	$RCONH_2$	$RCO\overline{N}H$	17
24.	RCH_2OH	RCH_2O^-	18

25.	$HC\equiv CH$	$HC\equiv C^-$	25
26.	NH_3	NH_2^-	34
27.	$Ar.CH_3$	$ArCH_2^-$	35
28.	$CH_2{=}CH_2$	$CH_2{=}CH^-$	36.5
29.	PhH	Ph^-	37
30.	CH_4	CH_3^-	40
31.	C_2H_6	$C_2H_5^-$	42
32.	Cyclohexane (C_6H_{12})	$C_6H_{11}^-$	45

(i) **Relative strengths of acids:** For weak acid $K_a = C\alpha^2$. For two acids with dissociation constants K_{a_1} and K_{a_2} at the same concentration C,

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} = \frac{\text{Strength of acid HA}_1}{\text{Strength of acid HA}_2}$$

(ii) **Relative strengths of bases :** For weak base $K_b = C\alpha^2$. For two bases with dissociation constants K_{b_1} and K_{b_2} at the same concentration C.

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}} = \frac{\text{Strength of base B}_1\text{OH}}{\text{Strength of base B}_2\text{OH}}$$

LEVELLING EFFECT :

All the strong acids in aqueous, solution appear almost equally strong since water acts as **strong base**. For example $HClO_4$, HBr, H_2SO_4, HCl and HNO_3 appear equally strong.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Hence relative strengths in aqueous solution cannot be compared. This phenomenon is known as **levelling effect**.

EFFECT OF SOLVENT ON ACID STRENGTH :

(i) **In acetic acid :**

$$HA + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + A^-$$

As acetic acid has a little tendency to accept proton, even strong acids are feebly ionised in acetic acid. For example $HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$

(ii) **In liquid NH_3 :** $HA + \ddot{N}H_3 \rightleftharpoons NH_4^+ + A^-$

As ammonia has a great tendency to accept proton, even weak acids appear strong in liquid ammonia. For example HCl, HNO_3 and CH_3COOH appear equally strong in liquid ammonia.

(iii) **In HF :** Since HF is a strong acid, the other acids act as a base when dissolved in HF eg.

$$HNO_3 + HF \rightleftharpoons H_2\overset{+}{N}O_3 + F^-$$

RELATION BETWEEN K_a AND K_b :

$K_a \times K_b = K_w$ or $pK_a + pK_b = pK_w = 14$ at 25°C.

Ionisation of polybasic acids : Polybasic acids ionise in various steps e.g. Orthophosphoric acid H_3PO_4.

$$H_3PO_4 \overset{K_1}{\rightleftharpoons} H^+ + H_2PO_4^-$$

$$H_2PO_4^- \overset{K_2}{\rightleftharpoons} H^+ + HPO_4^{--}$$

$$HPO_4^{--} \overset{K_3}{\rightleftharpoons} H^+ + PO_4^{--}$$

$K_1 > K_2 > K_3$ and overall dissociation const. $K = K_1 \times K_2 \times K_3$

AMPHOTERIC OR AMPHIPROTIC SUBSTANCE OR AMPHOLYTES :

A substance acting as an acid as well as a base, eg. water acts as an acid with ammonia and as base with acetic acid. A substance acting as proton donor and proton acceptor.

COMMON ION EFFECT :

The degree of ionisation of an electrolyte is suppressed by the addition of another electrolyte having a common ion. This is known as common ion effect e.g. ionisation of CH_3COOH is suppressed by the addition of HCl or CH_3COONa.

(i) It helps in controlling the concentration of ions furnished by weak electrolytes.

(ii) It effects the solubility of salts.

***Mixture of weak acid and its salt with a strong base**:*

The hydrogen ion (H^+) concentration of a mixture of a weak acid HA and its highly dissociated salt say NaA is given by

(I) $HA \rightleftharpoons H^+ + A^-$

(II) $NaA \rightleftharpoons Na^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = \frac{K_a[HA]}{[A^-]} = \frac{K_a[ACID]}{[SALT]}$$

HA being weak acid and secondly due to common ion (A^-) remains almost unionized. Salts are almost 100% ionised.

Mixture of weak base and its salt with a strong acid

The hydroxyl ion (OH^-) concentration of mixture of weak base BOH and its highly dissociated salt say BCl is given by

(I) ionisation of $BOH \rightleftharpoons B^+ + OH^-$ (negligible)

(II) ionisation of $BCl \rightleftharpoons B^+ + Cl^-$ (100%)

$$K_b = \frac{[B^+][OH^-]}{[BOH]};\ [OH^-] = \frac{K_b[BOH]}{[B^+]}$$

$$[OH^-] = \frac{K_b[BASE]}{[SALT]}$$

Ex.: Calculate the $[H^+]$ concentration of solution which is 0.1 M in HA and 0.5M in NaA. K_a of HA is 1.8×10^{-6}.

Sol. : $[H^+] = \dfrac{K_a[ACID]}{[SALT]} = \dfrac{1.8\times10^{-6}\times0.1}{0.5} = 3.6\times10^{-7}$ M

Ex. : What will be the H^+ ion concentration of a solution obtained by mixing 500 ml of 0.20 M CH_3COOH and 500 ml of 0.30 M CH_3COONa (K_a of $CH_3COOH = 1.8 \times 10^{-5}$)

Sol. : Concentration of CH_3COOH in the mixture

$$= \frac{0.20 \times 500}{1000} = 0.10 \text{ mol}/1$$

Concentration of CH_3COONa in the mixture

$$= \frac{0.30 \times 500}{1000} = 0.15 \text{ mol}/1$$

$$[H^+] = \frac{1.8 \times 10^{-5} \times 0.10}{0.15} = 1.2 \times 10^{-5} \text{ mol}/1$$

SOLUBILITY PRODUCT (K_{sp}) :

At constant temperature and pressure the saturated solution of a sparingly soluble salt has an equilibrium between the excess of the solute and the ions furnished by it. e.g.

$$\underset{\substack{\text{Solid} \\ \text{undissolved}}}{AgCl} \rightleftharpoons \underset{\substack{\text{dissolved but} \\ \text{not ionised}}}{AgCl} \rightleftharpoons \underset{\text{ions in sol.}}{Ag^+ + Cl^-}$$

Applying law of mass action, $K = \dfrac{[Ag^+][Cl^-]}{[AgCl]}$

or $K[AgCl] = [Ag^+][Cl^-]$, $K_{sp} = [Ag^+][Cl^-]$

The constant K_{sp} is known as solubility product. It is equal to the product of the concentration of ions in saturated solution.

When $K_{sp} > [Ag^+][Cl^-]$ Solution is not saturated

When $K_{sp} < [Ag^+][Cl^-]$ Solution is supersaturated and precipitation takes place

When $K_{sp} = [Ag^+][Cl^-]$ Solution is saturated

For general electrolyte A_xB_y.

$K_{sp} = [A^{+y}]^x [B^{-x}]^y$

(I) K_{sp} is independent of the source of ions.

(II) Helps to know the solubility of electrolytes.

(III) Predicting ionic reactions.

(IV) Qualitative analysis.

(V) Purification of common salt, salting out of soap and Solvay ammonia soda process.

Relation between solubility product (K_{sp}) and solubility (S).

1. For binary electrolyte e.g. AgCl, $BaSO_4$

$$S = \sqrt{K_{sp}}$$

2. For ternary electrolyte e.g. CaF_2, PbI_2

$$S = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$$

Representation of K_{sp} for various electrolytes.

$Mg(OH)_2$ $K_{sp} = [Mg^{++}][OH^-]^2$

Ag_2S $K_{sp} = [Ag^+]^2 [S^{--}]$

Sb_2S_3 $K_{sp} = [Sb^{3+}]^2 [S^{--}]^3$

Ex.: K_{sp} of AgCl is 2.8×10^{-10} at 25°C. Calculate the solubility of AgCl in (I) Pure Water (II) 0.1 M $AgNO_3$ solution (III) 0.1 M NaCl.

Sol. (I) Let S mole/l be the solubility of AgCl

$K_{sp} = [Ag^+][Cl^-] = S \times S = S^2$;

$$\therefore S = \sqrt{K_{sp}} = \sqrt{2.8 \times 10^{-10}} = 1.67 \times 10^{-5} \text{ mol}/1$$

(II) $AgCl \rightleftharpoons Ag^+ + Cl^-$

$K_{sp} = [Ag^+][Cl^-]$

Solubility of AgCl will be equal to

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{2.8 \times 10^{-10}}{0.1} = 2.8 \times 10^{-9} \text{ mol}/1$$

(III) Solubility of AgCl will be equal to

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{2.8 \times 10^{-10}}{0.1} = 2.8 \times 10^{-9} \text{ mol}/1$$

Ex. : Solubility product of SrF_2 in water is 8×10^{-10}. Calculate the solubility in 0.1 M NaF aqueous solution.

Sol. : $SrF_2 \rightleftharpoons Sr^{++} + 2F^-$

Solubility of SrF_2 will be equal to

$$[Sr^{++}] = \frac{K_{sp}}{[F^-]^2} = \frac{8 \times 10^{-10}}{(0.1)^2} = 8 \times 10^{-8} \text{ mol/lit}$$

DISSOCIATION CONSTANT OF WATER / IONIC PRODUCT OF WATER (K_W) :

Water being weak electrolyte is slightly ionised as follows :

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \quad \text{or} \quad K[H_2O]^2 = [H_3O^+][OH^-]$$

$$\text{or} \quad K_W = [H_3O^+][OH^-]$$

K_w is known as ionic product of water or dissociation constant of water. It is equal to the product of concentration of $[H_3O^+]$ and $[OH^-]$ ions in water. At constant temperature of 25°C, the value of K_w is 1.0×10^{-14}.

In pure water $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ at 298 K

Molar concentration of water is 55.55 mol/lit

$K[H_2O] = [H^+][OH^-]$

$K \times 55.5 = K_w$.

Hence ionic product of water is 55.5 times greater than K. K_w increases with temperature.

The addition of salt, acid or base does not change value of K_W. Its value changes with temperature only.

Hydrogen and hydroxyl ion concentration in aqueous solution of Acids and Bases.

When an acid is added to water H^+ (aq.) ion combine with OH^- (aq.) ions so that K_w remains constant. Thus addition of an acid decreases the conc. of OH^- (aq.) ions and addition of base decreases the conc. of H^+ ions. In both cases the self ionisation of water is suppressed due to extra supply of H^+ or OH^- ions.

EXPRESSING HYDROGEN ION CONCENTRATION : pH SCALE

Any aqueous solution of some electrolyte or non electrolyte having equal concentrations of H^+ and OH^- ions, is neutral. It has been observed that H^+ ion concentrations can usually vary from 0 to 1×10^{-14} moles/l. Sorensen represented the acidic or basic character of an aqueous solution in terms of pH. The pH of a solution is the numerical value of the negative power to which ten must be raised to express the H^+ ion concentration.

$[H^+] = 10^{-pH}$

In pure water $[H^+] = 10^{-7} = 10^{-pH}$ at 25ºC or 298 K

Hence pH of pure water is 7.

$\log [H^+] = -pH \log 10$

$$\therefore pH = -\log (H^+) = \log \frac{1}{[H^+]}$$

Thus pH of a solution is the negative logarithm of hydrogen ion concentration. Similarly, negative logarithm of hydroxyl ion concentration is known as pOH.

$$pOH = -\log[OH^-]$$

An aqueous solution having pH value less than 7, is acidic and more than 7 at 298 K is basic.

Strongly acidic	Moderate acidic	Weakly acidic	Weakly basic	Moderate	Strongly basic	
0 1 2	3 4	5 6 7	8 9	10 11 12	13 14	(pH values)

$pH + pOH = 14$

The pH changes with temperature. It decreases with rise in temperature.

pH range of some important substances:

Subs.	pH range	Subs.	pH range
Tears	7.4	Vinegar	2.4 - 3.4
Blood plasma	7.3 - 7.42	Soft drinks	2.0 - 4.0
Human saliva	6.5 - 7.5	Gastric Juice	1.0 - 3.0
Human Urine	4.8 - 8.4	Boiling water	6.56

Ex. : What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12).

Sol. : HCl and NaOH are strong electrolytes.

pH of HCl = 2 $[HCl] = 10^{-2}$ M

pH of NaOH = 12 $[NaOH] = 10^{-2}$ M

Mev. of HCl = $200 \times 10^{-2} = 2$

Mev. of NaOH = $300 \times 10^{-2} = 3$

On mixing mev. of NaOH left = (3–2) = 1,

gev of NaOH = 0.001

$[OH^-] = 2 \times 0.001 = 0.002$

$-\log [OH^-] = pOH.$

$\therefore pOH = 2.6989;\quad pH = 14 - 2.6989 = 11.3011$

SALT HYDROLYSIS :

Salts are strong electrolytes and on dissolution in water split into ions which react with H^+ or OH^- ions furnished by water yielding acidic or basic solution. The process is known as salt hydrolysis.

1. ***Hydrolysis of salt of a strong acid and strong base :*** e.g. KCl, NaCl, Na_2SO_4 etc.

$$KCl + H_2O \rightleftharpoons KOH + HCl$$

Representing strong electrolytes as ions

$$K^+ + Cl^- + H_2O \rightleftharpoons K^+ + OH^- + H^+ + Cl^-$$

we have overall reaction $H_2O \rightleftharpoons H^+ + OH^-$

The solution is neutral since $[H^+] = [OH^-]$, pH = 7, thus salts of strong acids and strong bases are not hydrolysed.

2. ***Salts of Weak Acids and Strong Bases :*** e.g. CH_3COONa, KCN

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

or $CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

(i) Due to OH^- ions, the solution becomes basic, hence salt is hydrolysed.

(ii) Hydrolysis is known as anionic hydrolysis because CH_3COO^- is an anion.

(iii) Salt hydrolysis constant $K_h = \dfrac{K_w}{K_a}$

(iv) pH of solution more than 7

(v) Degree of hydrolysis $\alpha = \sqrt{\dfrac{K_w}{K_a \times C}}$

(vi) $[H^+] = \sqrt{\dfrac{K_w \times K_a}{C}}$

(vii) $pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$,

where C is conc. of anion i.e. CH_3COO^-

3. ***Hydrolysis of salts of weak bases and strong acids :*** e.g. NH_4Cl

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

or $NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

(i) Due to H^+ ions, the solution becomes acidic, hence salt is hydrolysed

(ii) Hydrolysis is known as cationic hydrolysis. because NH_4^+ is a cation

(iii) Salt hydrolysis const. $K_h = \dfrac{K_w}{K_b}$

(iv) pH of solution less than 7

(v) Degree of hydrolysis $\propto = \sqrt{\dfrac{K_w}{K_b \times C}}$

(vi) $[H^+] = \sqrt{\dfrac{K_w.C}{K_b}}$

(vii) $pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$

4. ***Hydrolysis of salts of weak bases and weak acids :*** e.g. CH_3COONH_4

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

or $CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

(i) The solution may be neutral, acidic or basic depending upon the relative strength of weak acid CH_3COOH and weak base NH_4OH formed. The salt is said to be hydrolysed.

(ii) Hydrolysis is known as cationic as well as anionic hydrolysis.

(iii) Salt hydrolysis Const., $K_h = \dfrac{K_w}{K_a \times K_b}$

(iv) pH of the solution may be 7, > 7 or <7

(v) Degree of hydrolysis, $\alpha = \sqrt{\dfrac{K_w}{K_a \times K_b}}$

(vi) $H^+ = \sqrt{\dfrac{K_w \times K_a}{K_b}}$

(vii) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$

Ex. : Calculate the degree of hydrolysis and hydrolysis constant of decinormal solution of NaCN. The dissociation constant of HCN is 7.2×10^{-10} at 25°C.

Sol. $\alpha = \sqrt{\dfrac{K_w}{C \times K_a}} = \sqrt{\dfrac{1 \times 10^{-14}}{0.1 \times 7.2 \times 10^{-10}}} = 1.178 \times 10^{-2}$

$$K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{7.2 \times 10^{-10}} = 1.388 \times 10^{-5}$$

Ex. : How many grams of sodium acetate must be added to 500 ml of water to give a solution of pH = 8.52 ($K_a = 1.8 \times 10^{-5}$)

Sol. Sodium acetate is salt of weak acid and strong base

$$pH = 7 + \frac{1}{2}pK_a + \log C$$

$$8.52 = \frac{1}{2}(14 + 4.74 + \log C)$$

$(-\log K_a = pK_a \quad \therefore -\log 1.8 \times 10^{-5} = 4.74)$

C = 0.02 mol/litre

Hence wt. of CH_3COONa in 500 ml = 0.01 × 82 = 0.82 g

Ex. : Calculate the pH of an aqueous soln. of 1.0 M ammonium formate assuming complete dissociation (pK_a of formic acid = 3.8 and ammonia = 4.8) (IIT 1995)

Sol. $pH = \frac{1}{2}(pK_w + pK_a - pK_b) = \frac{1}{2}(14 + 3.8 - 4.8) = 6.5$

BUFFERS :

Solutions which resist the change in the value of pH when small amount of acid or base is added to them are known as buffers. Types

(I) Simple buffers : Solution of salt of weak acid and weak base CH_3COONH_4, NH_4CN.

(II) Mixed buffers :

- **(a)** ***Acidic buffers :*** Solution of equimolar mixture of a weak acid and its salt with a strong base e.g. (CH_3COOH + CH_3COONa); (H_2CO_3 + $NaHCO_3$); (Boric acid + borax); (H_3PO_4 + NaH_2PO_4)
- **(b)** ***Basic buffers :*** Solution of equimolar mixture of a weak base and its salt with a strong acid e.g. (NH_4OH + NH_4Cl)

Buffer action of simple buffer : CH_3COONH_4 exist as ions CH_3COO^- and N^+H_4 in solution. Added acid (H^+) combine with CH_3COO^- to give feebly ionised CH_3COOH and added base (OH^-) combine with NH_4^+ to give feebly ionised NH_4OH. Thus pH remains unchanged

Buffer action of mixed buffers :

(a) ***Acidic buffer :***

$$CH_3COONa \rightleftharpoons \underset{H^+}{CH_3COO^- + \overset{+}{Na}} \rightleftharpoons CH_3COOH$$

When small amount of an acid is added to the buffer the added H^+ ions combine with CH_3COO^- to form feebly ionised CH_3COOH and when small amount of a base is added to the buffer the added OH^- ions combine with H^+ to form feebly ionised H_2O. In the latter case more CH_3COOH ionises to keep K_a of acid constant and hence constant concentration of H^+ ions. Thus whether we add acid or a base, the H^+ concentration remain constant and pH of solution does not change

(b) Basic buffer :

$$NH_4Cl \rightleftharpoons \underset{OH^-}{NH_4^+} + Cl^- \rightleftharpoons NH_4OH$$

When small amount of an acid is added to the buffer the added H^+ ions combine with OH^- to form feebly ionised H_2O, equilibrium is disturbed. More NH_4OH ionises to keep $[OH^-]$ fixed.

When small amount of a base is added to the buffer the added OH^- ions combine with NH_4^+ to form feebly ionised NH_4OH to keep $[OH^-]$ fixed. Hence there is no change of pH in both cases.

Buffer capacity =

$$\frac{\text{Moles of acid or a base added to 1 litre of buffer}}{\text{Change in pH}}$$

Calculation of pH value of buffers : Acidic buffer contains weak acid and its salt with strong base.

The H^+ ion concentration is given by

$$[H^+] = \frac{K_a[ACID]}{[SALT]}$$

$$-\log[H^+] = -\log K_a + \log\frac{[SALT]}{[ACID]}$$

$$pH = pK_a + \log\frac{[SALT]}{[ACID]}$$

This is known as Henderson's equation.

Basic buffer contains a weak base and its salt with strong acid. The OH^- ion concentration is given by

$$[OH^-] = \frac{K_b[BASE]}{[SALT]}$$

$$-\log[OH^-] = -\log K_b + \log\frac{[SALT]}{[BASE]}$$

$$pOH = pK_b + \log\frac{[SALT]}{[BASE]}$$

Note : $pH + pOH = 14 = pK_w$

A buffer has maximum buffer capacity when

$$\frac{[SALT]}{[ACID]} \text{ or } \frac{[SALT]}{[BASE]} = 1$$

In such case pH = pK_a for acid buffer and pOH = pK_b for basic buffer. For a buffer the ratio of concentration of salt to acid or base must lie between 0.1 and 10. Thus pH range for acid buffer is from $pK_a - 1$ to $pK_a + 1$. For basic buffer the pOH range is $pK_b - 1$ to $pK_b + 1$.

NEUTRALISATION :

The combination of $H^+_{(aq)}$ and $OH^-_{(aq)}$ furnished by an acid and a base in aqueous solution to produce undissociated water to maintain the value of K_W at 1×10^{-14}, is known as neutralisation.

$$HA + Water \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

$$BOH + Water \rightleftharpoons OH^-_{(aq)} + B^+_{(aq)}$$

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O$$

(I) Neutralisation of a strong acid with strong base : The strong acids and strong bases are almost completely ionised in aqueous solutions. When their solutions are mixed, the only effective change is the formation of unionised water.

$$\overset{+}{H}\overset{-}{Cl} + \overset{+}{Na}\overset{-}{OH} \rightleftharpoons \overset{+}{Na}\overset{-}{Cl} + H_2O$$

Net reaction $H^+ (aq) + OH^- (aq) \rightleftharpoons H_2O$,

$\Delta H = -13.7$ kcal/mole

Neutralisation is complete. pH of resulting solution is 7.

(II) Neutralisation of a weak acid with a strong base : While sodium hydroxide is completely ionised in aqueous solution, the acid is only weakly ionised.

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

Net reaction $CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$,

$\Delta H = -13.20$ kcal/mole.

Solution remains basic (pH > 7) due to presence of OH^- ions. Heat of neutralisation is less by 0.5 kcal/mol which is utilised for the dissociation of acetic acid.

(III) Neutralisation of a strong acid and weak base : The strong acid is completely ionised in aqueous solution and weak base is feebly ionised.

$$NH_4OH + HCl \rightleftharpoons NH_4Cl + H_2O$$

Net reaction $NH_4OH + H^+ \rightleftharpoons NH_4^+ + H_2O$,

$\Delta H = -12.3$ kcal/mole.

The solution remains acidic due to presence of H^+ ions (pH < 7) 1.4 kcal/mole is utilised for dissociation of NH_4OH.

(IV) Neutralisation of a weak acid and a weak base : The acid and base are weakly ionised in aqeous solution.

(1) $CH_3COOH + Water \rightleftharpoons CH_3COO^- + H^+$

(2) $NH_4OH + water \rightleftharpoons NH_4^+ + OH^-$

Net reaction $H^+ + OH^- \rightleftharpoons H_2O$,

$\Delta H = -11.8$ kcal/mol

The combination of H^+ and OH^- take place to a limited extent only. This combination is suffiecient to disturb., the equilibrium in (1) and (2) and dissociation is complete.

When neutralisation is completed, pH is almost 7. Heat evolved during neutralisation is even less, due to effecting the ionisation of weak acid and weak base.

HYDROGEN ION INDICATORS OR ACID BASE INDICATORS :

Such indicators change their colour with the change of the pH of solution. They are either weakly acidic or basic in nature e.g. phenolphthalein which is colourless below pH 8 and pink at 9.8.

Theory of Acid-Base indicators :

(1) Ostwald's theory : The unionised molecule of the indicator has one colour while the ionised form has another colour.

$$\underset{\text{Colour A}}{HIn} \rightleftharpoons H^+ + \underset{\text{Colour B}}{In^-}$$

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

Consider the ionisation of phenolphthalein which is weakly acidic in nature

$$\underset{\text{Colourless}}{HPh} \rightleftharpoons \underset{\text{Pink}}{H^+ + Ph^-}$$

Addition of a strong base will disturb the equilibrium ($OH^- + H^+ \rightleftharpoons H_2O$) and more phenolphthalein will ionise giving pink solution. Addition of a strong acid will suppress the ionisation of phenolphthalein by common ion effect, solution will be colourless. The indicator is not suitable for titrating weak base like NH_4OH against strong acid. The OH^- ions furnished by weak base are insufficient to shift the equilibrium and pink colour does not appear just at the end point. Excess of weak base is required.

Action of methyl orange : Methyl orange is a weak base and is ionised as follows :

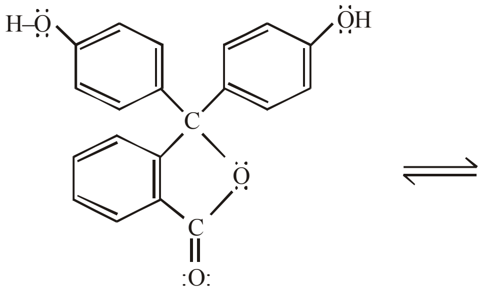
$$\underset{\text{Yellow}}{MeOH} \rightleftharpoons \underset{\text{Red}}{Me^+ + OH^-}$$

Addition of a strong acid will disturb the equilibrium ($H^+ + OH^- \rightleftharpoons H_2O$) and more methyl orange will ionise giving red solution. Addition of a strong base will suppress the ionisation of methyl orange by common ion effect hence solution will be yellow in colour. The indicator is not suitable for titrating weak acid like CH_3COOH against strong base. The H^+ ions furnished by weak acid are not sufficient to shift the equilibrium and red colour does not appear just at the end point. Excess of weak acid is required.

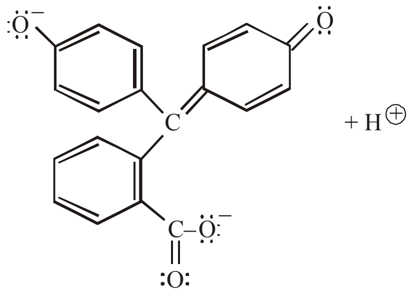
(2) Quinonoid theory :

In the unionised form the indicator is generally in the benzenoid form which is less intense in colour and in the ionised form it is in the Quinonoid form which is more intense in colour.

Phenolphthalein :

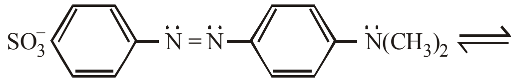


Benzenoid form (colourless)

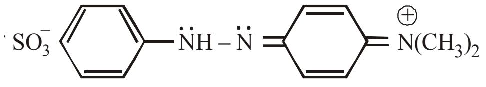


Quinonoid form (Pink)

Methyl Orange :



Benzenoid form (Yellow)



Quinonoid form (Red)

Types of indicators

1. ***Internal :*** Which can be added to reacting substances further they can be ***acid base*** indicator (phenolphthalein, methyl orange etc.) ***redox* indicators**, used for redox titrations (N-phenyl anthranilic acid) ***adsorption indicators*** (starch).
2. ***External :*** Which can not be added to reacting substances e.g. potassium ferricyanide for titration of $K_2Cr_2O_7$ vs. $FeSO_4(NH_4)_2SO_4.6H_2O$.
3. ***Radioactive :*** ${}_8O^{18}$ and D^2 for studying reaction mechanism.

Choice of indicator

1. For strong acid and strong base - methyl orange, phenolphthalein and Litmus.
2. For weak acid and strong base - phenolphthalein.
3. For strong acid and weak base - methyl orange.
4. For weak acid and weak base - Phenol red.

Some important Acid Base Indicators

Indicator	**pH** *range*	*Colour in acidic sol.*	*Colour in alkaline sol.*
Cresol red (acid)	1.2 - 1.8	Red	Yellow
Thymol blue (acid)	1.2 - 2.8	Red	Yellow
Methyl Orange	3.1 - 4.5	Red	Yellow
Methyl red	4.2 - 6.3	Red	Yellow
Phenol red	6.4 - 8.2	Yellow	Red
Cresol red (base)	7.0 - 8.1	Yellow	Red
Thymol blue (base)	8.1 - 9.6	Yellow	Red
Phenolphthalein	8.1 - 9.8	Colourless	Pink
Alizarin yellow	10.1 - 12.1	Yellow	Lilac (violet)

SALTS :

The compounds containing positive and negative ions are known as salts. Their solutions may be acidic, basic or neutral. They are classified as

(i) ***Simple salts :*** Formed by neutralisation of an acid and a base. They may be further classified as follows.

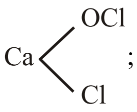
- (a) ***Normal salts :*** Salts not containing replaceable hydrogen or a hydroxyl group e.g. Na_2SO_4, KNO_3, $Al_2(PO_4)_3$, $CaCl_2$.
- (b) ***Acidic salts :*** Salts containing replaceable hydrogen atoms $NaHSO_4$, Na_2HPO_4, $NaHCO_3$.
- (c) ***Basic salts :*** Salts containing replaceable hydroxyl groups $Zn(OH)Cl$, $Mg(OH)Cl$, $Fe(OH)_2Cl$.

(ii) Double Salts : Formed by the combination of two simple salts

$FeSO_4.(NH_4)_2SO_4.6H_2O$, $K_2SO_4.Al_2(SO_4)_3.24H_2O$.

(iii) Complex Salts : Salts containing complex ion e.g. $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$.

(iv) Mixed Salts : Salts containing more than one type of cation or anion e.g.



$Ca(OCl)Cl$; $NaKSO_4$.

All salts are strong electrolytes.

SOLVENTS :

The substances which provide medium to carry out chemical reactions. They are classified as

(I) ***Protophilic :*** Such solvents have a tendency to accept proton e.g. H_2O, liquour ammonia and alcohol etc.

(II) ***Protogenic :*** Such solvents have a tendency to donate proton e.g. HCl (*l*), glacial CH_3COOH and H_2O etc.

(III) ***Amphiprotic :*** Solvents capable of donating and accepting a proton e.g. H_2O, alcohol etc.

(IV) ***Aprotic :*** Solvents which neither donate nor accept a proton e.g. benzene, CS_2, CCl_4 etc.

Miscellaneous Solved Examples

1. Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) has formula HNiC. Calculate its percent dissociation in a solution which contains 0.10 mole of nicotinic acid per 2.0 litre of solution.

Sol. $HNiC + H_2O \rightleftharpoons H_3O^+ + NiC^-$

Molar concentration of nicotinic acid = 0.05 mole/lit.

% Degree of dissociation

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.4\times10^{-5}}{0.05}} \times 100 = 1.67.$$

2. Enthalpy of neutralisation of CH_3COOH by NaOH is –55.9 kJ/mol. ΔH for the ionisation of CH_3COOH is

Sol. 57.1 – 55.9 = 1.2 KJ/mol

3. Calculate the amount of heat released when (I) 100 ml of 0.2 M HCl soution is mixed with 200 ml of 0.2 M KOH

(II) 200 ml of 0.2 M H_2SO_4 is mixed with equal volume of 0.2 M KOH

Sol. (I) Moles of H^+ ions $= \dfrac{100\times0.2}{1000} = 0.02$

Moles of OH^- ion $= \dfrac{200\times0.2}{1000} = 0.04$

H_2O formed is = 0.02 Moles

Hence heat released = 57.1 × 0.02 = 1.142 kJ

(II) Moles of H^+ ions $= \dfrac{200\times0.2}{1000} = 0.04$

and Moles of OH^- $= \dfrac{200\times0.2}{1000} = 0.04$

Moles of H_2O formed is = 0.04

Heat released = 57.1 × 0.04 = 2.18 kJ

4. A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the concentration of S^{--} and SH^- ions in solution. Given K_{a_1} and K_{a_2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively.

Sol. (I) $H_2S \overset{K_{a_1}}{\rightleftharpoons} H^+ + HS^-$

(II) $HS^- \overset{K_{a_2}}{\rightleftharpoons} H^+ + S^{--}$

$$K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]} \qquad K_{a_2} = \frac{[H^+][S^{--}]}{[SH^-]}$$

$$K_{a_1} \times K_{a_2} = \frac{[H^+]^2[S^{--}]}{[H_2S]}$$

H_2S is weak electrolyte in presence of HCl its ionisation is suppressed due to common ion effect.

$$[S^{--}] = \frac{K_{a_1} \times K_{a_2}[H_2S]}{[H^+]^2}$$

$$= \frac{1.0\times10^{-7}\times1.3\times10^{-13}\times0.1}{(0.3)^2} = 1.44\times10^{-20}\,M$$

Putting $[S^{--}]$ in equation (II)

$$[SH^-] = \frac{[H^+][S^{--}]}{K_{a_2}} = \frac{0.3\times1.44\times10^{-20}}{1.3\times10^{-13}} = 3.3\times10^{-8}\,M$$

5. The pH of 0.1 M hydrocyanic acid solution is 5.2. What is the value of K_a for hydrocyanic acid.

Sol. $\log\dfrac{1}{[H^+]} = pH = 5.2$

$[H^+] = 6.2 \times 10^{-6}\,M$, $\quad [H^+] = c\alpha = \sqrt{C\times K_a}$

$$\frac{(6.3\times10^{-6})^2}{0.1} = K_a; \qquad \therefore K_a = 3.96\times10^{-10}\,M$$

6. Calculate the pH of

(I) 1.0×10^{-8} M HCl (II) 1.0×10^{-8} M NaOH

Sol.

(I) $[H^+]$ conc. due to water and HCl $= [1 \times 10^{-7} + 1 \times 10^{-8}]$

$[H^+] = 10^{-8}(10 + 1) = 10^{-8} \times 11$

$-\log[H^+] = 8 \log 10 - \log 11$

$pH = 8 - 1.04 = 6.96.$

(II) Total $[OH^-] = [1 \times 10^{-7} + 1 \times 10^{-8}]$

Solving as in case (I) pOH = 6.96. $\therefore$ pH = 7.04.

7. What is the hydrogen ion concentration of 0.1 N CH_3COOH solution. The ionisation constant of CH_3COOH is 1.8×10^{-5}. What is the pH of solution.

Sol. $[H^+] = \sqrt{C \times K_a} = \sqrt{0.1 \times 1.8 \times 10^{-5}} = 1.34 \times 10^{-3}\,M$

$pH = -\log[H^+] = -\log 1.34 \times 10^{-3} = 2.8729.$

8. What volume of 0.10 M sodium formate solution should be added to 50 ml of 0.05 M formic acid to produce a buffer solution of pH 4.0, pK_a of formic acid is 3.80.

Sol. $pH = pK_a + \log\dfrac{\text{Salt}}{\text{Acid}}$

Let the volume added be V ml. then

$$4 = 3.8 + \log\frac{V \times 0.10}{0.05 \times 50}$$

Solving for V we get V = 39.5 ml.

9. Freshly precipitated aluminium and magnesium hydroxides are stirred vigrously in a buffer solution containing 0.05 mol L^{-1} of NH_4OH and 0.25 mol L^{-1} of NH_4Cl. Calculate the conc. of aluminium and magnesium ions in solution. K_{sp} of $Al(OH)_3 = 6 \times 10^{-32}$, K_{sp} of $Mg(OH)_2 = 6 \times 10^{-10}$, K_b of $NH_4OH = 1.8 \times 10^{-5}$.

Sol. The $[OH^-] = \dfrac{K_b \times [\text{BASE}]}{[\text{SALT}]}$

$$= \frac{1.8 \times 10^{-5} \times 0.05}{0.25} = 0.36 \times 10^{-5}\ \text{mol L}^{-1}$$

$$[Al^{3+}] = \frac{K_{sp}\ \text{of Al(OH)}_3}{[OH^-]^3}$$

$$= \frac{6 \times 10^{-32}}{(0.36 \times 10^{-5})^3} = 1.29 \times 10^{-10}\ \text{mol L}^{-1}$$

$$[Mg^{2+}] = \frac{K_{sp}\ \text{of Mg(OH)}_2}{[OH^-]^2} = \frac{6 \times 10^{-10}}{(0.36 \times 10^{-5})^2} = 46.3\ \text{mol L}^{-1}$$

10. An aqueous solution of metal bromide MBr_2 (0.05 M) is saturated with H_2S what is the minimum pH at which MS will precipitate? K_{sp} for MS $= 6.0 \times 10^{-21}$. Conc. of saturated $H_2S = 0.1$ M. $K_1 = 10^{-7}$ and $K_2 = 1.3 \times 10^{-13}$ for H_2S.

Sol. The minimum concentration of S^{--} ion required to precipitate MS is

$$(S^{--}) = \frac{K_{sp}}{[M^{++}]} = \frac{6.0 \times 10^{-21}}{0.05} = 1.2 \times 10^{-19}\,M$$

ionisation of H_2S; $H_2S \rightleftharpoons H^+ + HS^-$

$$K_1 = 10^{-7}, \quad K_1 = \frac{[H^+][SH^-]}{[H_2S]}$$

$$HS^- \rightleftharpoons H^+ + S^{--}; \quad K_2 = 1.3 \times 10^{-13}$$

$$K_2 = \frac{[H^+][S^{--}]}{[SH^-]}$$

On multiplying,

$$K_1 \times K_2 = \frac{[H^+]^2[S^{--}]}{[H_2S]}$$

$$10^{-7} \times 1.3 \times 10^{-13} = \frac{[H^+]^2 \times 1.2 \times 10^{-19}}{0.1}$$

Solving for $[H^+] = 1.04 \times 10^{-1}$

$pH = -\log[H^+] = -\log(1.04 \times 10^{-1}) = 0.98.$

11. The pH of 0.05 M aqueous solution of diethylamine is 12. Calculate its K_b.

Sol. pH + pOH = 14

pOH = 14 – 12 = 2; $[OH^-] = 10^{-2}$

$$(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$$

$0.05 - 0.01$ $\quad 0.01 \quad 0.01$

$$K_b = \frac{0.01 \times 0.01}{0.04} = 2.5 \times 10^{-3}$$

12. K_a for butyric acid is 2×10^{-5}. Calculate the pH and hydroxyl ion concentration of 0.2 M aqs. solution of sodium butyrate.

Sol. Sodium butyrate is a salt of weak acid and strong base

$$[H^+] = \sqrt{\frac{K_w \times K_a}{C}} = \sqrt{\frac{1 \times 10^{-14} \times 2 \times 10^{-5}}{0.2}} = 10^{-9}$$

Hence pH = 9

$10^{-14} = [H^+][OH^-]$

$10^{-14} = 10^{-9}[OH^-]$

$[OH^-] = 10^{-5}$

13. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation p_{K_a} for formic acid = 3.8 and p_{K_b} of ammonia = 4.8.

Sol. Ammonium formate is a salt of weak acid and weak base.

$$\text{Hence pH} = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

$$= 7 + \frac{1}{2} \times 3.8 - \frac{1}{2} \times 4.8 = 6.5$$

14. A certain weak acid has $K_a = 1.0 \times 10^{-4}$. Calculate the equilibrium constant for its reaction with strong base.

Sol. $HA \rightleftharpoons H^+ + A^- \quad K_a = 1\times10^{-4}$

$$\underset{\text{Weak}}{HA} + \underset{\text{Strong}}{BOH} \rightleftharpoons BA + H_2O$$

$$HA + OH^- \rightleftharpoons A^- + H_2O$$

$$K = \frac{[A^-]}{[HA][OH]} = \frac{[A^-][H^+]}{[HA][OH^-][H^+]} = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = 10^{10}$$

15. Calculate for 0.01 N solution of sodium acetate.

(a) Hydrolysis constant (b) Degree of Hydrolysis

(c) pH. Given $K_a = 1.9 \times 10^{-5}$.

Sol. Sodium acetate is salt of weak acid and strong base

(a) $K_h = \dfrac{K_w}{K_a} = \dfrac{10^{-14}}{1.9\times10^{-5}} = 5.26\times10^{-10}$

(b) Degree of hydrolysis

$$= \sqrt{\frac{K_w}{C\times K_a}} = \sqrt{\frac{10^{-14}}{0.1\times1.9\times10^{-5}}} = 2.29\times10^{-4}$$

(c) $pH = 7 + \frac{1}{2}p_{Ka} + \frac{1}{2}\log C = 7 - \frac{1}{2}\log K_a + \frac{1}{2}\log C$

$$= 7 - \frac{1}{2}\log 1.9\times10^{-5} + \frac{1}{2}\log 0.01 = 8.36$$

16. K_a for ascorbic acid (HAsc) is 5×10^{-5}. Calculate the hydrogen ion concentration and percentage of hydrolysis in aqueous solution in which the concentration of Asc^- ions is 0.02 M.

Sol. Degree of hydrolysis

$$\alpha = \sqrt{\frac{K_w}{C\times K_a}} = \sqrt{\frac{1\times10^{-14}}{0.02\times5\times10^{-5}}} = 10^{-4} = 0.01\%$$

$$pH = 7 - \frac{1}{2}\log K_a + \frac{1}{2}\log C = 7 - \frac{1}{2}\log 5\times10^{-5} + \frac{1}{2}\log 0.02 = 8.3$$

$[H^+] = 5 \times 10^{-9}$.

17. When 0.2 M acetic acid is neutralised with 0.2 M NaOH in 0.5 litre of water the resulting solution is slightly alkaline. Calculate the pH of the resulting solution. K_a for acetic acid is $= 1.8 \times 10^{-5}$

Sol. $CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$

The concentration of $[CH_3COONa]$ will be 0.1 $mol\,L^{-1}$. It is salt of weak acid and strong base

$$pH = 7 + \frac{1}{2}p_{K_a} + \frac{1}{2}\log C$$

$$= 7 + \frac{1}{2}(-\log K_a) + \frac{1}{2}\log C$$

$$= 7 + \frac{1}{2}(-\log 1.8\times10^{-5}) + \frac{1}{2}\log 0.1 = 8.87$$

18. The K_a for formic acid and acetic acid are 2.1×10^{-4} and 1.1×10^{-5} respectively. Calculate the relative strength of acids.

Sol. Relative strengths of weak acids = $\sqrt{\dfrac{K_{a_1}C_1}{K_{a_2}C_2}}$

Assuming $C_1 = C_2$

Relative strength = $\sqrt{\dfrac{K_{a_1}}{K_{a_2}}} = \sqrt{\dfrac{2.1\times10^{-4}}{1.1\times10^{-5}}} = 4.37:1$

Formic acid is 4.37 times more acidic than acetic acid

19. Calcium lactate is a salt of weak organic acid and is represented by $Ca(Lac)_2$. A saturated solution of $Ca(Lac)_2$ contains 0.13 mole of this salt in 0.50 litre solution. The pOH of this solution is 5.60. Assuming the complete dissociation of the salt. Calculate K_a of lactic acid.

Sol. For salt of weak acid and strong base

$$pH = \frac{1}{2}(pK_w + pK_a + \log a)$$

where a is concentration of lactate ion i.e. $2\times0.26)\ mol\,L^{-1}$

$$(14 - 5.6) = \frac{1}{2}(14 - \log K_a + \log 0.52)$$

$$\log K_a = -3.084 = \bar{4}.916$$

on taking antilog $K_a = 8.24 \times 10^{-4}$

20. Calculate the hydrolysis constant for NH_4Cl, pH value and $[OH^-]$ in 0.1 M NH_4Cl solution.

$K_{NH_4OH} = 1.75\times10^{-5}$

$K_w = 1 \times 10^{-14}$

Sol. Salt hydrolysis constant

$$K_h = \frac{K_w}{K_b} = 5.7 \times 10^{-10}$$

Hydrolysis of NH_4Cl is represented as

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

$$pH = \frac{1}{2}(pK_w - pK_b - \log C)$$

$$= \frac{1}{2}(14 + \log K_b - \log C)$$

$$= \frac{1}{2}(14 + \log 1.75 \times 10^{-5} - \log 0.1) = 5.12$$

$\log [H^+] = -pH;$

$[H^+] = 7.55 \times 10^{-6}$ M

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1 \times 10^{-14}}{7.55 \times 10^{-6}} = 1.32 \times 10^{-9} \text{ M}$$

21. Calculate the amount of ammonium chloride required to dissolve in 500 ml water to have pH = 4.5 (K_b for $NH_4OH = 1.8 \times 10^{-5}$)

Sol. $pH = 4.5;$

$\log[H^+] = -4.5;$

$[H^+] = 3.162 \times 10^{-5}$ M

Let the concentration of NH_4Cl be C

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

$$C(1-\alpha) \qquad\qquad C\alpha \qquad C\alpha$$

$$K_h = C\alpha^2 = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$$

$$\alpha = \frac{K_h}{C\alpha} = \frac{K_h}{[H^+]} = \frac{5.5 \times 10^{-10}}{3.162 \times 10^{-5}} = 1.739 \times 10^{-5}$$

$$C = \frac{[H^+]}{\alpha} = \frac{3.162 \times 10^{-5}}{1.739 \times 10^{-5}} = 1.8 \text{ mol L}^{-1}$$

500 ml of water contains = 0.9 mole

The weight of $NH_4Cl = 0.9 \times 53.5 = 48.15$ g

22. Calculate the change in pH of one litre buffer solution containing 0.1 mole each of NH_3 and NH_4Cl upon addition of

(a) 0.02 mole of dissolved HCl gas

(b) 0.02 mole of dissolved NaOH

Assume no change in volume $K_{NH_3} = 1.8 \times 10^{-5}$

Sol. Use Henderson's equation

$$pOH = -\log K_b + \log \frac{[Salt]}{[Base]}$$

$$= -\log 1.8 \times 10^{-5} + \log \frac{0.1}{0.1}$$

$pOH = 4.7447$

$pH = 14 - 4.7447 = 9.2553$

(a) Addition of 0.02 mole of HCl

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$

0.02	0.1	0.1	Mole initially
0	0.1 − 0.02	0.1+0.02	mole after reaction
0	0.08	0.12	

Hence

$$[NH_4OH] = \frac{0.08}{1}; \; [NH_4Cl] = \frac{0.12}{1}$$

$$pOH = -\log 1.8 \times 10^{-5} + \log \frac{0.12}{0.08} = 4.9208$$

$pH = 14 - 4.9208 = 9.6792$

Change in $pH = 9.2553 - 9.0792$

$= 0.1761$

(b) Addition of 0.02 moles of NaOH

$$NaOH + NH_4Cl \longrightarrow NaCl + NH_4OH$$

0.02	0.1	0	0.1 (Before reaction)
0	0.1 − 0.02	0.02	0.1 + 0.02 (After reaction)
	0.08	0.12	

$$pOH = -\log 1.8 \times 10^{-5} + \log \frac{[0.08]}{[0.12]}$$

$pOH = 4.5686;$

$pH = 14 - 4.5686 = 9.4314$

Change in $pH = 9.4314 - 9.2553$

$= 0.1761$

23. The pH of bloodstream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution should be mixed with 10 ml of sample of blood which is 2 M in H_2CO_3 in order to maintain a pH of 7.4? K_a for H_2CO_3 in blood is 7.8×10^{-7}

Sol. $[H_2CO_3]$ in blood = 2.0 M

$[NaHCO_3] = V$ ml

Total volume on mixing (10 + V) ml

$$pH = -\log K_a + \log \frac{[Salt]}{[Acid]}$$

$$= -\log 7.8 \times 10^{-7} + \log \frac{5V/(V+10)}{20/(V+10)}$$

$\therefore \; V = 78.36$ ml

24. Zn salt is mixed with $(NH_4)_2S$ of molarity = 0.021 M, what amount of Zn^{2+} will remain unprecipitated in 12ml of the solution . K_{sp} of ZnS = 4.51×10^{-24}

Sol. $(NH_4)_2S = 0.021$ M ; $[S^{--}] = 0.021$ M

At equilibrium $[Zn^{++}]\,[S^{--}] = K_{sp}$ of ZnS

$$[Zn^{++}] = \frac{4.51 \times 10^{-24}}{0.021} = 2.15 \times 10^{-22} \text{ M}$$

$[Zn^{2+}]$ left in solution $= 2.15 \times 10^{-22} \times 65$ g/litre

$$= \frac{2.15 \times 10^{-22} \times 65 \times 12}{1000} \text{ g/12ml}$$

$= 1.677 \times 10^{-22}$ g/12 ml

25. Will a precipitate of $Mg(OH)_2$ be formed in a 0.001 M solution of $Mg(NO_3)_2$ if the pH of the solution is adjusted to 9? K_{sp} of $Mg(OH)_2 = 8.9 \times 10^{-12}$

Sol. $pH = 9; \quad \therefore \quad [H^+] = 10^{-9}$ M

or $[OH^-] = 10^{-5}$ M

Product of ionic conc. $= [Mg^{2+}]\,[OH^-]^2$

$= [0.001]\,[10^{-5}]^2 = 10^{-13}$

Which is less, than K_{sp} of $Mg(OH)_2$ i.e. 8.9×10^{-12}. Hence $Mg(OH)_2$ will not precipitate.

26. Calculate pH of a saturated solution of $Mg(OH)_2$. Ksp for $Mg(OH)_2$ is 8.9×10^{-12}

Sol. $$\underset{}{Mg(OH)_2} \rightleftharpoons \underset{S}{Mg^{2+}} + \underset{2S}{2\,OH^-}$$

Let the solubility of $Mg(OH)_2$ be S mole lit^{-1};

$K_{sp} = 4S^3$

$= 4S^3 = 8.9 \times 10^{-12}$;

$S = 1.305 \times 10^{-4}$ M

$[OH^-] = 2S = 2 \times 1.305 \times 10^{-4}$

pOH = 3.5832

pH = 10.4168

Exercise-1 | NCERT BASED QUESTIONS

Very Short/Short Answer Questions

1. The equilibrium constants for HCN and HAc are 4.0×10^{-10} and 1.9×10^{-5} mole/L respectively. Which acid is stronger?

2. A certain metal sulphide MS, has a solubility product 1.3×10^{-18} mole^2/l^2 . What must be $[S^{-2}]$ be in a 0.10M solution of M^{2+} when MS just starts to precipitate.

3. pK_a values of acids A, B, C, D are 1.5, 3.5, 2.0 and 5.0. Which of them is strongest acid ?

4. Which of the following is strongest Lewis acid ? CCl_4, $AlCl_3$, NCl_3, OCl_2.

5. Which of the following is strongest conjugate base? CH_3^-, NH_2^-, OH^-, F^-.

6. What happens to ionic product of water if temperature is increased?

7. All Bronsted acids are not Lewis acids. Explain.

8. Calculate the molar concentration of an acetic acid solution which is 2% ionized? ($K_a = 1.8 \times 10^{-5}$)

9. Which has the greater molarity in water, AgCl or $Mg(OH)_2$
$(K_{sp}\,(AgCl) = 1.8 \times 10^{-10}$,
$(K_{sp} Mg(OH)_2 = 1.2 \times 10^{-11})$

10. Calculate the pH of the solution produced when an aqueous solution of pH = 5 is mixed with equal volume of an aqueous solution of pH = 3.

11. A sparingly soluble salt gets precipitated only when the product of concentration of its ions in the solution (Q_{sp}) becomes greater than its solubility product. If the solubility of $BaSO_4$ in water is 8×10^{-4} mol dm^{-3}. Calculate its solubility in 0.01 mol dm^{-3} of H_2SO_4.

Long Answer Questions

12. (i) A sample of orange juice was found to have a pH of $10^{-3.80}$. What were the H^+ and OH^- concentrations in the juice?
(ii) What is the pH of a 5.0×10^{-4} M solution of NaOH at 25°C?

13. (i) What is the pH of a solution that contains 0. 10 M HCl and 0.10 M CH_3COOH? For acetic acid, $K_a = 1.8 \times 10^{-5}$.
(ii) What are the concentrations of all the species present in a 0. 50 M solution of acetic acid. For CH_3COOH $K_a = 1.8 \times 10^{-5}$.

14. Carbonic acid, H_2CO_3, is a weak diprotic acid formed by the reaction of carbon dioxide with water, For this acid, $K_{a_1} = 4.3 \times 10^{-7}$ and $K_{a_2} = 5.6 \times 10^{-11}$. What are the equilibrium concentrations of each species in a 0. 10 M solution of carbonic acid?

15. **(i)** How much of 0.3 M ammonium hydroxide should be mixed with 30 mL of 0.2 M solution of ammonium chloride to give buffer solution of pH 8.65 and 10?
$[pK_b = 4.75]$
(ii) How much volume of 0.1 M HAc should be added to 50 mL of 0.2 M NaAc solution if we want to prepare a buffer solution of pH 4.91. ($pK_a = 4.76$)

Multiple Choice Questions

16. Which of the following can act both as Bronsted acid and Bronsted base?
(a) Na_2CO_3
(b) OH^-
(c) HCO_3^-
(d) NH_3

17. Which equilibrium can be described as an acid-base reaction using the Lewis acid-base definition but not using the Bronsted-Lowry definition?
(a) $2NH_3 + H_2SO_4 \rightleftharpoons 2NH_4^+ + SO_4^{2-}$
(b) $NH_3 + CH_3COOH \rightleftharpoons NH_4^+ + CH_3COO^-$
(c) $H_2O + CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$
(d) $[Cu(H_2O)_4]^{2-} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 4H_2O$

18. The ionisation constant of an acid, K_a, is the measure of strength of an acid. The K_a values of acetic acid, hypochlorous acid and formic acid are 1.74×10^{-5}, 3.0×10^{-8} and 1.8×10^{-4} respectively. Which of the following orders of pH of 0.1 mol dm^{-3} solutions of these acids is correct?
(a) acetic acid > hypochlorous acid > formic acid
(b) hypochlorous acid > acetic acid > formic acid
(c) formic acid > hypochlorous acid > acetic acid
(d) formic acid > acetic acid > hypochlorous acid

19. K_{a_1}, K_{a_2} and K_{a_3} are the respective ionisation constants for the following reactions.

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

The correct relationship between K_{a_1}, K_{a_2} and K_{a_3} is
(a) $K_{a_3} = K_{a_1} \times K_{a_2}$
(b) $K_{a_3} = K_{a_1} + K_{a_2}$
(c) $K_{a_3} = K_{a_1} - K_{a_2}$
(d) $K_{a_3} = K_{a_1} / K_{a_2}$

20. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be
(a) 9.58 (b) 4.79
(c) 9.22 (d) 7.01

21. What will be the value of pH of 0.01 mol dm^{-3} CH_3COOH $\left(K_a = 1.74 \times 10^{-5}\right)$?
(a) 3.4 (b) 3.6
(c) 3.9 (d) 3.0

22. The pH of a solution which is 0.1 M in HA and 0.5 M in NaA. K_a for HA is 1.8×10^{-6}
(a) 5.44 (b) 6.44
(c) 6.0 (d) 4.73

23. Which of the following will produce a buffer solution when mixed in equal volumes?
(a) 0.1 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl
(b) 0.05 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl
(c) 0.1 mol dm^{-3} NH_4OH and 0.05 mol dm^{-3} HCl
(d) 0.1 mol dm^{-3} CH_4COONa and 0.1 mol dm^{-3} NaOH

24. A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-6} M sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively which one will precipitate first
(a) FeS (b) MgS
(c) HgS (d) ZnS

Exercise-2 | CONCEPTUAL MCQs

1. Which will not affect the degree of ionization?
(a) Temperature (b) Concentration
(c) Type of solvent (d) Current

2. At infinite dilution, the percentage ionisation for both strong and weak electrolytes is
(a) 1% (b) 20%
(c) 50% (d) 100%

3. A 0.2 molar solution of formic acid is 3.2% ionized. Its ionisation constant is
(a) 9.6×10^{-3} (b) 2.1×10^{-4}
(c) 1.25×10^{-6} (d) 4.8×10^{-5}

4. The hydrogen ion concentration of 0.2 N CH_3COOH which is 40% dissociated is
(a) 0.08 N (b) 0.12 N
(c) 0.80 N (d) 1.2 N

5. Degree of dissociation of 0.1 N CH_3COOH is (Dissociation constant = 1×10^{-5})
(a) 10^{-5} (b) 10^{-4}
(c) 10^{-3} (d) 10^{-2}

6. A monoprotic acid in a 0.1 M solution ionizes to 0.001%. Its ionisation constant is
(a) 1.0×10^{-3} (b) 1.0×10^{-6}
(c) 1.0×10^{-8} (d) 1.0×10^{-11}

7. The concentration of water molecules in one litre of water at 298 K is
(a) 10^{-7} M (b) 55.5 M
(c) 5.55 M (d) 7.26 M

8. Which of the following will occur if 0.1 M solution of a weak acid is diluted to 0.01 M at constant temperature
(a) $[H^+]$ will decrease to 0.01 M
(b) pH will decrese
(c) Percentage ionization will increase
(d) K_a will increase

9. Which of the following is not a Lewis base?
(a) CH_4 (b) C_2H_5OH
(c) Acetone (d) Sec amine

10. Which of the following is not a Lewis acid?
(a) BF_3 (b) $AlCl_3$
(c) $FeCl_3$ (d) PH_3

11. In the given anions, the strongest Bronsted base is
(a) ClO^- (b) ClO_2^-
(c) ClO_3^- (d) ClO_4^-

12. Which of the following can act as both Bronsted acid and Bronsted base?
(a) Na_2CO_3 (b) OH^-
(c) HCO_3^- (d) NH_3

13. Which of the following is the strongest Lewis acid?
(a) BI_3 (b) BBr_3
(c) BCl_3 (d) BF_3

14. The strongest conjugate base is
(a) NO_3^- (b) Cl^-
(c) SO_4^{2-} (d) CH_3COO^-

15. A base, as defined by Bronsted theory, is a substance which can
(a) lose a pair of electrons
(b) donate protons
(c) gain a pair of electrons
(d) accept protons

16. Which of the following is strongest Lewis base?
(a) CH_3^- (b) NH_2^-
(c) OH^- (d) F^-

17. Aluminium chloride is
(a) Bronsted Lowry acid (b) Arrhenius acid
(c) Lewis acid (d) Lewis base

18. BF_3 is an acid according to
(a) Arrhenius concept (b) Bronsted-Lowry concept
(c) Lewis Concept (d) Both (b) and (c)

19. Which of the following is not a Lewis acid?
(a) CO (b) $SiCl_4$
(c) SO_3 (d) Zn^{2+}

20. Ammonium ion is
(a) a conjugate acid
(b) a conjugate base
(c) both an acid and a base
(d) neither an acid nor a base

21. Among the following, the weakest base is
(a) H^- (b) CH_3^-
(c) CH_3O^- (d) Cl^-

22. In the equation $I_2 + I^- \longrightarrow I_3^-$, which is the Lewis base?
(a) I_2 (b) I^-
(c) I_3^- (d) None of these

23. Which one of the following compounds is not a protonic acid
(a) $PO(OH)_3$ (b) $SO(OH)_2$
(c) $SO_2(OH)_2$ (d) $B(OH)_3$

24. Which equilibrium can be described as an acid-base reaction using the Lewis acid-base definition but not using the Bronsted-Lowry definition?
(a) $2NH_3 + H_2SO_4 \rightleftharpoons 2NH_4^+ + SO_4^{2-}$
(b) $NH_3 + CH_3COOH \rightleftharpoons NH_4^+ + CH_3COO^-$
(c) $H_2O + CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$
(d) $[Cu(H_2O)_4]^{2-} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 4H_2O$

25. Which one of the following is the strongest acid?
(a) ClO_3OH (b) $ClO_2(OH)$
(c) $SO(OH)_2$ (d) $SO_2(OH)_2$

26. Why are strong acids generally used as standard solutions in acid-base titrations?
(a) The pH at the equivalent point will always be 7
(b) They can be used to titrate both strong and weak bases
(c) Strong acids form more stable solutions than weak acids
(d) The salts of strong acid do not hydrolyse

27. At a certain temperature the dissociation constants of formic acid and acetic acid are 1.8×10^{-4} and 1.8×10^{-6} respectively. The concentration of acetic acid solution in which the hydrogen ion has the same concentration as in 0.001 M formic acid solution is equal to
(a) 0.001 M (b) 0.01 M
(c) 0.1 M (d) 0.0001 M

28. What is the decreasing order of basic strengths of OH^-, NH_2^-, $H-C\equiv C^-$ and $CH_3-CH_2^-$
(a) $CH_3-CH_2^- > NH_2^- > H-C\equiv C^- > OH^-$
(b) $H-C\equiv C^- > CH_3CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > H-C\equiv C^- > CH_3-CH_2^-$
(d) $NH_2^- > H-C\equiv C^- > OH^- > CH_3-CH_2^-$

29. A compound having the formula NH_2CH_2COOH may behave
(a) only as an acid
(b) only as a base
(c) both as an acid and base
(d) Neither acid nor base

30. Water is a
(a) protophobic solvent (b) protophilic solvent
(c) amphiprotic solvent (d) aprotic solvent

31. To Ag_2CrO_4 solution over its own precipitate, CrO_4^{2-} ions are added. This results in
(a) increase in Ag^+ concentration
(b) decrease in Ag^+ concentration
(c) increase in solubility product
(d) shifting of Ag^+ ions from the precipitate into the solution

32. To suppress the dissociation of acetic acid, the compound to be added to it is
(a) sodium oxalate (b) sodium acetate
(c) sodium carbonate (d) sodium nitrate

33. Addition of which chemical will decrease the hydrogen ion concentration of an acetic acid solution
(a) NH_4Cl (b) $Al_2(SO_4)_3$
(c) $AgNO_3$ (d) NaCN

34. Why only As^{+3} gets precipitated as As_2S_3 and not Zn^{+2} as ZnS when H_2S is passed throgh an acidic solution containing As^{+3} and Zn^{+2}?
(a) Solubility product of As_2S_3 is less than that of ZnS
(b) Enough As^{+3} are present in acidic medium
(c) Zinc salt does not ionise in acidic medium
(d) Solubility product changes in presence of an acid

35. The precipitation occurs if ionic concentration is
(a) less than solubility product
(b) more than solubility product
(c) equal to solubility product
(d) None of these

36. The solubility of AgCl will be minimum in
(a) 0.001 M $AgNO_3$ (b) pure water
(c) 0.01 M $CaCl_2$ (d) 0.01 M NaCl

37. The solubility of $PbCl_2$ is
(a) $\sqrt{K_{sp}}$ (b) $(K_{sp})^{1/3}$
(c) $(K_{sp}/4)^{1/3}$ (d) $(8K_{sp})^{1/2}$

38. The solubility of calcium phosphate in water is x mol L^{-1} at 25°C. Its solubility product is equal to
(a) $108\,x^2$ (b) $36\,x^3$
(c) $36\,x^5$ (d) $108\,x^5$

39. Which of the following sulphides has the lowest solubility product?
(a) FeS (b) MnS
(c) PbS (d) ZnS

40. The K_{sp} of CuS, Ag_2S and HgS are 10^{-31}, 10^{-44} and 10^{-54} respectively. The solubility of these sulphides are in the order
(a) $Ag_2S > CuS > HgS$ (b) $AgS > HgS > CuS$
(c) $HgS > Ag_2S > CuS$ (d) $CuS > Ag_2S > HgS$

41. Which of the following on reaction with H_2S does not produce metallic sulphide?
(a) $CdCl_2$ (b) $ZnCl_2$
(c) $COCl_2$ (d) $CuCl_2$

42. What is the correct representation for the solubility product of SnS_2?
(a) $[Sn^{2+}][S^{2-}]^2$ (b) $[Sn^{4+}][S^{2-}]^2$
(c) $[Sn^{2+}][2S^{2-}]$ (d) $[Sn^{4+}][2\,S^{2-}]^2$

43. How do we differentiate between Fe^{3+} and Cr^{3+} in group III?
(a) By taking excess of NH_4OH
(b) By increasing NH_4^+ ion concentration
(c) By decreasing OH^- ion concentration
(d) Both (b) and (c)

44. The solubility product of barium sulphate is 1.5×10^{-9} at 18°C. Its solubility in water at 18°C is
(a) 1.5×10^{-9} mol L^{-1} (b) 1.5×10^{-5} mol L^{-1}
(c) 3.9×10^{-9} mol L^{-1} (d) 3.9×10^{-5} mol L^{-1}

45. The solubility product of AgCl is 4.0×10^{-10} at 298 K. The solubility of AgCl in 0.04 M $CaCl_2$ will be
(a) 2.0×10^{-5} M (b) 1.0×10^{-4} M
(c) 5.0×10^{-9} M (d) 2.2×10^{-4} M

46. The solubility of AgCl at 20°C is 1.435×10^{-3} gm/lit. The solubility product of AgCl is
(a) 1.0×10^{-10} (b) 2×10^{-10}
(c) 1.035×10^{-5} (d) 108×10^{-3}

47. The solubility product of Ag_2CrO_4 is 32×10^{-12}. What is the concentration of CrO_4^{-2} ions in that solution (in g ions L^{-1})
(a) 2×10^{-4} (b) 8×10^{-4}
(c) 8×10^{-8} (d) 16×10^{-4}

48. The solubility product of silver chloride is 1.8×10^{-10} at 298 K. The solubility of AgCl in 0.01 M HCl solution in mol/dm^3 is
(a) 2.4×10^{-9} (b) 3.6×10^{-8}
(c) 0.9×10^{-10} (d) 1.8×10^{-8}

49. K_{sp} for $HgSO_4$ is 6.4×10^{-5}, then solubility of the salt is
(a) 8×10^{-6} (b) 8×10^{-3}
(c) 4.6×10^{-5} (d) None of these

50. The maximum amount of $BaSO_4$ precipitated on mixing $BaCl_2$ (0.5 M) with H_2SO_4 (1M) will correspond to
(a) 0.5 M (b) 1.0 M
(c) 1.5 M (d) 2.0 M

51. At 20°C, the Ag^+ ion concentration in a saturated solution of Ag_2CrO_4 is 1.5×10^{-4} mole/litre. At 20°C, the solubility product of Ag_2CrO_4 will be
(a) 3.3750×10^{-12} (b) 1.6875×10^{-10}
(c) 1.6875×10^{-12} (d) 1.6875×10^{-11}

52. The solubility of $BaSO_4$ in water is 2.33×10^{-3} g L^{-1}. Its solubility product will be (molecular weight of $BaSO_4 = 233$)
(a) 1×10^{-5} (b) 1×10^{-10}
(c) 1×10^{-15} (d) 1×10^{-20}

53. What is the minimum concentration of SO_4^{2-} required to precipitate $BaSO_4$ in a solution containing 1.0×10^{-4} mole of Ba^{2+}? K_{sp} for $BaSO_4 = 4 \times 10^{-10}$
(a) 4×10^{-10} M (b) 2×10^{-7} M
(c) 4×10^{-6} M (d) 2×10^{-3} M

54. Solubility of an MX_2 type electrolyte is 0.5×10^{-4} mole/lit, then K_{sp} of the electrolyte is
(a) 5×10^{-12} (b) 25×10^{-10}
(c) 1×10^{-13} (d) 5×10^{-13}

55. The pH of blood does not appreciably change by a small addition of acid or a base because blood
(a) contains serum protein which acts as buffer
(b) contains iron as a part of the molecule
(c) can be easily coagulated
(d) is body fluid

56. The pH of solutions A, B, C, D are respectively 9.5, 2.5, 3.5, 5.5. The most acidic solution is
(a) A (b) B
(c) C (d) D

57. pH of 10 M solution of HCl is
(a) 1 (b) 0
(c) 2 (d) less than 0

58. It is found that 0.1 M solution of four sodium salts NaA, NaB, NaC and NaD have the following pH values 7.0, 9.0, 10.0 and 11.0 respectively.
(a) NaD (b) NaC
(c) NaB (d) NaA
Which one of the corresponding acids is strongest ?

59. A white salt is readily soluble in water and gives a colourless solution with a pH of about 9. The salt would be
(a) NH_4NO_3 (b) CH_3COONa
(c) CH_3COONH_4 (d) $CaCO_3$

60. The value of ionic product of water at 393 K is
(a) less than 1×10^{-14} (b) greater than 1×10^{-14}
(c) equal to 1×10^{-14} (d) equal to 1×10^{-7}

61. Which has the highest pH?
(a) CH_3COOK (b) Na_2CO_3
(c) NH_4Cl (d) $NaNO_3$

62. A solution of $MgCl_2$ in water has pH
(a) < 7 (b) > 7
(c) 7 (d) 14.2

63. A solution of an acid has pH = 4.70. Find out the number of OH^- ions ($pK_w = 14$)
(a) 5×10^{-10} (b) 4×10^{-10}
(c) 2×10^{-5} (d) 9×10^{-4}

64. The pH of a solution whose $[H^+]$ is 3.0×10^{-4} M is
(a) 4.45 (b) 3.75
(c) 4.36 (d) 3.523

65. pH of 4.0 gm/litre NaOH solution is
(a) 13 (b) 11
(c) 13.5 (d) 12

66. Highest pH (14) is given by
(a) 0.1 M H_2SO_4 (b) 0.1 M NaOH
(c) 1 N NaOH (d) 1 N HCl

67. The pH of 0.0001 M NaOH is
(a) 4 (b) 10
(c) 12 (d) 11

68. The pOH value of a solution whose hydroxide ion concentration is 6.2×10^{-9} mol/litre is
(a) 8.21 (b) 6.21
(c) 7.75 (d) 7.21

69. The pH of a solution obtained by mixing 50 ml of 0.4 N HCl and 50 ml of 0.2 N NaOH is
(a) – log 2 (b) – log 0.2
(c) 1.0 (d) 2.0

70. The pH of 1.0 M aqueous solution of a weak acid HA is 6.0. Its dissociation constant is
(a) 1.0×10^{-12} (b) 1.0×10^{-6}
(c) 1.0 (d) 6.0

71. The pH of a solution is increased from 3 to 6; its H^+ ion concentration will be
(a) reduced to half (b) doubled
(c) reduced by 1000 times (d) increased by 1000 times

72. When CO_2 dissolves in water, the following equilibrium is established $CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^-$
for which the equilibrium constant is 3.8×10^{-7} and pH = 6.0. The ratio of $[HCO_3^-]$ to $[CO_2]$ would be
(a) 3.8×10^{-13} (b) 3.8×10^{-1}
(c) 6.0 (d) 13.4

73. An example of a salt that will not hydrolyse is
(a) NH_4Cl (b) KCl
(c) CH_3COONH_4 (d) CH_3COOK

74. pH of 2 M NaCl will be
(a) 3 (b) 6.5
(c) 7 (d) 10

75. Dissociation constant of NH_4OH is 1.8×10^{-5}. The hydrolysis constant of NH_4Cl would be
(a) 1.80×10^{-19} (b) 5.55×10^{-10}
(c) 5.55×10^{-5} (d) 1.80×10^{-5}

76. What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for HCN is 1.3×10^{-9} and $K_w = 1.0 \times 10^{-14}$
(a) 2.48 (b) 5.26
(c) 8.2 (d) 9.6

77. The pH of a 1 M CH_3COONa solution in water will be nearly
(a) 2.4 (b) 5.4
(c) 7.4 (d) 9.4

78. A physician wishes to prepare a buffer solution at pH = 3.58 that efficiently resists a change in pH yet contains only small conc. of the buffering agents. Which one of the following weak acid together with its sodium salt would be best to use?
(a) *m*-chloro benzoic acid ($pK_a = 3.98$)
(b) *p*-chloro cinnamic acid ($pK_a = 4.41$)
(c) 2,5-dihydroxy benzoic acid ($pK_a = 2.97$)
(d) Acetoacetic acid ($pK_a = 3.58$)

79. Which one is Buffer solution?
(a) $[PO_4^{-3}]\,[HPO_4^{2-}]$ (b) $[PO_4^{3-}]\,[H_2PO_4^-]$
(c) $[HPO_4^{2-}]\,[H_2PO_4^-]$ (d) All of these

80. Which of the following solution cannot act as a buffer?
(a) $NaH_2PO_4 + H_3PO_4$
(b) $CH_3COOH + CH_3COONa$
(c) $HCl + NH_4Cl$
(d) $H_3PO_4 + NaH_2PO_4$

81. A buffer solution of pH 9 can be prepared by mixing
(a) CH_3COONa and CH_3COOH
(b) NaCl and NaOH
(c) NH_4Cl and NH_4OH
(d) KH_2PO_4 and K_2HPO_4

82. Which of the following is the buffer solution of strong acidic nature?
(a) $HCOOH + HCOO^-$
(b) $CH_3COOH + CH_3COO^-$
(c) $H_2C_2O_4 + C_2O_4^{2-}$
(d) $H_3BO_3 + BO_3^{3-}$

83. One litre of a buffer solution containing 0.01 M NH_4Cl and 0.1 M NH_4OH having pK_b of 5 has pH of
(a) 9 (b) 10
(c) 4 (d) 6

84. A certain buffer solution contains equal concentration of X^- and HX. The K_a for HX is 10^{-8}. The pH of the buffer is
(a) 3 (b) 8
(c) 11 (d) 14

85. In a mixture of a weak acid and its salt, the ratio of the concentration of acid to salt is increased tenfold. The pH of the solution
(a) decreases by one (b) decreases by one tenth
(c) increases by one (d) increases by ten-fold

86. How much sodium acetate should be added to 0.1 M solution of CH_3COOH to give a solution of pH 5.5
(pK_a of $CH_3COOH = 4.5$)
(a) 0.1 M (b) 0.2 M
(c) 1.0 M (d) 10.0 M

87. For preparing a buffer solution of pH 6 by mixing sodium acetate and acetic acid, the ratio of the concentration of salt and acid should be ($K_a = 10^{-5}$)
(a) 1 : 10 (b) 10 : 1
(c) 100 : 1 (d) 1 : 100

88. What is $[H^+]$ of a solution that is 0.1 M HCN and 0.2 M NaCN? (K_a for HCN = 6.2×10^{-10})
(a) 3.1×10^{10} (b) 6.2×10^{5}
(c) 6.2×10^{-10} (d) 3.1×10^{-10}

89. The pH of a buffer containing equal molar concentrations of a weak base and its chloride
(K_b for weak base = 2×10^{-5}, log 2 = 0.3) is
(a) 5 (b) 9
(c) 4.7 (d) 9.3

90. How many ml of 1 M H_2SO_4 is required to neutralise 10 ml of 1 M NaOH solution?
(a) 2.5 (b) 5.0
(c) 10.0 (d) 20.0

91. Molar heat of neutralization of NaOH with HCl in comparison to that of KOH with HNO_3 is

(a) less (b) more

(c) equal (d) depends on pressure

92. The mutual heat of neutralization of 40 g NaOH and 60 g CH_3COOH will be

(a) 57.4 kJ (b) Less than 57.4 kJ

(c) More than 57.4 kJ (d) 13.7 kJ

93. Heat of neutralization of NH_4OH and HCl is

(a) equal to 13.7 kcal (b) more than 13.7 kcal

(c) less than 13.7 kcal (d) more than one is correct

94. The pH indicators are

(a) salts of strong acids and strong bases

(b) salts of weak acids and weak bases

(c) either weak acids or weak bases

(d) either strong acids or strong bases

95. Identify the indicator used to titrate Na_2CO_3 solution with HCl

(a) Phenolphthalein (b) dil. H_2SO_4

(c) Methyl orange (d) None of these

96. The solubility product of AgI at 25°C is 1.0×10^{-16} mol^2 L^{-2}. The solubility of AgI in 10^{-4}N solution of KI at 25°C is approximately (in mol L^{-1})

(a) 1.0×10^{-12} (b) 1.0×10^{-10}

(c) 1.0×10^{-8} (d) 1.0×10^{-16}

97. When rain is accompanied by a thunderstorm, the collected rain water will have a pH value

(a) slightly lower than that of rain water without thunderstorm

(b) slightly higher than that when the thunderstorm is not there

(c) uninfluenced by occurrence of thunderstorm

(d) depends on the amount of dust in air

98. H_3BO_3 is

(a) monobasic and weak Lewis acid

(b) monobasic and weak Bronsted acid

(c) monobasic and strong Lewis acid

(d) tribasic and weak Bronsted acid

99. A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-6} M sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively which one will precipitate first

(a) FeS (b) MgS

(c) HgS (d) ZnS

Exercise-3 | PAST COMPETITION MCQs

1. A weak acid, HA, has a K_a of 1.0×10^{-5}. If 0.1 mole of this acid dissolved in one litre of water, the percentage of acid dissociated at equilbrium is closest to **[CBSE-PMT 2007]**

(a) 1.0% (b) 99.9% (c) 0.1% (d) 99.0%

2. Calculate the pOH of a solution at 25°C that contains 1×10^{-10} M of hydronium ions, i.e. H_3O^+. **[CBSE-PMT 2007]**

(a) 4.0 (b) 9.0 (c) 1.0 (d) 7.0

3. Equal volumes of three acid solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture ? **[CBSE-PMT 2008]**

(a) 1.11×10^{-4} M (b) 3.7×10^{-4} M

(c) 3.7×10^{-3} M (d) 1.11×10^{-3} M

4. If the concentration of OH^- ions in the reaction

$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$ is

decreased by $\frac{1}{4}$ times, then equilibrium concentration of Fe^{3+} will increase by : **[CBSE-PMT 2008]**

(a) 8 times (b) 16 times (c) 64 times (d) 4 times

5. Equimolar solutions of the following were prepared in water separately. Which one of the solutions will record the highest pH ? **[CBSE-PMT 2008]**

(a) $SrCl_2$ (b) $BaCl_2$

(c) $MgCl_2$ (d) $CaCl_2$

6. The dissociation constants for acetic acid and HCN at 25°C are 1.5×10^{-5} and 4.5×10^{-10} respectively. The equilibrium constant for the equilibrium **[CBSE-PMT 2009]**

$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$ would be:

(a) 3.0×10^{-5} (b) 3.0×10^{-4}

(c) 3.0×10^{4} (d) 3.0×10^{5}

7. Which of the following molecules acts as a Lewis acid ? **[CBSE-PMT 2009]**

(a) $(CH_3)_2O$ (b) $(CH_3)_3P$ (c) $(CH_3)_3N$ (d) $(CH_3)_3B$

8. The ionization constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. Hydrolysis constant of ammonium chloride is: **[CBSE-PMT 2009]**

(a) 6.50×10^{-12} (b) 5.65×10^{-13}

(c) 5.65×10^{-12} (d) 5.65×10^{-10}

9. If pH of a saturated solution of $Ba(OH)_2$ is 12, the value of its $K_{(sp)}$ is : **[CBSE-PMT 2010]**

(a) $4.00 \times 10^{-6} M^3$ (b) $4.00 \times 10^{-7} M^3$

(c) $5.00 \times 10^{-6} M^3$ (d) $5.00 \times 10^{-7} M^3$

10. What is $[H^+]$ in mol/L of a solution that is 0.20 M in CH_3COONa and 0.10 M in CH_3COOH? K_a for CH_3COOH $= 1.8 \times 10^{-5}$. **[CBSE-PMT 2010]**

(a) 3.5×10^{-4} (b) 1.1×10^{-5}

(c) 1.8×10^{-5} (d) 9.0×10^{-6}

11. In a buffer solution containing equal concentration of B^- and HB, the K_b for B^- is 10^{-10}. The pH of buffer solution is : **[CBSE-PMT 2010]**

(a) 10 (b) 7 (c) 6 (d) 4

12. Which one of the following molecular hydrides acts as a Lewis acid? **[CBSE-PMT 2010]**

(a) NH_3 (b) H_2O (c) B_2H_6 (d) CH_4

13. A buffer solution is prepared in which the concentration of NH_3 is 0.30M and the concentration of NH_4^+ is 0.20 M. If the equilibrium constant, K_b for NH_3 equals 1.8×10^{-5}, what is the pH of this solution ? (log 2.7 = 0.433). **[CBSE-PMT 2011]**

(a) 9.08 (b) 9.43 (c) 11.72 (d) 8.73

14. Which of the following is least likely to behave as Lewis base ? **[CBSE-PMT 2011]**

(a) H_2O (b) NH_3 (c) BF_3 (d) OH^-

15. In qualitative analysis, the metals of Group I can be separated from other ions by precipitating them as chloride salts. A solution initially contains Ag^+ and Pb^{2+} at a concentration of 0.10 M. Aqueous HCl is added to this solution until the Cl^- concentration is 0.10 M. What will the concentrations of Ag^+ and Pb^{2+} be at equilibrium? **[CBSE-PMT 2011M]**

(K_{sp} for AgCl = 1.8×10^{-10}, K_{sp} for $PbCl_2 = 1.7 \times 10^{-5}$)

(a) $[Ag^+] = 1.8 \times 10^{-7}$ M ; $[Pb^{2+}] = 1.7 \times 10^{-6}$ M

(b) $[Ag^+] = 1.8 \times 10^{-11}$ M ; $[Pb^{2+}] = 8.5 \times 10^{-5}$ M

(c) $[Ag^+] = 1.8 \times 10^{-9}$ M ; $[Pb^{2+}] = 1.7 \times 10^{-3}$ M

(d) $[Ag^+] = 1.8 \times 10^{-11}$ M ; $[Pb^{2+}] = 8.5 \times 10^{-4}$ M

16. pH of a saturated solution of $Ba(OH)_2$ is 12. The value of solubility product (K_{sp}) of $Ba(OH)_2$ is : **[CBSE-PMT 2012 S]**

(a) 3.3×10^{-7} (b) 5.0×10^{-7} (c) 4.0×10^{-6} (d) 5.0×10^{-6}

17. Buffer solutions have constant acidity and alkalinity because **[CBSE-PMT 2012S]**

(a) these give unionised acid or base on reaction with added acid or alkali.

(b) acids and alkalies in these solutions are shielded from attack by other ions.

(c) they have large excess of H^+ or OH^- ions

(d) they have fixed value of pH

18. Identify the correct order of solubility in aqueous medium: **[NEET 2013]**

(a) ZnS > Na_2S > CuS (b) Na_2S > CuS > ZnS

(c) Na_2S > ZnS > CuS (d) CuS > ZnS > Na_2S

19. Which of these is least likely to act as Lewis base? **[NEET 2013]**

(a) F^- (b) BF_3

(c) PF_3 (d) CO

20. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is **[AIEEE 2002]**

(a) not a buffer solution with pH < 7

(b) not a buffer solution with pH > 7

(c) a buffer solution with pH < 7

(d) a buffer solution with pH > 7.

21. Species acting as both Bronsted acid and base is

(a) $(HSO_4)^{-1}$ (b) Na_2CO_3

(c) NH_3 (d) OH^{-1}.

22. Let the solubility of an aqueous solution of $Mg(OH)_2$ be x then its K_{sp} is **[AIEEE 2002]**

(a) $4x^3$ (b) $108x^5$

(c) $27x^4$ (d) $9x$.

23. The solubility of $Mg(OH)_2$ is S moles/litre. The solubility product under the same condition is **[AIEEE 2002]**

(a) $4S^3$ (b) $3S^4$

(c) $4S^2$ (d) S^3

24. Which one of the following statements is not true? **[AIEEE 2003]**

(a) pH + pOH = 14 for all aqueous solutions

(b) The pH of 1×10^{-8} M HCl is 8

(c) 96,500 coulombs of electricity when passed through a $CuSO_4$ solution deposits 1 gram equivalent of copper at the cathode

(d) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}

25. The solubility in water of a sparingly soluble salt AB_2 is 1.0 × 10^{-5} mol L^{-1}. Its solubility product number will be **[AIEEE 2003]**

(a) 4×10^{-10} (b) 1×10^{-15}

(c) 1×10^{-10} (d) 4×10^{-15}

26. The conjugate base of $H_2PO_4^-$ is **[AIEEE 2004]**

(a) H_3PO_4 (b) P_2O_5

(c) PO_4^{3-} (d) HPO_4^{2-}

27. The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is 'S'. The corresponding solubility product is K_{sp}. 'S' is given in term of K_{sp} by the relation : **[AIEEE 2004]**

(a) $S = (256 K_{sp})^{1/5}$ (b) $S = (128 K_{sp})^{1/4}$

(c) $S = (K_{sp}/128)^{1/4}$ (d) $S = (K_{sp}/256)^{1/5}$

28. The solubility product of a salt having general formula MX_2, in water is : 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is **[AIEEE 2005]**

(a) 4.0×10^{-10} M (b) 1.6×10^{-4} M

(c) 1.0×10^{-4} M (d) 2.0×10^{-6} M

29. Hydrogen ion concentration in mol/L in a solution of $pH = 5.4$ will be : **[AIEEE 2005]**

(a) 3.98×10^{-6} (b) 3.68×10^{-6}

(c) 3.88×10^{6} (d) 3.98×10^{8}

30. What is the conjugate base of OH^- ? **[AIEEE 2005]**

(a) O^{2-} (b) O^-

(c) H_2O (d) O_2

31. Which of the following statements is true? **[AIEEE 2006]**

(a) $HClO_4$ is a weaker acid than $HClO_3$

(b) HNO_3 is a stronger acid than HNO_2

(c) H_3PO_3 is a stronger acid than H_2SO_3

(d) In aqueous medium HF is a stronger acid than HCl

32. Given the data at 25°C **[AIEEE 2006]**

$$Ag + I^- \longrightarrow AgI + e^- \quad E° = 0.152\text{ V}$$

$$Ag \longrightarrow Ag^+ + e^- \quad E° = -0.800\text{ V}$$

What is the value of $\log K_{sp}$ for AgI? ($2.303\,RT/F = 0.059$ V)

(a) –37.83 (b) –16.13

(c) –8.12 (d) +8.612

33. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be **[AIEEE 2007]**

(a) 0.2×10^{5} (b) 5.0×10^{-5}

(c) 5.0×10^{15} (d) 5.0×10^{-15}.

34. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffer solution of HA in which 50% of the acid is ionized is **[AIEEE 2007]**

(a) 7.0 (b) 4.5 (c) 2.5 (d) 9.5

35. In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283) the equilibrium which sets is $AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$. If the solubility product constant K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 ml of its saturated solution? **[AIEEE 2007]**

(a) 1.0×10^{-4} g (b) 28.3×10^{-2} g

(c) 2.83×10^{-3} g (d) 1.0×10^{-7} g.

36. For the following three reactions a, b and c, equilibrium constants are given: **[AIEEE 2008]**

(i) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g); K_1$

(ii) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g); K_2$

(iii) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g); K_3$

(a) $K_1\sqrt{K_2} = K_3$ (b) $K_2K_3 = K_1$

(c) $K_3 = K_1 K_2$ (d) $K_3.K_2^3 = K_1^2$

37. Four species are listed below: **[AIEEE 2008]**

i. HCO_3^- ii. H_3O^+ iii. HSO_4^- iv. HSO_3F

Which one of the following is the correct sequence of their acid strength?

(a) iv < ii < iii < i (b) ii < iii < i < iv

(c) i < iii < ii < iv (d) iii < i < iv < ii

38. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the correspondng salt, BA, will be **[AIEEE 2008]**

(a) 9.58 (b) 4.79 (c) 7.01 (d) 9.22

39. Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$) **[AIEEE 2009]**

(a) 5.1×10^{-5} M (b) 8.1×10^{-8} M

(c) 8.1×10^{-7} M (d) 4.1×10^{-5} M

40. Three reactions involving $H_2PO_4^-$ are given below :

(i) $H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$

(ii) $H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+$

(iii) $H_2PO_4^- + OH^- \rightarrow H_3PO_4 + O^{2-}$

In which of the above does $H_2PO_4^-$ act as an acid ? **[AIEEE 2010]**

(a) (ii) only (b) (i) and (ii) (c) (iii) only (d) (i) only

41. In aqueous solution the ionization constants for carbonic acid are

$K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$.

Select the correct statement for a saturated 0.034 M solution of the carbonic acid. **[AIEEE 2010]**

(a) The concentration of CO_3^{2-} is 0.034 M.

(b) The concentration of CO_3^{2-} is greater than that of HCO_3^-.

(c) The concentrations of H^+ and HCO_3^- are approximately equal.

(d) The concentration of H^+ is double that of CO_3^{2-}.

42. Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is **[AIEEE 2010]**

(a) 1.2×10^{-10} g (b) 1.2×10^{-9} g

(c) 6.2×10^{-5} g (d) 5.0×10^{-8} g

43. At 25°C, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions? **[AIEEE 2010]**

(a) 9 (b) 10 (c) 11 (d) 8

44. An acid HA ionises as

$$HA \rightleftharpoons H^+ + A^-$$

The pH of 1.0 M solution is 5. Its dissociation constant would be : **[AIEEE 2011RS]**

(a) 5 (b) 5×10^{-8}

(c) 1×10^{-5} (d) 1×10^{-10}

45. The K_{sp} for $Cr(OH)_3$ is 1.6×10^{-30}. The solubility of this compound in water is : **[AIEEE 2011RS]**

(a) $\sqrt[4]{1.6\times10^{-30}}$ (b) $\sqrt[4]{1.6\times10^{-30}/27}$

(c) $1.6\times10^{-30/27}$ (d) $\sqrt{1.6\times10^{-30}}$

46. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is : **[AIEEE 2011]**

(a) 1.8 atm (b) 3 atm (c) 0.3 atm (d) 0.18 atm

47. The equilibrium constant (K_c) for the reaction $N_2(g) + O_2(g) \rightarrow 2NO(g)$ at temperature T is 4×10^{-4}. The value of K_c for the reaction **[AIEEE 2012]**

$NO(g) \rightarrow \frac{1}{2}N_2(g)+\frac{1}{2}O_2(g)$ at the same temperature is:

(a) 0.02 (b) 2.5×10^2 (c) 4×10^{-4} (d) 50.0

48. The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, K_a of the acid is : **[AIEEE 2012]**

(a) 3×10^{-1} (b) 1×10^{-3} (c) 1×10^{-5} (d) 1×10^{-7}

49. How many litres of water must be added to 1 litre an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ? **[JEE Main 2013]**

(a) 0.1 L (b) 0.9 L

(c) 2.0 L (d) 9.0 L

50. 2.5 ml of (2/5) M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°) is titrated with (2/15) M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C) **(IIT-JEE 2008S)**

(a) 3.7×10^{-14} M (b) 3.2×10^{-7} M

(c) 3.2×10^{-2} M (d) 2.7×10^{-2} M

51. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature T are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (mol dm^{-3}) of the salts at temperature 'T' are in the order – **(IIT-JEE 2008S)**

(a) $MX > MX_2 > M_3X$ (b) $M_3X > MX_2 > MX$

(c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$

Exercise-4 | Applied MCQs

1. How many gms of CaC_2O_4 will dissolve in litre of saturated solution. K_{sp} of

CaC_2O_4 is 2.5×10^{-9} $mol^2 lit^{-2}$

(a) 0.0064 g (b) 0.0128 g

(c) 0.0032 g (d) None of these

2. For NH_3, $K_b = 1.8 \times 10^{-5}$ and K_a for NH_4^+ would be

(a) 1.8×10^{-5} (b) 5.56×10^{5}

(c) 1.8×10^{10} (d) 5.56×10^{-10}

3. The pH of a solution which is 0.1 M in HA and 0.5 M in NaA. K_a for HA is 1.8×10^{-6}

(a) 5.44 (b) 6.44

(c) 6.0 (d) 4.73

4. The pH of a solution obtained by mixing of 100.0 ml of 0.1 M HCl and 100 ml of 0.2 M NH_3, K_b for NH_3 is 1.8×10^{-5}

(a) 4.74 (b) 9.26

(c) Less than 7 (d) None of these

5. The percentage hydrolysis of 0.15 M solution of ammonium acetate, K_a for CH_3COOH is 1.8×10^{-5} and K_b for NH_3 is 1.8×10^{-5}

(a) 0.556 (b) 4.72

(c) 9.38 (d) 5.56

6. The solubility of CaF_2 in 0.01 M solution of NaF. The K_{sp} of CaF_2 is 3.4×10^{-11}

(a) 3.4×10^{-7} mol/l

(b) 3.4×10^{-5} mol/l

(c) 3.4 Mol/l

(d) None of these

7. If the reaction between CO_2 and H_2O is

$CO_2+H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons \overset{+}{H}+H\overset{-}{C}O_3.$

If CO_2 escapes from the system

(a) pH will decrease

(b) H^+ concentration will decrease

(c) H_2CO_3 concentration will be altered

(d) The forward reaction is promoted

8. A solution contains 0.1 M H_2S and 0.3 M HCl, the concentration of SH^- ions is ($K_a = 1.\times10^{-7}$)

(a) 3.3×10^{-8} M (b) 33×10^{-8} M

(c) 3.3×10^{-7} M (d) 10^{-7} M

9. 20 ml of 0.2 M. NaOH are added to 50 ml of 0.2 M CH_3COOH ($K_a = 1.8\times10^{-5}$) the pH of the solution is

(a) 4.56 (b) 4.73

(c) 9.45 (d) 6.78

10. The pH at which the $Mg(OH)_2$ begins to precipitate from a solution containing 0.10 M Mg^{++} ions. The K_{sp} of $Mg(OH)_2$ is 1×10^{-11}

(a) 9 (b) 5
(c) 11 (d) 4

11. The 0.001M Solution of $Mg(NO_3)_2$ is adjusted to pH 9, K_{sp} of $Mg(OH)_2$ is 8.9×10^{-12}. At this pH

(a) $Mg(OH)_2$ will be precipitated
(b) $Mg(OH)_2$ is not precipitated
(c) $Mg(OH)_3$ will be precipitated
(d) $Mg(OH)_3$ is not precipitated

12. Calculate the pH of 0.5 M aqueous solution of NaCN, the pK_b of CN^- is 4.70

(a) 4.70 (b) 11.5
(c) 7 (d) 6.5

13. The pH of aqueous solution of 1M $HCOONH_4$, pK_a of HCOOH is 3.8 and pK_b of NH_3 is 4.8

(a) 6.5 (b) 4.8
(c) 3.8 (d) 8.6

14. The hydrolysis of Na_2CO_3 involves the reaction between

(a) Na^+ ions and water
(b) Na^+ and OH^- ions
(c) CO_3^{2-} and H_2O
(d) CO_3^{2-} and H^+

15. The solubility of BaF_2 in a solution of $Ba(NO_3)_2$ will be represented by concentration term

(a) $[Ba^{2+}]$ (b) $\left[F^-\right]$
(c) $\frac{1}{2}\left[F^-\right]$ (d) $2[NO_3^-]$

16. The enthalpy of neutralization of HCl and HCN by NaOH are –55.9 and –12.1 kJ mol^{-1} respectively, the enthalpy of ionisation of HCN is

(a) -43.8 kJ mol^{-1}
(b) -68.0 kJ mol^{-1}
(c) 43.8 kJ mol^{-1}
(d) 68.0 kJ mol^{-1}

17. K_a for HCN is 5×10^{-10} at 25°C. For maintaining at constant pH of 9, the volume of 5M KCN solution required to be added to 10ml of 2M HCN solution is

(a) 4 ml (b) 7.95 ml
(c) 2 ml (d) 9.3 ml

18. An acid-base indicator has $K_a = 3.0 \times 10^{-5}$. The acid form of the indicator is red and the basic form is blue. The amount of change in $[H^+]$ required to change indicator from 75% red the 75% blue is

(a) 8×10^{-5} M (b) 9×10^{-5} M
(c) 1×10^{-5} M (d) 3×10^{-4} M

19. Which of the following statements(s) is (are) correct?

(a) The pH of 1.0×10^{-8} M solution of HCl is 8
(b) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
(c) Autoprotolysis constant of water decreases with temperature
(d) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point pH = $(1/2)pK_a$.

20. The pH of 0.1 M solution of the following salts increases in the order.

(a) $NaCl < NH_4Cl < NaCN < HCl$
(b) $HCl < NH_4Cl < NaCl < NaCN$
(c) $NaCN < NH_4Cl < NaCl < HCl$
(d) $HCl < NaCl < NaCN < NH_4Cl$

21. What will be the H^+ ion concentration in a solution prepared by mixing 50 mL of 0.20 M NaCl, 25 mL of 0.10 M NaOH and 25 mL of 0.30 N HCl?

(a) 0.5 M (b) 0.05 M
(c) 0.02 M (d) 0.10 M

22. Determine the pH of the solution that results from the addition of 20.00 mL of 0.01 M $Ca(OH)_2$ to 30.00 mL of 0.01 M HCl.

(a) 11.30 (b) 10.53
(c) 2.70 (d) 8.35

23. Two weak solutions are isohydric when their

(a) hydrogen-ion concentrations are the same before mixing
(b) hydrogen-ion concentrations are same before and after mixing
(c) degree of dissociation are the same
(d) chemical properties are the same

24. The dissociation constant of monobasic acids A, B and C are 10^{-4}, 10^{-6} and 10^{-10} respectively. The concentration of each is 0.1 M. Which of the following has been arranged in order of increasing pH?

(a) $A < B < C$ (b) $C < A < B$
(c) $B < C < A$ (d) $B < A \approx C$

25. Calculate the molar solubility of $Fe(OH)_2$ at a pH of 8.00 [K_{sp} of $Fe(OH)_2 = 1.6 \times 10^{-14}$]

(a) 0.06 (b) 0.016
(c) 0.010 (d) 0.16

26. K_1 and K_2 for oxalic acid are 6.5×10^{-2} and 6.1×10^{-5} respectively. What will be $[HO^-]$ in a 0.01 M solution of sodium oxalate ?

(a) 9.6×10^{-6} (b) 1.4×10^{-1}
(c) 1.3×10^{-6} (d) 1.3×10^{-8}

27. Calculate the pH of a solution containing 0.1 M HCO_3^- and 0.2 M CO_3^{2-} $[K_1(H_2CO_3) = 4.2\times10^{-7}\times10$ and $K_2(HCO_3^-) = 4.8\times10^{-11}]$.

(a) 3.18 (b) 10.62
(c) 6.62 (d) 9.31

28. At what pH will a 1×10^{-4} M solution of an indicator will (K_b indicator) = 1×10^{-11} change colour?

(a) 7.0 (b) 3.0
(c) 5.5 (d) 11.0

29. Calculate the pH of a 0.01 M $NaHCO_3$ solution $[K_1(H_2CO_3) = 4\times10^{-7}, K_2(HCO_3^-) = 4.8\times10^{-11}]$.

(a) 9.38 (b) 6.38
(c) 8.38 (d) 7.38

30. Blood plasma is maintained at a pH of 7.4 largely by the

(a) HCO_3^- / H_2CO_3 buffer

(b) HPO_4^{2-} / PO_4^{3-} buffer

(c) HCO_3^- / H_2CO_3

and $HPO_4^{2-} / H_2PO_4^-$ buffer

(d) HPO_4^{2-} / H_3PO_4 and haemoglobin buffers

31. In the titration of a weak diprotic acid (H_2A) with a strong base (NaOH), $[H^+]$ is given by

(a) $\sqrt{K_{a_1} C_a}$ (b) $K_a \sqrt{C_{a_1}}$

(c) $K_a C_{a_1}$ (d) K_{a_1}

32. The pH of a solution prepared by mixing 2.0 ml of a strong acid (HCl) solution of pH 3.0 and 3.0 ml of a strong base (NaOH) of pH 10.0

(a) 4.5 (b) 3.4
(c) 2.5 (d) 6.5

33. For a sparingly soluble salt A_pB_q, the relationship of its solubility product $Ls \rightarrow K_{sp}$ with its solubility (S) is

(a) $Ls \rightarrow K_{sp} = S^{pq}\ (pq)^{P+q}$

(b) $Ls = S^{p+q}.p^p q^q$

(c) $Ls \rightarrow K_{sp} = S^{p+q}.p^q q^p$

(d) $Ls \rightarrow K_{sp} = S^{pq} p^p q^q$

34. The correct order of increasing solubility of AgCl in (A) water, (B) 0.1 M NaCl, (C) 0.1 M, $BaCl_2$, (D) 0.1 M NH_3 is

(a) D > A > B > C (b) D > C > B > A
(c) B > A > D > C (d) A > D > B > C

35. If pK_b for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is

(a) 3.52×10^{-3} (b) 6.75×10^{-4}

(c) 5.38×10^{-2} (d) 1.74×10^{-5}

36. The degree of dissociation of 0.1M weak acid HA is 0.5%. If 2 ml of 1.0 M HA solution is diluted to 32 ml the degree of dissociation of acid and H_3O^+ ion concentration in the resulting solution will be respectively

(a) 0.02 and 3.125×10^{-4} (b) 1.25×10^{-3} and 0.02

(c) 6.02 and 1.25×10^{-3} (d) 0.02 and 8.0×10^{-12}

37. The dissociation constants of a weak acid HA and weak base BOH are 2×10^{-5} and 5×10^{-6} respectively. The equilibrium constant for the neutralisation reaction of the two is

(a) 1.0×10^{4} (b) 1.0×10^{-4}

(c) 1.0×10^{-10} (d) 2.5×10^{-1}

38. The ionisation constant of an acid-base indicator (a weak acid) is 1.0×10^{-6}. The ionised form of the indicator is red whereas the unionised form is blue the pH change required to alter the colour of the indicator from 80% blue to 80% red is

(a) 1.40 (b) 1.20
(c) 0.80 (d) 2.00

39. The pH at the equivalence point in the titration of 25 ml of 0.10 M formic acid with a 0.1 M NaOH solution (given that pK_a of formic acid = 3.74)

(a) 8.74 (b) 8.37
(c) 4.74 (d) 6.06

40. In $H\overline{S}$, $\bar{I}$, RNH_2, NH_3 the order of proton accepting tendency will be

(a) $H\overline{S} > RNH_2 > NH_3 > \bar{I}$

(b) $\bar{I} > NH_3 > RNH_2 > H\overline{S}$

(c) $NH_3 > RNH_2 > H\overline{S} > \bar{I}$

(d) $RNH_2 > NH_3 > H\overline{S} > \bar{I}$

41. The pH of a weak monoacid base at 80% neutralisation with a strong acid in a dilute solution is 7.40. The ionisation constant of the base is

(a) 1.6×10^{-7} (b) 1.0×10^{-5}

(c) 1.0×10^{-6} (d) 2.0×10^{-7}

42. What will be the volume of 1 M NH_3 and 1 M HCl required to prepare 300 ml of a buffer of pH = 9.26 (pK_a = 9.26 for NH_4^+)

(a) 225 ml, 75 ml (b) 200 ml, 100 ml
(c) 100 ml, 200 ml (d) 150 ml, 150 ml

43. K_{sp} of $M(OH)_2$ is 3.2×10^{-11}. The pH of saturated solution in water is

(a) 3.40 (b) 10.30

(c) 10.60 (d) 3.70

44. The concentration of hydroxyl ion in a solution left after mixing 100 ml of 0.1 M $MgCl_2$ and 100 ml of 0.2 M NaOH (K_{sp} of $Mg(OH)_2 = 1.2 \times 10^{-11}$) is

(a) 2.8×10^{-4} (b) 2.8×10^{-3}

(c) 2.8×10^{-2} (d) 2.8×10^{-5}

45. In the titration of monoacid base (weak) with a strong acid the pH at half of the equivalence point.

(a) $14 - pK_b$ (b) $= pK_b$

(c) $7 - pK_b$ (d) $7 + pK_b$

46. The pK_a value for the A → B, B → C and C → D dissociations are 2.09, 3.86 and 9.82 respectively. Since only B has an equal number of positive and negative charges, the value of the isoelectric point is

(a) 5.26 (b) 2.98.

(c) 3.86 (d) 15.77

47. Mass loss of 1.0000 g of the AgCl ($K_{sp} = 1.0 \times 10^{-10}$) on repeated washing with 10 L of water is (Ag = 108, Cl = 35.5)

(a) 1.43×10^{-2} g (b) 1.43×10^{-3} g

(c) 1.0×10^{-4} g (d) 1.34×10^{-3} g

48. 0.1 M acetic acid solution is titrated against 0.1 M NaOH solution what would be the difference in pH between 1/4 and 3/4 stages of neutralisation of acid

(a) 2 log 1/4 (b) 2 log 3/4

(c) log 1/3 (d) 2 log 3

49. pH of a solution obtained on mixing 50 ml of 0.1M NaCN and 50 ml of 0.2 M HCl will be (pK_a for HCN = 9.40)

(a) 1.00 (b) 9.40

(c) 9.10 (d) 1.30

50. On addition of increasing amount of $AgNO_3$ to 0.1 M each of NaCl and NaBr in a solution, what % of Br^- ion get precipitated when Cl^- ion starts precipitating. K_{sp} (AgCl) = 1.0×10^{-10}, K_{sp}(AgBr) = 1×10^{-13}

(a) 0.11 (b) 99.9

(c) 0.01 (d) 9.99

51. A solution of NH_4Cl and NH_3 has pH = 8.0. Which of the following hydroxides may be precipitated when this solution is mixed with equal volume of 0.2 M of metal ion.

(a) $Ba(OH)_2 (K_{sp} = 1.1 \times 10^{-4})$

(b) $Mg(OH)_2 (K_{sp} = 3.5 \times 10^{-4})$

(c) $Fe(OH)_2$ $(K_{sp} = 8.1 \times 10^{-16})$

(d) $Ca(OH)_2$ $(K_{sp} = 2.1 \times 10^{-5})$.

52. In order to prepare a buffer of pH 8.26, the amount of $(NH_4)_2SO_4$ required to be mixed with 1L of 0.1 M $NH_3 (pK_b = 4.74)$ is

(a) 5 mol (b) 0.5 mol

(c) 10.0 mol (d) 1.0 mol

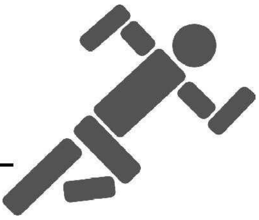
53. Assuming that the buffer in the blood is $CO_2 - HCO_3^-$. Calculate the ratio of conjugate base to acid necessary to maintain blood at its proper pH of 7.4.

$K_1(H_2CO_3) = 4.5 \times 10^{-7}$

(a) 11 (b) 8

(c) 6 (d) 14

Hints & Solutions



EXERCISE 1

1. HAc is stronger
2. $[S^{-2}] = 1.3 \times 10^{-17}$ M
3. Acid 'A' with $pK_a = 1.5$ is strongest acid, lower the value of pK_a stronger will be the acid.
4. $AlCl_3$ is strongest Lewis acid because its octet is not complete.
5. CH_3^- is strongest conjugate base.
6. It increases with increase in temperature because dissociation of water is endothermic process.
8. 0.045 M
9. 1.4×10^{-4} M, $Mg(OH)_2$ has greater.
10. pH = 3.301
11. $S = 6 \times 10^{-4}$ mol dm^{-3}
16. (c) **17.** (d) **18.** (d) **19.** (a) **20.** (d)
21. (a) **22.** (b) **23.** (c) **24.** (c)

EXERCISE 2

1. (d) Current does not effect the degree of ionisation.

2. (d) Ionisation is 100% at infinite dilution.

3. (b) $K = C\alpha^2 = 0.2\,(0.032)^2 = 2.1 \times 10^{-4}$.

4. (a) $[H^+] = C\alpha = 0.2 \times 0.40 = 0.08$ M. ($\alpha = \frac{40}{100} = 0.40$)

5. (d)

6. (d) $K_a = C\alpha^2 = 0.1 \times (1 \times 10^{-5})^2 = 1 \times 10^{-11}$

7. (b) 1 litre of H_2O = 1000 ml = 1000 g;
($\because$ density of water 1 g/ml)

$$\therefore \frac{1000}{18} = 55.5 \text{ moles}$$

8. (c) Ostwald's dilution law, dilution increases ionisation.

9. (a) Methane cannot donate electrons. While others can donate electrons. Lewis bases are electron doners.

10. (d) PH_3 is Lewis base and not Lewis acid.

11. (a) The weaker the conjugate acid, the stronger is the base and vice versa. HClO is a weak acid, hence ClO^- is a strong base.

12. (c) $H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H^+ + CO_3^{-}$.
HCO_3^- can donate and accept H^+.

13. (a) Back bond formation decreases with increase in size of halogen atom. Hence B in BI_3 is more electron deficient.

14. (d) CH_3COOH is a weak acid, hence CH_3COO^- is a strong base.

15. (d) Base accepts protons and acid donates protons.

16. (a)

17. (c) $AlCl_3$ electron deficient hence Lewis acid.

18. (c) Lewis concept.

19. (a) CO cannot accept electrons. Hence it is not Lewis acid.

20. (a) $\ddot{N}H_3 + H^+ \rightleftharpoons NH_4^+$ (Acid)

21. (d) HCl is strongest hence Cl^- weakest.

22. (b) I^- is electron donor. Hence it is Lewis base

23. (d) The acids are H_3PO_4 (orthophosphoric acid), H_2SO_3 (Sulphurous acid) and H_2SO_4 (Sulphuric acid) are protonic acid whereas Orthoboric acid is not protonic acid.

24. (d) $[Cu(H_2O)_4]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 4H_2O$ involves lose and gain of electrons. H_2O is coordinated to Cu by donating electrons (LHS). It is then removed by withdrawing electrons.

25. (a) $HClO_4$ (perchloric acid) is strongest.

26. (b) Strong acid can ionise the weak base also.

27. (b) $[H^+] = \sqrt{C \times K_a} = \sqrt{0.001 \times 1.8 \times 10^{-4}}$ for formic acid

$[H^+] = \sqrt{C_2 \times 1.8 \times 10^{-5}}$ for acetic acid Equating and solving for $C_2 = 0.01$ M.

28. (a) Follow Lowry Bronsted concept for conjugate pair. Acid strength follows the order $H_2O > C_2H_2 > NH_3 > C_2H_6$ conjugate base will follow the order

$$C_2H_5^- > N\overline{H}_2 > C_2\overline{H} > O\overline{H}$$

29. (c) $H_2\ddot{N}.CH_2COOH$ can donate and accept H^+ ions.

30. (c) H_2O can donate and accept protons.

31. (b) To keep K_{sp} constant addition of CrO_4^{2-} will decrease $[Ag^+]$.

32. (b) Common ion effect. CH_3COONa will suppress ionisation of CH_3COOH.

33. (d) $NaCN + H_2O \rightleftharpoons NaOH + HCN$ (hydrolysis)
Strong NaOH will give OH^- ions and react with H^+ to form H_2O hence decrease the concentration of H^+ ions.

34. (a) K_{sp} of As_2S_3 is less than ZnS. In acid medium ionisation of H_2S is suppresed (common ion effect) and K_{sp} of ZnS does not exceed.

35. (b) For precipitation the product of concentration of ions > K_{sp}.

36. (c) Due to common ion effect.

37. (c) $PbCl_2 \rightleftharpoons Pb^{++} + 2Cl^-$, $K_{sp} = (S)(2S)^2$

$$\therefore S = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}} \qquad S = \text{solubility}$$

38. (d) $Ca_3(PO_4)_2 \rightleftharpoons \underset{3S}{3Ca^{++}} + \underset{2S}{2PO_4^{--}}$

$K_{sp} = (3S)^3 (2S)^2 = 108\ S^5$

39. (c) Sulphides of IIA and IIB have low value of K_{sp}.

40. (a) For CuS solubility is $(10^{-31})^{1/2}$;

$$\text{For } Ag_2S = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}} = \left(\frac{10^{-44}}{4}\right)^{\frac{1}{3}} \text{ and for HgS} = \left(10^{-54}\right)^{\frac{1}{2}}$$

41. (c) $COCl_2$ is phosgene hence will not give any metal sulphide.

42. (b) $SnS_2 \rightleftharpoons Sn^{4+} + 2S^{--} \quad K_{sp} = [Sn^{4+}]\,[S^{--}]^2$

43. (d) When NH_4Cl is added for III group NH_4^+ concentration increases and OH^- concentration decreases (by common ion effect).

44.(d) Solubility of

$$BaSO_4 = \sqrt{K_{sp}} = (1.5\times10^{-9})^{1/2} = 3.87\times10^{-5}$$

45. (c) Solubility of AgCl

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{4\times10^{-10}}{0.08} = 5.0\times10^{-9}\,M$$

0.08 M is concentration of $[Cl^-]$ from $CaCl_2$.

46. (a) $\text{Solubility of AgCl} = \dfrac{1.435\times10^{-3}}{143.5} = 10^{-5}\ \text{moles}\ L^{-1}$

$K_{sp} = s^2 = (10^{-5})^2 = 10^{-10}$

47. (a) For ternary electrolyte solubility

$$= \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}} = \left(\frac{32\times10^{-12}}{4}\right)^{\frac{1}{3}} = 2\times10^{-4}$$

48. (d) Solubility in AgCl is 0.01 M HCl

$$= \frac{K_{sp}}{[Cl^-]} = \frac{1.8\times10^{-10}}{0.01} = 1.8\times10^{-8}$$

49. (b) $\text{Solubility} = \sqrt{K_{sp}} = \sqrt{6.4\times10^{-5}} = 8\times10^{-3}\,M$

50. (a) $\underset{0.5}{BaCl_2} + \underset{0.5}{H_2SO_4} \longrightarrow \underset{0.5}{BaSO_4} + 2HCl$

($BaCl_2$ is limiting reagent)

51. (c) $Ag_2CrO_4 \longrightarrow 2Ag^+ + CrO_4^{2-}$

$$[CrO_4^{2-}] = \frac{1}{2}[Ag^+] = \frac{1.5\times10^{-4}}{2} = 0.75\times10^{-4}$$

$$K_{sp} = (1.5\times10^{-4})^2(0.75\times10^{-4}) = 1.68\times10^{-12}$$

52. (b) $\text{Solubility of } BaSO_4 = \dfrac{2.33\times10^{-3}}{233} = 10^{-5}\,ML^{-1}$

$\therefore K_{sp} = (10^{-5})^2 = 10^{-10}$

53. (c) $[Ba^{++}]\,[SO_4^{--}]$

$K_{sp=}(1.0 \times 10^{-4})\,[SO_4^{--}] = 4 \times 10^{-10}$

$\therefore [SO_4^{--}] = 4\times10^{-6}$

54. (d) MX_2 is ternary salt. $K_{sp} = 4S^3 = 4\ (0.5 \times 10^{-4})^3 = 5 \times 10^{-13}$

55. (a) Blood contains serum protein which acts as buffer.

56. (b) Smaller the pH, the more the acidic character.

57. (d) – log [H⁺] = pH; – log 10 = pH. Hence pH = –1 less than 0.

58. (d) The pH values indicate that NaD, NaC and NaB are salts of strong base and weak acid. pH of NaA = 7 it is salt of strong acid and strong base.

59. (b) Salt must be of strong base and weak acid as pH = 9, hence the salt CH_3COONa.

60. (b) K_w increases with temperature.

61. (b) The higher the pH more, the basic character, pH of $Na_2CO_3 > CH_3COOK$.

62. (a) $MgCl_2$ gives acidic solution hence pH < 7.

63. (a) $-\log [H^+] = 4.70.\ \therefore [H^+] = 2\times10^{-5}$,

$$[OH^-] = \frac{10^{-14}}{2\times10^{-5}} = 5\times10^{-10}$$

64. (d) $-\log [H^+] = pH; -\log 3 \times 10^{-4} = pH;\ \therefore\ pH = 3.523.$

65. (a) Molar concentration of NaOH $\dfrac{4}{40} = 0.1M$.

$\therefore [OH^-] = 10^{-1};\ [H^+] = 10^{-13};\ pH = 13.$

66. (c) 1 N NaOH = 1 M NaOH.

$\therefore [OH^-] = 10^0;\ [H^+] = 10^{-14};\ pH = 14.$

67. (b) 0.0001 M NaOH.

$\therefore [OH^-] = 10^{-4};\ [H^+] = 10^{-10};\ pH = 10.$

68. (a) $-\log (OH) = pOH; -\log 6.2 \times 10^{-9} = pOH;$

$\therefore\ pOH = 8.21$

69. (c) mev. of HCl = 50 × 0.4 = 20, mev. of NaOH = 50 × 0.2 = 10
mev. of acid left = 10 or gev. of acid = 0.01, volume 100 ml

$$[HCl] = \frac{0.01\times1000}{100} = 0.1;\ \therefore [H^+] = 10^{-1};\ pH = 1$$

70. (a) For weak acid $[H^+] = C\alpha$.

$$\therefore \alpha = \frac{10^{-6}}{1};\ (pH = 6,\ \therefore [H^+] = 10^{-6});$$

$K_a = C\alpha^2 = 1 \times (10^{-6})^2 = 1 \times 10^{-12}$

71. (c) $pH = 3.\ \therefore\ [H^+] = 10^{-3}; pH = 6\ \therefore\ [H^+] = 10^{-6}.$
Hence $[H^+]$ reduced by 10^{-3} times.

72. (b) $CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^-$;

$$K_c = \frac{[H_3O^+][HCO_3^-]}{[CO_2]};\ \frac{[HCO_3^-]}{[CO_2]} = \frac{3.8\times10^{-7}}{10^{-6}} = 3.8\times10^{-1}$$

73. (b) Salt of strong acid and strong base give neutral solution (pH = 7). Hence such salts are not hydrolysed. pH = 7

74. (c) NaCl solution (salt of strong base and strong acid) hence pH = 7.

75. (b) $K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8\times10^{-5}} = 5.5\times10^{-10}$.

76. (a) $\alpha = \sqrt{\frac{K_w}{K_a \times c}} = \sqrt{\frac{10^{-14}}{1.3\times10^{-9}\times\frac{1}{80}}} = 2.48\%$.

77. (d) $pH = \frac{1}{2}(14 + 4.75 - 0) = 9.4$ Salt of weak acid and strong base. Remember for CH_3COOH, $pK_a = 4.75$

78. (d) $pH = pk_a + \log\frac{[SALT]}{[ACID]}$.

For maximum buffer capacity $\frac{[SALT]}{[ACID]} = 1$.

79. (b) PO_4^{3-} and $H_2PO_4^-$ is combination of acid and salt.

80. (c) $HCl + NH_4Cl$. HCl is strong acid hence not used in buffer.

81. (c) The pH of basic buffer is more than 7. NH_4Cl and NH_4OH combination provides basic buffer.

82. (a) Formic acid is stronger than other acids given.

83. (b) $pOH = pk_b + \log\frac{[SALT]}{[BASE]} = 5 + \log\frac{0.01}{0.1} = 4$.

$\therefore pH = 10 \quad (\because pH + pOH = 14)$

84. (b) $pH = -\log K_a + \log\frac{[SALT]}{[ACID]} = -\log 10^{-8} + 0 = 8$.

85. (a) $pH = pK_a - \log\frac{[ACID]}{[SALT]} = pK_a - \log\frac{10[SALT]}{[SALT]}$

$\because$ [Acid] = 10 [Salt]

Hence pH will decrease by 1.

86. (c) $pH = pK_a + \log\frac{[SALT]}{[ACID]}$

$5.5 = 4.5 + \log\frac{[SALT]}{0.1}$ [SALT] = 1 M.

87. (b) $6 = -\log 10^{-5} + \log\frac{SALT}{ACID} = 5 + \log\frac{SALT}{ACID}$

$\log\frac{SALT}{ACID}$ must be 1. $\therefore \frac{SALT}{ACID} = \frac{10}{1}$ or $10:1$.

88. (d) $[H^+] = K_a \times \frac{[ACID]}{[SALT]} = 6.2\times10^{-10}\times\frac{0.1}{0.2} = 3.1\times10^{-10}$

89. (d) $pOH = -\log K_b + \log\frac{[SALT]}{[BASE]}$

$= -\log K_b \left(\text{since } \frac{SALT}{BASE} = 1\right)$

$= -\log 2\times10^{-5} = 4.7. \quad \therefore pH = 9.3$

90. (b) $N_1V_1 = N_2V_2 \quad (1\,M\,H_2SO_4 = 2N\,H_2SO_4)$

$2\times V_1 = 10\times 1 \quad V_1 = 5\,ml$

91. (c) (NaOH + HCl) (KOH + HNO_3). Both constitute the pair of strong base and strong acid.

92. (b) 57.4 kJ mol^{-1} is heat of neutralisation for strong acid and strong base. Since acetic acid is weak, the value will be less than 57.4 kJ mol^{-1}.

93. (c) Less than 13.7 kcal. NH_4OH is a weak base. It requires less energy for ionisation.

94. (c) Weak acids or weak bases e.g. phenolphthalein (weak acid) or methyl orange. (weak base)

95. (c) Methyl orange is a weak base hence must be used with strong acid.

96. (a) Solubility of AgI in KI soln. $= \frac{K_{sp}\text{ of AgI}}{[I^-]} = \frac{1.0\times10^{-16}}{10^{-4}}$

$= 1.0\times10^{-12}\ mol^{-1}$

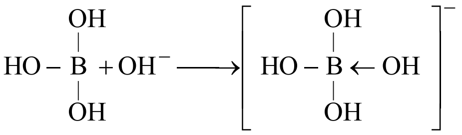
97. (a) Rain water is acidic due to dissolved oxides of nitrogen

$(N_2 + O_2 \longrightarrow 2NO \text{ and } NO + O_2 \longrightarrow 2NO_2)$

formed by thunderstorm.

Hence pH less than 7.

98. (a) H_3BO_3 is not proton donor but behaves as a Lewis acid by accepting a lone pair of electrons from OH^- ions



99.(c) Since K_{sp} of HgS is minimum among others, HgS will precipitate first.

EXERCISE 3

1. (a) Given $K_a = 1.00\times10^{-5}$, $c = 0.100$ mol for a weak electrolyte, degree of dissociation

$(\alpha) = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1\times10^{-5}}{0.100}} = 10^{-2} = 1\%$

2. (a) Given $[H_3O^+] = 1\times10^{-10}$ M

at 25° $[H_3O^+][OH^-] = 10^{-14}$

$\therefore [OH^-] = \frac{10^{-14}}{10^{-10}} = 10^{-4}$

$pOH = -\log[OH^-] = -\log[10^{-4}] = 4$

$\therefore pOH = 4$

3. **(b)** $[H_3O]^+$ for a solution having pH = 3 is given by
$[H_3O]^+ = 1\times10^{-3}$ moles/litre

$[\therefore\ [H_3O]^+ = 10^{-pH}]$

Similarly for solution having pH = 4,
$[H_3O]^+ = 1 \times 10^{-4}$ moles/ litre and for pH=5
$[H_3O^+] = 1\times10^{-5}$ moles/ litre

Let the volume of each solution in mixture be IL, then total volume of mixture solution L = (1 + 1 + 1) L =3L

Total $[H_3O]^+$ ion present in mixture solution $= (10^{-3} + 10^{-4} + 10^{-5})$ moles

Then $[H_3O]^+$ ion concentration of mixture solution

$$= \frac{10^{-3}+10^{-4}+10^{-5}}{3}\text{M} = \frac{0.00111}{3}\text{M}$$

$= 0.00037\ \text{M} = 3.7 \times10^{-4}$ M.

4. **(c)** For this reaction $K_{eq.}$ is given by

$$K = \frac{\left[Fe^{3+}\right]\left[OH^-\right]^3}{\left[Fe(OH)_3\right]}$$

$= [Fe^{3+}]\,[OH^-]^3 \qquad [\therefore\ [\text{solid}]=1].$

If $[OH^-]$ is decreased by $\frac{1}{4}$ times then for reaction equilibrium constant to remain constant, we have to increase the concentration of $[Fe^{3+}]$ by a factor of 4^3 i.e $4\times 4 \times 4 = 64$. Thus option (c) is correct answer.

5. **(b)** The highest pH will be recorded by the most basic solution. The basic nature of hydroxides of alkaline earth metals increase as we move from Mg to Ba and thus the solution of $BaCl_2$ in water will be most basic and so it will have highest pH.

6. **(c)** Given, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$;

$K_{a_1} = 1.5 \times 10^{-5} \quad$ ....(i)

$HCN \rightleftharpoons H^+ + CN^-$; $K_{a_2} = 4.5 \times 10^{-10}$

or $H^+ + CN^- \rightleftharpoons HCN$;

$$K'_{a_2} = \frac{1}{K_{a_2}} = \frac{1}{4.5\times10^{-10}} \qquad \text{...(ii)}$$

$\therefore$ From (i) and (ii), we find that the equilibrium constant (K_a) for the reaction ,

$CN^- + CH_3COOH \rightleftharpoons CH_3COO^- + HCN$, is

$$K_a = K_{a_1} \times K'_{a_2} = \frac{1.5\times10^{-5}}{4.5\times10^{-10}} = \frac{1}{3}\times10^5 = 3.33\times10^4$$

7. **(d)** $(CH_3)_3$ B - is an electron deficient, thus behave as a lewis acid.

8. **(d)** Ammonium chloride is a salt of weak base and strong acid. In this case hydrolysis constant K_h can be calculated as

$$K_h = \frac{K_w}{K_b} = \frac{1\times10^{-14}}{1.77\times10^{-5}} = 5.65\times10^{10}$$

9. **(d)** $Ba(OH)_2(s) \longrightarrow Ba^{2+}(aq) + 2\,OH^-(aq)$

pH = 12 or pOH = 2

$[OH^-] = 10^{-2}$ M

$$\begin{array}{lll} Ba(OH)_2 \longrightarrow & Ba^{2+} & +\,2\,OH^- \\ & 0.5\times10^{-2} & 10^{-2} \end{array}$$

$[\therefore$ Concentration of Ba^{2+} is half of $OH^-]$

$K_{sp} = [Ba^{2+}]\,[OH^-]^2$

$= [0.5 \times 10^{-2}]\,[1 \times 10^{-2}]^2$

$= 0.5 \times 10^{-6} = 5 \times 10^{-7}\ M^3$

10. **(d)** $$pH = pK_a + \log\left[\frac{\text{Salt}}{\text{Acid}}\right]$$

$$\log\left[H^+\right] = \log K_a - \log\left[\frac{\text{Salt}}{\text{Acid}}\right]$$

$$\log\left[H^+\right] = \log K_a + \log\left[\frac{\text{Acid}}{\text{Salt}}\right]$$

$$\left[H^+\right] = K_a\left[\frac{\text{Acid}}{\text{Salt}}\right]$$

$$= 1.8 \times 10^{-5} \times \frac{0.1}{0.2} = 9 \times 10^{-6}\ \text{M}$$

11. **(d)** $K_b = 10^{-10}$; $K_a = 10^{-4}$ or $pK_a = 4$

For the buffer solution containing equal concentration of B^- and HB

$pH = pK_a + \log 1$

$pH = pK_a = 4$

12. **(c)** Boron in B_2H_6 is electron deficient

13. **(b)** Given $[NH_3] = 0.3$ M, $[NH_4^+] = 0.2$ M, $K_b = 1.8 \times 10^{-5}$.

$$pOH = pK_b + \log\frac{[\text{salt}]}{[\text{base}]} \quad [pK_b = -\log K_b;$$

$pK_b = -\log 1.8 \times 10^{-5}]$

$\therefore\ pK_b = 4.74$

$$= 4.74 + \log\frac{0.2}{0.3} = 4.74 + 0.3010 - 0.4771 = 4.56$$

$pH = 14 - 4.56 = 9.436$

14. **(c)** BF_3 behaves as lewis acid.

15. **(c)** $K_{sp} = [Ag^+]\,[Cl^-]$

$1.8 \times 10^{-10} = [Ag^+]\,[0.1]$

$[Ag^+] = 1.8 \times 10^{-9}$ M

$K_{sp} = [Pb^{+2}]\,[Cl^-]^2$

$1.7 \times 10^{-5} = [Pb^{+2}]\,[0.1]^2$

$[Pb^{+2}] = 1.7 \times 10^{-3}$ M

16. **(b)** Given pH = 12
or $[H^+] = 10^{-12}$
Since, $[H^+][OH^-] = 10^{-14}$

$$\therefore \quad [OH^-] = \frac{10^{-14}}{10^{-12}} = 10^{-2}$$

$$Ba(OH)_2 \rightleftharpoons \underset{s}{Ba^{2+}} + \underset{2s}{2OH^-}$$

$[OH^-] = 10^{-2}$

$$2s = 10^{-2} \quad \text{or} \quad s = \frac{10^{-2}}{2}$$

$$K_{sp} = 4s^3 = 4 \times \left(\frac{10^{-2}}{2}\right)^3 = 5 \times 10^{-7}$$

17. **(a)** Lets take an example of an acidic buffer CH_3COOH and CH_3COONa.
$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$;
$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$
when few drops of HCl are added to this buffer, the H^+ of HCl immediatly combine with CH_3COO^- ions to form undissociated acetic acid molecules. Thus there will be no appreciable change in its pH value. Like wise if few drops of NaOH are added, the OH^- ions will combine with H^+ ions to form unionised water molecule. Thus pH of solution will remain constant.

18. **(c)** Solubility of alkali metal is maximum among the following. Among ZnS (1.7×10^{-5}) & CuS (8×10^{-37}) ZnS has higher value of K_{sp}.

19. **(b)** BF_3 is Lewis acid(e^- pair acceptor)

20. **(a)** A buffer is a solution of weak acid and its salt with strong base and vice versa. HCl is strong acid and NaCl is its salt with strong base. pH is less than 7 due to HCl

21. **(a)** $(HSO_4)^-$ can accept and donate a proton
$(HSO_4)^- + H^+ \rightarrow H_2SO_4$ (conjugate acid)
$(HSO_4)^- - H^+ \rightarrow SO_4^{2-}$. (conjugate base)

22. **(a)** $Mg(OH)_2 \rightarrow \underset{x}{[Mg^{2+}]} + \underset{2x}{2[OH^-]}$
$k_{sp} = [Mg][OH]^2 = [x][2x]^2 = x.4x^2 = 4x^3$.

23. **(a)** $Mg(OH)_2 \rightleftharpoons \underset{S}{Mg^{++}} + \underset{2S}{2OH^-}$;
$K_{sp} = (s)(2s)^2 = 4s^3$

24. **(b)** An acidic solution cannot have a pH > 7.

25. **(d)** $[A] = 1.0 \times 10^{-5}, [B] = [1.0 \times 10^{-5}]$,
$k_{sp} = [2.B]^2[A] = [2 \times 10^{-5}]^2[1.0 \times 10^{-5}]$
$= 4 \times 10^{-15}$

26. **(d)** $$\underset{\text{Acid}}{H_2PO_4^-} \xrightarrow{-H^+} \underset{\text{conjugate base}}{HPO_4^{2-}}$$

27. **(d)** $$MX_4 \rightleftharpoons \underset{S}{M^{4+}} + \underset{4S}{4X^-}$$

$$k_{sp} = [S][4S]^4 = 256\,S^5 \quad \therefore S = \left(\frac{K_{sp}}{256}\right)^{1/5}$$

28. **(c)** $$MX_2 \rightleftharpoons \underset{1S}{M^{++}} + \underset{2S}{2X^-}$$

Where S is the solubility of MX_2
then $K_{sp} = 4S^3$; $S \times (2S)^2 = 4 \times 10^{-12} = 4S^3$; $S = 1 \times 10^{-4}$
$\therefore S = 1[M^{++}] = 1 \times 10^{-4}$

29. **(a)** $pH = -\log[H^+] = \log\frac{1}{[H^+]}$

$$5.4 = \log\frac{1}{[H^+]}$$

On solving $[H^+] = 3.98 \times 10^{-6}$

30. **(a)** Conjugate acid-base pair differ by only one proton.

$OH^- \longrightarrow H^+ + O^{2-}$ Conjugate base of OH^- is O^{2-}

31. **(b)** The $H\overset{+5}{N}O_3$ is stronger than $H\overset{+3}{N}O_2$. The more the oxidation state of N, the more is the acid character.

32. **(b)** Given

(i) $Ag \longrightarrow Ag^+ + e^- \quad E^\circ = -0.800$ V

(ii) $Ag^+ + I^- \longrightarrow AgI + e^- \quad E^\circ = 0.152$ V

From the eqn (i) and (ii) we have,

$AgI \longrightarrow Ag^+ + I^- \quad E^\circ = -0.952$ V

$$E^o_{cell} = \frac{0.059}{n}\log K$$

$$-0.952 = \frac{0.059}{1}\log[Ag^+][I^-]$$

$$-\frac{0.952}{0.059} = \log K_{sp}$$

$-16.13 = \log K_{sp}$

33. **(d)** $H_2A \rightleftharpoons H^+ + HA^-$

$$\therefore K_1 = 1.0 \times 10^{-5} = \frac{[H^+][HA^-]}{[H_2A]} \text{(Given)}$$

$$HA^- \longrightarrow H^+ + A^{--}$$

$$\therefore K_2 = 5.0 \times 10^{-10} = \frac{[H^+][A^{--}]}{[HA^-]} \text{(Given)}$$

$$K = \frac{[H^+]^2[A^{2-}]}{[H_2A]} = K_1 \times K_2$$

$= (1.0 \times 10^{-5}) \times (5 \times 10^{-10}) = 5 \times 10^{-15}$

34. **(d)** For acidic buffer $pH = pK_a + \log\left[\frac{\text{salt}}{\text{acid}}\right]$

$$\text{or } pH = pK_a + \log\frac{[A^-]}{[HA]}$$

Given $pK_a = 4.5$ and acid is 50% ionised.
$[HA] = [A^-]$ (when acid is 50% ionised)
$\therefore\ pH = pK_a + \log 1$
$\therefore\ pH = pK_a = 4.5$
$pOH = 14 - pH = 14 - 4.5 = 9.5$

35. (c) Let s = solubility

$$\underset{}{AgIO_3} \rightleftharpoons \underset{s}{Ag^+} + \underset{s}{IO_3^-}$$

$K_{sp} = [Ag^+]\,[IO_3^-] = s \times s = s^2$
Given $K_{sp} = 1 \times 10^{-8}$

$$\therefore\quad s = \sqrt{K_{sp}} = \sqrt{1\times10^{-8}}$$
$$= 1.0 \times 10^{-4}\ \text{mol/lit} = 1.0 \times 10^{-4} \times 283\ \text{g/lit}$$
$$(\because \text{Molecular mass of Ag IO}_3 = 283)$$
$$= \frac{1.0\times10^{-4}\times283\times100}{1000}\ \text{gm}/100\text{ml}$$
$$= 2.83 \times 10^{-3}\ \text{gm}/100\ \text{ml}$$

36. (c) Reaction (c) can be obtained by adding reactions (a) and (b) therefore $K_3 = K_1 . K_2$
Hence (c) is the correct answer.

37. (c) The correct order of acidic strength of the given species

$$\underset{(iv)}{HSO_3F} > \underset{(ii)}{H_3O^+} > \underset{(iii)}{HSO_4^-} > \underset{(i)}{HCO_3^-}$$

or (i) < (iii) < (ii) < (iv)
It corresponds to choice (c) which is correct answer.

38. (c) In aqueous solution BA(salt) hydrolyses to give

$$BA + H_2O \rightleftharpoons \underset{\text{Base}}{BOH} + \underset{\text{acid}}{HA}$$

Now pH is given by

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pKa - \frac{1}{2}pK_b$$

substituting given values, we get

$$pH = \frac{1}{2}(14 + 4.80 - 4.78) = 7.01$$

39. (a)
$$\underset{1\times10^{-4}M}{Na_2CO_3} \longrightarrow \underset{1\times10^{-4}M}{2Na^+} + \underset{1\times10^{-4}M}{CO_3^{2-}}$$

$$K_{sp(BaCO_3)} = [Ba^{2+}][CO_3^{2-}]$$

$$[Ba^{2+}] = \frac{5.1\times10^{-9}}{1\times10^{-4}} = 5.1\times10^{-5}M$$

40. (a)
(i) $\underset{acid_1}{H_3PO_4} + \underset{base_2}{H_2O} \longrightarrow \underset{acid_2}{H_3O^+} + \underset{base_1}{H_2PO_4^-}$

(ii) $\underset{acid_1}{H_2PO_4^-} + \underset{base_2}{H_2O} \longrightarrow \underset{base_1}{HPO_4^{--}} + \underset{acid_2}{H_3O^+}$

(iii) $\underset{base_1}{H_2PO_4^-} + \underset{acid_2}{OH^-} \longrightarrow \underset{acid_1}{H_3PO_4} + \underset{base_2}{O^{--}}$

Hence only in (ii) reaction $H_2PO_4^-$ is acting as an acid.

41. (c)
$$\underset{0.034-x}{H_2CO_3(aq)} + H_2O(l) \rightleftharpoons \underset{x}{HCO_3^-(aq)} + \underset{x}{H_3O^+(aq)}$$

$$K_1 = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = \frac{x \times x}{0.034 - x}$$

$$\Rightarrow 4.2\times10^{-7} \simeq \frac{x^2}{0.034} \Rightarrow x = 1.195\times10^{-4}$$

As H_2CO_3 is a weak acid so the concentration of H_2CO_3 will remain 0.034 as 0.034 >> x.

$x = [H^+] = [HCO_3^-] = 1.195 \times 10^{-4}$

Now, $\underset{x-y}{HCO_3^-(aq)} + H_2O(l) \rightleftharpoons \underset{y}{CO_3^{2-}(aq)} + \underset{y}{H_3O^+(aq)}$

As HCO_3^- is again a weak acid (weaker than H_2CO_3) with $x >> y$.

$$K_2 = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = \frac{y\times(x+y)}{(x-y)}$$

Note : $[H_3O^+] = H^+$ from first step (x) and from second step (y) = ($x + y$)
[As $x >> y$ so $x + y \simeq x$ and $x - y \simeq x$]

$$\text{So, } K_2 \simeq \frac{y\times x}{x} = y$$

$$\Rightarrow K_2 = 4.8\times10^{-11} = y = [CO_3^{2-}]$$

So the concentration of $[H^+] \simeq [HCO_3^-]$ = concentrations obtained from the first step. As the dissociation will be very low in second step so there will be no change in these concentrations.
Thus the final concentrations are

$[H^+] = [HCO_3^-] = 1.195 \times 10^{-4}$ & $[CO_3^{2-}] = 4.8\times10^{-11}$

42. (b)
$$AgBr \rightleftharpoons Ag^+ + Br^-$$

$K_{sp} = [Ag^+]\,[Br^-]$
For precipitation to occur
Ionic product > Solubility product

$$[Br^-] = \frac{K_{sp}}{[Ag^+]} = \frac{5\times10^{-13}}{0.05} = 10^{-11}$$

i.e., precipitation just starts when 10^{-11} moles of KBr is added to $1\,\ell$ $AgNO_3$ solution
$\therefore$ Number of moles of Br^- needed from KBr = 10^{-11}
$\therefore$ Mass of KBr = $10^{-11} \times 120 = 1.2 \times 10^{-9}$ g

43. (b)
$$Mg(OH)_2 \rightleftharpoons Mg^{++} + 2OH^-$$

$K_{sp} = [Mg^{++}][OH^-]^2$
$1.0 \times 10^{-11} = 10^{-3} \times [OH^-]^2$

$$[OH^-] = \sqrt{\frac{10^{-11}}{10^{-3}}} = 10^{-4}$$

$\therefore$ pOH = 4
$\therefore$ pH + pOH = 14
$\therefore$ pH = 10

44. **(d)** pH = 5

$\therefore$ $[H^+] = 10^{-5}$

$$\begin{array}{llll} & HA & \rightleftharpoons & H^+ + A^- \\ t = 0 & c & & 0 \quad 0 \\ t_{eq} & c(1-\alpha) & & c\alpha \quad c\alpha \end{array}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(c\alpha)^2}{c(1-\alpha)} = \frac{[H^+]^2}{c-[H^+]}$$

(As $[H^+]) = [A^-] = c\alpha)$

But, $[H^+] << c$

$\therefore$ $K_a = (10^{-5})^2 = 10^{-10}$

45. **(b)** $Cr(OH)_3(s) \rightleftharpoons Cr^{3+}(aq.) + 3OH^-(aq.)$

$\qquad\qquad\qquad s \qquad\quad 3s$

$(s)\ (3s)^3 = K_{sp}$

$27S^4 = K_{sp}$

$$s = \left(\frac{K_{sp}}{27}\right)^{1/4} = \left(\frac{1.6\times10^{-30}}{27}\right)^{1/4}$$

46. **(a)** $CO_2 + C_{(graphite)} \rightleftharpoons 2CO$

$P_{initial}$ 0.5atm $\qquad$ 0

P_{final} $(0.5 - x)$atm $\qquad$ $2x$ atm

Total P at equilibrium $= 0.5 - x + 2x = 0.5 + x$ atm

$0.8 = 0.5 + x$

$\therefore$ $x = 0.8 - 0.5 = 0.3$ atm

Now $K_p = (P_{CO})^2/P_{CO_2}$

$$= \frac{(2\times0.3)^2}{(0.5-0.3)} = \frac{(0.6)^2}{(0.2)} = 1.8 \text{ atm}$$

47. **(d)** For the reaction

$N_2 + O_2 \longrightarrow 2NO \qquad K = 4\times10^{-4}$

Hence for the reaction

$$NO \longrightarrow \frac{1}{2}N_2 + \frac{1}{2}O_2 \quad K' = \frac{1}{\sqrt{K}} = \frac{1}{\sqrt{4\times10^{-4}}} = 50$$

48. **(c)** $HQ \rightleftharpoons H^+ + Q^-$

$c(1-\alpha) \quad c\alpha \quad c\alpha$

$$[H^+] = c\alpha; \alpha = \frac{[H^+]}{c}$$

$$\text{or} \quad \alpha = \frac{10^{-3}}{0.1} = 10^{-2}$$

$$K_a = c\alpha^2 = 0.1\times10^{-2}\times10^{-2} = 10^{-5}$$

49. **(d)** $\because$ pH = 1 ; $H^+ = 10^{-1} = 0.1$ M

pH = 2 ; $H^+ = 10^{-2} = 0.01$ M

$\therefore$ $M_1 = 0.1 \quad V_1 = 1$

$M_2 = 0.01 \quad V_2 = ?$

From

$M_1V_1 = M_2V_2$

$0.1\times1 = 0.01\times V_2$

$V_2 = 10$ litres

$\therefore$ Volume of water added $= 10 - 1 = 9$ litres

50. **(d)** Let the weak monoacidic base be BOH, then the reaction that occurs during titration is

$BOH + HCl \rightarrow BCl + H_2O$

$$\text{Equilibrium: } \underset{c(1-h)}{B^+} + H_2O \rightleftharpoons \underset{c.h}{BOH} + \underset{c.h}{H^+}$$

Using the normality equation, $\underset{(acid)}{N_1V_1} = \underset{(base)}{N_2V_2}$

Substituting various given values, we get

$$\frac{2}{15}\times V_1 = 2.5\times\frac{2}{5}$$

$$\text{or } V_1 = 2.5\times\frac{2}{5}\times\frac{15}{2} = 2.5\times3 = 7.5 \text{ ml}$$

Then the concentration of BCl in resulting solution is given by

$$[BCl] = \frac{\frac{2}{5}\times2.5}{10} = \frac{1}{10} \text{ or } 0.1 \text{ M}$$

[Total volume = 2.5 + 7.5 = 10 ml]

$$\text{Since } K_h = \frac{K_w}{K_b}$$

$$\therefore K_h = \frac{1\times10^{-14}}{1\times10^{-12}} = 10^{-2}$$

$$\text{Thus } K_h = \frac{0.1h^2}{(1-h)} \quad \text{or} \quad 10^{-2} = \frac{0.1h^2}{(1-h)}$$

or $10^{-2} - 10^{-2}\,h = 0.1\,h^2$

or $0.1\,h^2 + 10^{-2}\,h - 10^{-2} = 0$

(Solving this quadratic equation for h, we get)

$$\text{Using} \left[x = \frac{-b\pm\sqrt{b^2-4ac}}{2a}\right]$$

$$h = \frac{-10^{-2}\pm\sqrt{(10^{-2})^2 + 4\times10^{-1}\times10^{-2}}}{2\times0.1}$$

$$= \frac{-10^{-2}\pm\sqrt{10^{-4}+4\times10^{-3}}}{2\times0.1}$$

$$= \frac{-0.01\pm\sqrt{.0001+0.004}}{0.2}$$

$$= \frac{-0.01\pm\sqrt{0.0041}}{0.2}$$

$$= \frac{-0.01 \pm 0.064}{0.2}$$

$$= \frac{0.54}{0.2} \quad \text{[Neglecting the negative term]}$$

$$= 0.27$$

$\therefore [H^+] = c.h = 0.1 \times 0.27 = 2.7 \times 10^{-2}$ M

Thus the correct answer is [d].

51. (d) $\underset{}{MX} \rightleftharpoons \underset{s}{M^+} + \underset{s}{X^-}$ (Where s is the solubility)

Then $K_{sp} = s^2$ or $s = \sqrt{K_{sp}}$

Similarly for $MX_2 \longrightarrow \underset{s}{M^{2+}} + \underset{2s}{2X^-}$

$$K_{sp} = s \times (2s)^2 = 4s^3 \quad \text{or} \quad s = \left[\frac{K_{sp}}{4}\right]^{\frac{1}{3}}$$

and for $M_3X \rightleftharpoons \underset{3s}{3M^+} + \underset{s}{X^{-3}}$

$$K_{sp} = (3s)^3 \times s = 27s^4 \quad \text{or} \quad s = \left[\frac{K_{sp}}{27}\right]^{\frac{1}{4}}$$

From the given values of K_{sp} for MX, MX_2 and M_3 X, we can find the solubilities of those salts at temperature, T.

Solubility of $MX = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}$

$$\text{Solubility of } MX_2 = \left[\frac{3.2 \times 10^{-14}}{4}\right]^{\frac{1}{3}} \text{ or } \left[\frac{32}{4} \times 10^{-15}\right]^{\frac{1}{3}}$$

$$= \left[8 \times 10^{-15}\right]^{\frac{1}{3}} \quad \text{or} \quad 2 \times 10^{-5}$$

$$\text{Solubility of } M_3X = \left[\frac{2.7 \times 10^{-15}}{27}\right]^{\frac{1}{4}}$$

$$= \left[10^{-16}\right]^{\frac{1}{4}} \text{ or } 10^{-4}$$

Thus the solubilities are in the order $MX > M_3X > MX_2$ i.e the correct answer is (d).

EXERCISE 4

1. (a) $CaC_2O_4 \rightleftharpoons \overset{2+}{Ca} + C_2\overset{2-}{O_4}$; $K_{sp} = S^2$

$\therefore S = \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-9}} = 5 \times 10^{-5}$ mol/litre

solubility $= 5 \times 10^{-5} \times 128 = 0.0064$ g

2. (d) $K_a \times K_b = K_w$

$\therefore 1.8 \times 10^{-5} \times K_a = 1 \times 10^{-14} \ \therefore k_a = 5.56 \times 10^{-10}$

3. (b) $[H^+] = \dfrac{K_a[ACID]}{[SALT]}; [H^+] = \dfrac{1.8 \times 10^{-6} \times 0.1}{0.5}$

$= 0.36 \times 10^{-6}; -\log[H^+] = -\log[0.36 \times 10^{-6}]$

$\therefore$ pH = 6.44

4. (b)

NH_4OH	+ $HCl \rightleftharpoons$	NH_4Cl	+ H_2O	
100×0.2	100×0.1	0	0	Initial millimoles
10		10	10	After neutrilisation

$pOH = -\log 1.8 \times 10^{-5} + \log\dfrac{0.01}{0.01}, \therefore pOH = 4.73;\ pH = 9.26$

5. (a) $\alpha = \sqrt{\dfrac{K_w}{K_a \times K_b}} = \sqrt{\dfrac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}} = 0.55$

6. (a) $[Ca^{++}] = \dfrac{K_{sp}}{[F^-]^2}$; Solubility $= \dfrac{3.4 \times 10^{-11}}{[0.01]^2} = 3.4 \times 10^{-7}$

7. (b) $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons \overset{+}{H} + HC\overset{-}{O_3}$.

If CO_2 escapes, the equilibrium will shift to LHS and $[H^+]$ concentration will decrease

8. (a) $H_2S \rightleftharpoons SH^- + H^+$;

$K_a = \dfrac{[SH^-][H^+]}{[H_2S]}; [SH^-] = \dfrac{10^{-7} \times 0.1}{0.3} = 3.3 \times 10^{-8}$

9. (a)

NaOH	+ $CH_3COOH \rightleftharpoons$	CH_3COONa	+ H_2O
20×0.2	50×0.2	0	0
4	10	0	0
0	6	4	4

$\text{Conc.} = \dfrac{\text{Millimoles}}{\text{Total Volume}}; [CH_3COOH] = \dfrac{6}{70}; [CH_3COONa] = \dfrac{4}{70}$

$pH = -\log 1.8 \times 10^{-5} + \log\dfrac{4/70}{6/70}, pH = 4.56$

10. (a) $[OH^-]^2 = \dfrac{K_{sp}}{[Mg^{++}]} = \dfrac{1 \times 10^{-11}}{0.1} = 10^{-10};$

$[OH^-] = 10^{-5}; [H^+] = 10^{-9}; pH = 9$

11. (b) pH = 9 ; $[H^+] = 10^{-9}; [OH^-] = 10^{-5}$;

$[Mg^{++}] = 1 \times 10^{-3}; [Mg^{++}][OH^-]^2 = 1 \times 10^{-13}$

given K_{sp} of $Mg(OH)_2 = 8.9 \times 10^{-12}$ which is more than 1×10^{-13}. Hence $Mg(OH)_2$ will not precipitate

12. (b) NaCN is a salt of strong base and weak acid ; pH

$$= 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

pK_a for HCN = 14–4.70 = 9.30

$$\therefore pH = 7 + \frac{1}{2} \times 9.30 + \frac{1}{2}\log 0.5; pH = 11.5$$

13. (a) $HCOONH_4$ is a salt of weak acid and weak base ;

$pH = ½\, pK_w + ½\, pK_a - ½\, pK_b$

$$\therefore pH = \frac{1}{2} \times 14 + \frac{1}{2} \times 3.8 - \frac{1}{2} \times 4.8 \ ; pH = 6.5$$

14. (c) $Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2CO_3$

$CO_3^{--} + 2H_2O \rightleftharpoons 2OH^- + H_2CO_3$ Anionic hydrolysis

15. (c) $BaF_2 \rightleftharpoons Ba^{++} + 2F^-, Ba(NO_3)_2$

F^- are obtained from BaF_2. Then ½ $[F^-] = [BaF_2]$

16. (c) HCN is a weak acid and energy is required to affect its ionisation. Hence the enthalpy of neutralisation of HCN is less than the enthalpy of neutralisation of strong acid. The difference of enthalpy gives the enthalpy of ionisation. 55.9 kJ-12.1 kJ = 43.8 kJ

17. (c) Let the volume of KCN to be added is V ml ; Conc. of KCN = S×V and

Conc. of HCN = 10 ×2 ; pH = 9 , $\therefore H^+ = 10^{-9}$

$$H^+ = \frac{K_a[ACID]}{[SALT]}; 10^{-9} = \frac{5 \times 10^{-10} \times 10 \times 2}{5 \times V}; V = 2ml$$

18. (c) An acid base indicator is InH. Its ionisation is as follows

$$InH \rightleftharpoons In^- + H^+$$

acid form (Red) basic form (blue)

$$K_a = \frac{[\bar{In}][H^+]}{[InH]}; [H^+] = \frac{K_a[InH]}{[\bar{In}]}; [H^+] = \frac{3 \times 10^{-5} \times 25}{75} = 1 \times 10^{-5}$$

19. (b) pH of 1 × 10^{-8} M HCl is below 7.

$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$

conjugate base of $H_2PO^-_4$ is H_3PO_4

$$H_2PO_4^- + H^+ \rightleftharpoons H_3PO_4$$

K (Autoprotolysis constant of water i.e. ionic product of water) increases with temperature. For half neutralisation of a weak acid by a weak base,

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

[Salt] = [Acid], $\therefore pH = pK_a$

20. (b) The characteristics of the given solutions are:

NaCl neutral solution

NH_4Cl slightly acidic due to the reaction

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

NaCN Slightly alkaline due to the reaction

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

HCl highly acidic

The pH of the solution will follow the order highly acidic < slightly acidic < neutral < slightly alkaline i.e. HCl < NH_4Cl < NaCl < NaCN

21. (b) $$[H^+] = \frac{(25 \times 0.3 - 25 \times 0.1)}{100} meq = 0.05M$$

22. (a) $$[OH^-] = \frac{(20 \times 0.02) - (30 \times 0.01)}{50} = 0.002M$$

$-\log [OH^-] = pOH = -\log .002 = 2.7$

$\therefore pH = 14 - 2.7 = 11.3$

23. (a) Isohydric solutions have the same $[H^+]$ concentration

24. (a)

	A	B	C
K_a	10^{-4}	10^{-6}	10^{-10}

The higher the value of K_a, the stronger the acid and the lower is pH. Hence order of pH A < B < C.

25. (b) $Fe(OH)_2 \rightleftharpoons Fe^{++} + 2\bar{O}H$

pH = 8, $[H^+] = 10^{-8}$, $[OH^-] = 10^{-6}$

$$Fe^{++} = \frac{K_{sp}}{[OH^-]^2} = \frac{1.6 \times 10^{-4}}{[10^{-6}]^2} = 0.016$$

26. (c) The hydrolysis of $C_2O_4^{2-}$ is as follows

$$C_2O_4^{2-} + H_2O \rightleftharpoons HC_2O_4^- + OH^-$$

$$K_h = \frac{K_w}{K_2} = \frac{1.0 \times 10^{-14}}{6.0 \times 10^{-5}} = \frac{x^2}{0.01}$$

$\therefore x = 1.3 \times 10^{-6}$

27. (b) $HCO_3^- \rightarrow H^+ + CO_3^{2-}$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.8 \times 10^{-11}$$

$$[H^+] = \frac{4.8 \times 10^{-11}[HCO_3^-]}{[CO_3^{2-}]} = 4.8 \times 10^{-11}(0.1/0.2)$$

$pH = -\log [H^+] = -\log (4.8 \times 10^{-11} \times 0.5) = 10.62$

28. (b) The basic indicator is InOH

$InOH \rightleftharpoons In^+ + OH^-$

$$K_b = \frac{[In^+][\bar{OH}]}{[InOH]}$$

Indicator will change colour when $\frac{[In^+]}{[InOH]} = 1$

$\therefore K_b = [OH^-] = 1 \times 10^{-11}$ and $[H^+] = 10^{-3}$

$\therefore pH = 3$

29. (c)

30. (c) The pH of blood plasma (7.4) is maintained by HCO_3^- / H_2CO_3 and $HPO_4^{2-} / H_2PO_4^-$ buffers

31. (a) $H_2A \rightleftharpoons H^+ + HA^-$

$$K_a = \frac{[H^+][HA^-]}{[H_2A]} = \frac{[H^+]^2}{C_a}$$

$$\therefore [H^+] = \sqrt{K_a.C_a}$$

32. (b) $pH = 3$, $[H^+] = 10^{-3}$ (2.0 ml); $pH = 10$,

$[H^+] = 10^{-10}$ (3.0 ml).

On mixing the volume becomes 5 ml

$$\therefore [H^+] = \frac{2\times10^{-3}}{5} + \frac{3}{5}\times10^{-10} = \frac{10^{-10}}{5}(2\times10^7 + 3)$$

$$\text{or} \quad [H^+] = \frac{10^{-10}}{5}\times 2\times10^7 = \frac{2}{5}\times10^{-3}$$

$$-\log[H^+] = -\log 2 + 3\log 10 + \log 5$$

$$\therefore \quad pH = -0.3010 + 3 + 7 = 3.4$$

33. (b) $ApBq \rightleftharpoons \underset{Sp}{pA^+} + \underset{Sq}{q\bar{B}}$

Let the solubility be s mol/liter

Thus,

$$K_{sp} = [A^+]^p[B^-]^q = [sp]^p[sq]^q = p^p\cdot q^q(s)^{p+q}.$$

34. (a) The solubility decreases by common ion effect.

$A[Cl^-] = 0,\ B[Cl^-] = 0.1$

$C[Cl^-] = 0.2\ \ D[Cl^-] = 0$

[Soluble complex is formed $[Ag(NH_3)_2]Cl$]

35. (b) $K_w = K_a \times K_b$

$$\therefore \quad K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{1.48\times10^{-11}} = 6.75\times10^{-4}$$

36. (c) $\alpha_1 = 0.005 = \sqrt{K_a \times C_1}$

Molarity of diluted solution $2\times1 = 32\times M$,

$M = \frac{1}{16}\ (C_2)$

$$\alpha_2 = \sqrt{\frac{K_a}{C_2}} = 0.005\sqrt{16} = 0.02$$

$$H_3\overset{+}{O} = C_2\alpha_2 = \frac{0.02}{16} = 1.25\times10^{-3}\ M$$

37. (a) $HA + BOH \rightleftharpoons BA + H_2O$ BA is Salt

$$\therefore \quad K_H = \frac{K_w}{K_a \times K_b}.$$

The inverse of K_H is $K_c = \frac{K_a \times K_b}{K_w}$

$$= \frac{2\times10^{-5}\times5\times10^{-6}}{1\times10^{-14}} = 1.0\times10^4$$

38. (b) $HIn \rightleftharpoons H^+ + \overline{In}$

$$pH = pK_{In} + \log\frac{[\overline{In}]}{[HIn]}$$

$$pH_1 = pK_{In} + \log\frac{20}{80} = pK_{In} - 2\log 2$$

$$pH_2 = pK_{In} + \log\frac{80}{20} = pK_{In} + 2\log 2$$

$$pH_2 - pH_1 = pK_{In} + 2\log 2 - (pK_{In} - 2\log 2)$$
$$= 4\log 2 = 1.20$$

39. (b) $HCOOH + NaOH \rightleftharpoons HCOONa + H_2O$,

HCOONa is salt of weak acid and strong base which is 0.10 M.

$$pH = \frac{1}{2}(K_w + pK_a + \log C)$$

$$= \frac{1}{2}(14 + 3.74 + \log 0.1) = 8.37$$

40. (d) The stronger the base, the more is proton accepting tendency RNH_2 is stronger than NH_3 and HI is strong acid, hence $\bar{I}$ is weak base

41. (c) $pH = 14 - pOH = 14 - \left[pK_b + \log\frac{[salt]}{[base]}\right]$

$$= 14 + \log K_b + \log\frac{80}{20}$$

$$\therefore \quad K_b = 1.0\times10^{-6}$$

42. (b) Let volume of HCl required be V ml then volume of NH_3 = 300 − V ml.

$$pH = pK_a + \log\frac{[salt]}{[base]};$$

$$9.26 = 9.26 - \log\frac{V}{(300-V)-V},\ ; V = 100\ ml.$$

43. (c) $K_{sp} = 4S^3 = 3.2 \times 16^{-11} \therefore S = 2 \times 10^{-4}$ M

$[\overline{OH}] = 2S = 2 \times 2 \times 10^{-4}$ M

$\therefore \quad pH = 14 - pOH = 14 + \log 4 \times 10^{-4} = 10.60$

44. (a) $MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$

$$\begin{array}{ccccl} 100 \times 0.1 & 100 \times 0.2 & 0 & 0 & \text{Initial moles} \\ 0 & 0 & 10 & 20 & \text{After mixing} \end{array}$$

$$\therefore K_{sp} = \left[\frac{10}{200}\right]\left[\frac{20}{200}\right]^2 = 5 \times 10^{-4}.$$

But actually K_{sp} of $Mg(OH)_2 = 1.2 \times 10^{-11}$

$\therefore \; 4S^3 = 1.2 \times 10^{-11}$

Find S then $[OH^-] = 2S$ which is 2.8×10^{-4}.

45. (a) At the half equivalence point we have equal concentrations of base left and the salt formed.

$$\therefore \quad pOH = pK_b + \log\frac{[\text{salt}]}{[\text{base}]};\; pOH = pK_b$$

and $pH = 14 - pK_b$

46. (b) The pH at which the dipolar ion does not migrate in the electric field is called isoelectric point. It is given by

$$\frac{pK_{a_1} + pK_{a_2}}{2} = \frac{2.09 + 3.86}{2} = 2.98.$$

47. (a) The solubility S of AgCl, $S^2 = K_{sp}$; $S^2 = 1.0 \times 10^{-10}$;

$S = 1 \times 10^{-5}$ mol L^{-1}.

The mass dissolved in 10 L

$= 10 \times 1.0 \times 10^{-5} \times 143.5 = 1.435 \times 10^{-2}$ g

48. (d) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

$$\begin{array}{lll} \frac{0.3}{4} & \frac{0.1}{4} & \text{at. 1/4 neutralisation} \\[1em] \frac{0.1}{4} & \frac{0.3}{4} & \text{at 3/4 neutralisation} \end{array}$$

$$pH_1 = pK_a + \log\frac{1}{3};\; pH_2 = pK_a + \log\frac{3}{1}$$

$$pH_1 - pH_2 = \log\frac{1}{3} - \log 3 = 2\log 3$$

49. (d) $NaCN(aq) + HCl(aq) \longrightarrow HCN(aq) + NaCl\,(aq)$.

Millimoles of NaCN = 50 × 0.1 = 5;

Millimoles of HCl = 50 × 0.2 = 10

Excess millimoles of HCl = 5 in 100 ml : $[H_3\overset{+}{O}] = 0.05$

$pH = -\log 0.05 = 1.30$

50. (b) To precipitate the AgCl

$[Ag^+]$ required

$$= \frac{K_{sp}(AgCl)}{[Cl^-]} = \frac{1.0 \times 10^{-10}}{0.1} = 1.0 \times 10^{-9}\,M$$

$$[Br^-] \text{ left at this stage} = \frac{K_{sp}(AgBr)}{[Ag^+]} = \frac{1.0 \times 10^{-13}}{1.0 \times 10^{-9}}$$

$= 1.0 \times 10^{-4}$ M

$$\%\text{ of remaining } [Br^-] = \frac{1.0 \times 10^{-4}}{0.1} \times 100 = 0.1$$

% of Br^- to be precipitated = 100 – 0.1 = 99.9

51. (c) pH = 8, pOH = 6; $[OH^-] = 10^{-6}$ M;

Ionic product of $Fe(OH)_2 = 0.2 \times (1 \times 10^{-6})^2$

$= 2 \times 10^{-13} > K_{sp} (= 8.1 \times 10^{-16})$

52. (b) pOH = 14 – pH = 14 – 8.26 = 5.74

$$= pK_a + \log\frac{[NH_4^+]}{[NH_3]}$$

$$= 4.74 + \log\frac{[NH_4^+]}{0.1}$$

$[\overset{+}{NH_4}] = 1$ molL^{-1}

$$\therefore \quad (NH_4)_2SO_4 = \frac{1}{2} \text{ of } [NH_4^+] = 0.5 \text{ mol}L^{-1})$$

53. (a) CO_2 with H_2O forms H_2CO_3

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.5 \times 10^{-7}$$

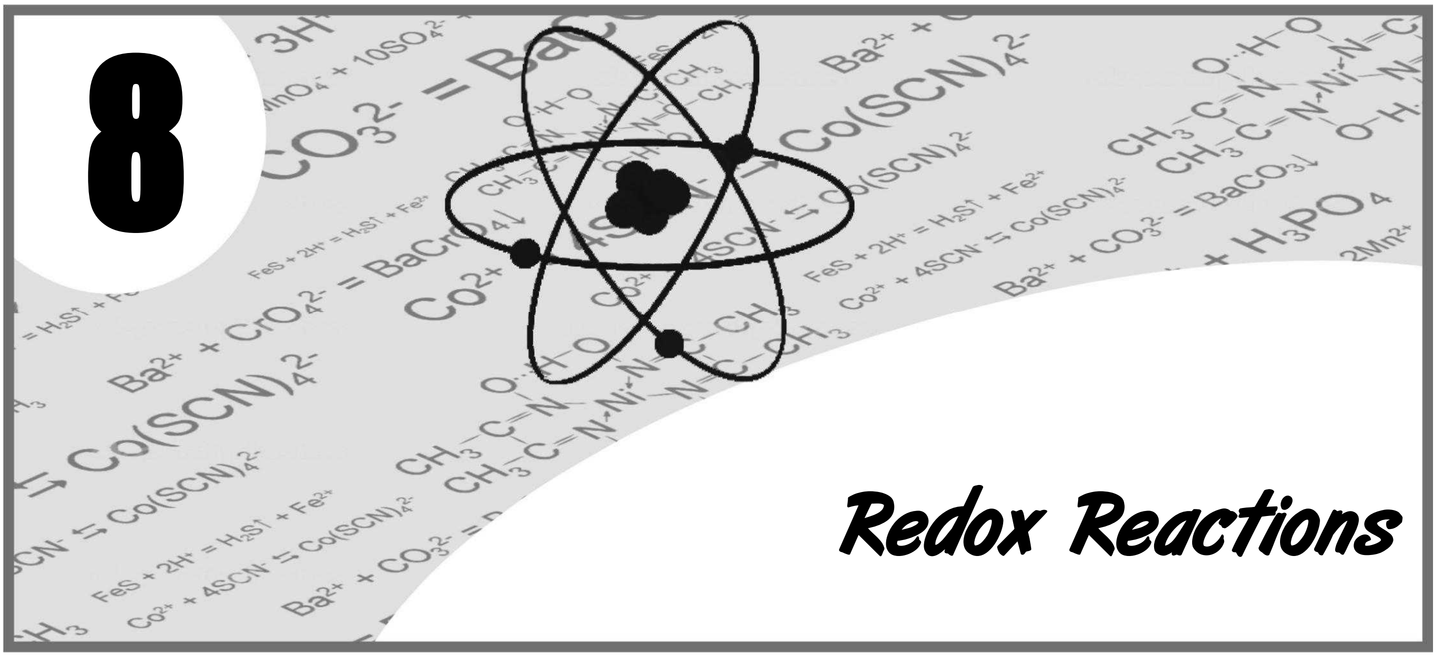
Again $pH = -\log[H^+] = 7.4$

$\therefore \quad [H^+] = 4.0 \times 10^{-8}$

$$\therefore \quad \frac{[HCO_3^-]}{[CO_2]} = \frac{4.5 \times 10^{-7}}{4 \times 10^{-8}} = 11$$

8

Redox Reactions



OXIDATION :

Oxidation may be defined in any of the following terms

(a) Addition of oxygen.
$2\,Mg + O_2 \rightarrow 2MgO$

(b) Removal of hydrogen
$3O_2 + 4NH_3 \rightarrow 2N_2 + 6H_2O$

(c) Addition of electronegative portion
$Cu + Cl_2 \rightarrow CuCl_2$

(d) Removal or decrease in the electropositive portion
$H_2S + Cl_2 \rightarrow 2\,HCl + S$

(e) De - electronation $M \longrightarrow M^{n+} + ne^-$

REDUCTION :

Reduction may be defined in any of the following terms

(a) Addition of hydrogen
$N_2 + 3H_2 \rightarrow 2NH_3$

(b) Addition of electropositive portion
$CuCl_2 + Cu \rightarrow Cu_2Cl_2$

(c) Removal of oxygen
$CuO + H_2 \rightarrow Cu + H_2O$

(d) Removal or decrease in the electronegative portion
$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$

(e) Electronation $M + ne^- \rightarrow M^{n-}$

OXIDANT OR OXIDISING AGENT :

As stated above the oxidising agent may be defined as a substance supplying oxygen or electronegative element, removing hydrogen or electropositive element and can accept electrons. They show decrease in oxidation number Examples.

$K_2Cr_2O_7$, $KMnO_4$, H_2O_2, Cl_2, Br_2, $KClO_3$, $FeCl_3$ etc.

REDUCTANT OR REDUCING AGENT :

A substance supplying hydrogen or electropositive element, removing oxygen or electro negative element and can donate electrons. They show increase in oxidation number.

Examples $SnCl_2$, H_2, H_2S, Mg, $FeSO_4$, $H_2C_2O_4$, H_2SO_3.

REDOX REACTIONS :

Reactions comprising of simultaneous oxidation and reduction and called oxidation - reduction or redox reactions.

$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + Hg_2Cl_2$

TYPES OF REDOX REACTIONS :

(*i*) ***Intermolecular redox reactions*** - In this case one substance is oxidised and another is reduced.
$4\,HCl + MnO_2 \rightarrow MnCl_2 + Cl_2 + 2H_2O$
Here HCl is oxidised and MnO_2 is reduced.

(*ii*) ***Disproportionation*** - In this case the same substance is oxidised and reduced eg.

$$4K\overset{+5}{Cl}O_3 \rightarrow 3K\overset{+7}{Cl}O_4 + KCl^{-1}$$

(*iii*) ***Intramolecular redox reactions*** - In this case one element of the compound is reduced while another element of the same compound is oxidised

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$$

Cr is reduced and N is oxidised

OXIDATION NUMBER :

It is the number of electrons lost or gained by an element during its change from free state in a particular compound.

Or

It is defined as the formal charge present on an atom in a particular compound determined by certain arbitrary rules.

RULES FOR DETERMINING OXIDATION NUMBER:

(i) O.N. of elements in free state is zero eg Cl_2, N_2, Mg, Ca

(ii) O.N. of hydrogen is always +1 except in ionic metal hydrides where it is – 1.

(iii) O.N. of oxygen is –2 except in OF_2 where it is + 2 and in peroxides where it is – 1.

(iv) O.N. of metals is always +ve. For IA group elements it is +1 and for IIA group elements it is +2.

(v) O.N. of halogens is –1 in metal halides.

(vi) O.N. of ion or radical is the number of electrons it must gain or lose to acquire neutrality *i.e.* it is equal to the electric charge for SO_4^{--} O.N. is –2.

(vii) O.N. of an atom within compound can be +ve, –ve integer, zero or fraction.

(viii) The algebraic sum of all the O.N. of elements is equal to zero.

(ix) The algebraic sum of all the O.N. of elements in an ion is equal to net charge on the ion.

(x) Maximum O.N. of an element is equal to number of valence electrons *i.e.* group number.

(xi) Minimum O.N. of an element (except metals) = (8 – group number).

(xii) In metal corbonyl, and amalgams, O.N. of metals is zero.

COVALENCY AND OXIDATION STATE

(i) Covalency : It is the number of hydrogen atoms which can combine with a given atom

or

It is the number of single bonds which an atom can form.

or

It is the number of electrons an atom can share. Valency is always a whole number.

(ii) Oxidation state : It is defined as the O.N. per atom.

STOCK NOTATION :

Representation of oxidation state of element by Roman numerals within parenthesis is known as stock notation eg $FeCl_3$ is written as Iron(III) chloride and $FeSO_4$ as Iron (II) sulphate.

CHEMICAL BONDING METHOD FOR DETERMINATION OF OXIDATION NUMBER

Sometimes wrong results are obtained when the O.N. is determined by applying the above mentioned simple rules. In such cases applying the chemical bonding method is very useful. The rules are

(i) For one covalent bond assign one unit negative charge to electronegative atom and one unit positive charge to less electronegative atom eg

$$A^{-1} - B^{+1} \text{ (electronegativity A> B).}$$

(ii) No charge when the covalent bond is between like atoms.

(iii) In case of coordinate bond assign two unit negative charge to acceptor atom and two unit positive charge to donor atom e.g. $A^{2-} \leftarrow B^{2+}$ (electronegavity A > B).

(iv) No charge when donor in coordinate bond is more electronegative than acceptor eg

$$A \rightarrow B \text{ (electronegavity A > B).}$$

(v) When coordinate bond is between similar atoms assign two unit negative charge to acceptor and two unit positive charge to donor e.g.,

$$A^{2-} \leftarrow A^{2+} \text{ (electronegativity same).}$$

CALCULATION/ DETERMINATION OF OXIDATION NUMBER OF UNDERLINED ELEMENT IN SOME COMPOUNDS:

(a) $K_2\underline{Cr}_2O_7$ -

Let the O.N. of Cr be x then

$2 \times (+1) + 2 \times (x) + 7 \times (-2) = 0$

$2 + 2x - 14 = 0 \quad \therefore x = +6$

(b) $K\underline{Mn}O_4$ -

Let the O.N. of Mn be x then

$1 \times (+1) + 1 \times (x) + 4 \times (-2) = 0$

$1 + 1x - 8 = 0 \quad \therefore x = +7$

(c) $H_2\underline{S}O_4$ -

Let the O.N. of S be x then

$2 \times (+1) + 1 \times (x) + 4 \times (-2) = 0$

$2 + x - 8 = 0 \quad \therefore x = +6$

(d) $\underline{N}H_4\underline{N}O_3$ - Split into two ions NH_4^+ and NO_3^-

Let O.N. of N be x in NH_4^+ ion then

$1 \times (x) + 4 \times (+1) = +1$

$x + 4 = +1 \quad \therefore x = -3$

Let the O.N. of N be x in NO_3^- ion then

$1 \times (x) + 3 \times (-2) = -1$

$x - 6 = -1 \quad \therefore x = +5$

(e) $\underline{P}O_4^{3-}$ -

Let the O. N. of P be x then

$1 \times (x) + 4 \times (-2) = -3$

$x - 8 = -3 \quad \therefore x = +5$

(f) $H\underline{N}O_3$ -

Let the O.N. of N be x then

$1 \times (+1) + 1 \times (x) + 3 \times (-2) = 0$

$1 + x - 6 = 0 \quad \therefore x = 5$

(g) $K\underline{I}_3$ -

Let the O.N. of I be x then

$1 \times (+1) + 3 \times (x) = 0$

$\therefore 1 + 3x = 0 \quad \therefore x = -1/3$

(h) $Na\underline{O}_2$ - It is super oxide.

Let O.N. of O be x then

$1 \times (+1) + 2 \times (x) = 0 \therefore 1 + 2x = 0 \quad \therefore x = -1/2$

(i) $\underline{Fe}_3O_4$ - It is mixed oxide $FeO.Fe_2O_3$ and Fe has O.N. +2 and +3 respectively.

(j) $\underline{Fe}_{0.96}O$

Let O.N. of Fe be x then $0.96x + (-2) = 0$

$\therefore 0.96x - 2 = 0$

$$\therefore x = \frac{+2}{0.96}$$

(k) $\underline{N}_3H$ (hydrazoic acid)

Let O.N. of N be x then

$3 \times (x) + 1 \times (+1) = 0$

$3x + 1 = 0 \quad \therefore x = -1/3$

(l) $K_4[\underline{Fe}(CN)_6]$ -

Let the O.N. of Fe be x then

$4 \times (+1) + 1 \times (x) + 6 \times (-1) = 0$

(sum of O.N. of $CN^- = -1$)

$4 + x - 6 = 0 \therefore x = 2$

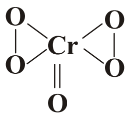
Determination of oxidation number by chemical bonding method

(m) $\underline{Cr}O_5$ - Let the O.N. of Cr be x then

$1 \times (x) + 5 \times (-2) = 0$

$x - 10 = 0 \quad \therefore x = 10$ (**wrong**)

Apply chemical bond method



$x \quad + \quad 1 \times (-2) \quad + \quad 4 \times (-1) \quad = 0$

(for Cr) (one=O) (four O – O)

$\therefore x = +6$

(n) HCN - Its structure is $H-C\equiv N$

for H – C bond H = +1, C = –1

for $C\equiv N$ bond C = +3, N = –3

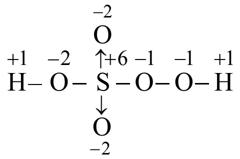
$\therefore$ sum of O.N. of H = +1, C = +2 and N = –3

(o) $H-\underline{N}\overset{\rightarrow}{=}C$ for H – N bond H = +1, N = –1

for $N\overset{\rightarrow}{=}C$, N = –2 and C = +2 (for two covalent bonds) No contribution of N → C bond since N more electronegative than C)

$\therefore$ O.N. of different atoms H = +1, C = +2, N = –3

(p) $H_2\underline{S}O_5$ (Caro acid) - Write structure and apply chemical bond method



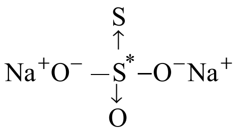
$$\overset{+1}{H}-\overset{-2}{O}-\underset{\underset{\underset{-2}{O}}{\downarrow}}{\overset{\overset{\overset{-2}{O}}{\uparrow}}{\overset{+6}{S}}}-\overset{-1}{O}-\overset{-1}{O}-\overset{+1}{H}$$

$2 \times (+1) + x + 3 \times (-2) + 2\,(-1) = 0$

for H for S for O for O – O $\therefore x = +6$

(q) $Na_2\underline{S}_2O_3$

(Structure I)



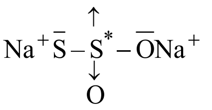
$$Na^+O^- - \underset{\underset{O}{\downarrow}}{\overset{\overset{S}{\uparrow}}{S^*}} - O^-Na^+$$

$2 \times (+1) + x + 1 \times (-2) + 3 \times (-2) = 0$

for Na for S* for S for O

$\therefore$ O.N. of S* = +6 and another S = –2

(Structure II)



$$Na^+\bar{S} - \underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S^*}} - \bar{O}Na^+$$

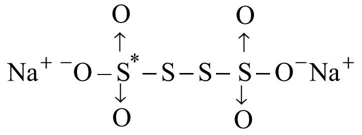
$2 \times (+1) + 1 \times (-1) + 1 \times (x) + 3 \times (-2) = 0$

for Na for S for S* for O

$2 - 1 + x - 6 = 0 \quad \therefore x = +5$

$\therefore$ O.N. of S* = +5 and another S = –1

(r) $Na_2\underline{S}_4O_6$ - Sodium tetra thionate - its structure is as follows



$$Na^{+\,-}O - \underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S^*}} - S - S - \underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}} - O^-Na^+$$

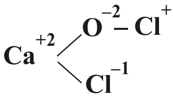
Let the O.N. of S* be x then

$2 \times (+1) + 6 \times (-2) + 2 \times (0) + 2 \times (x) = 0$

for Na for O for middle S

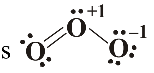
$\therefore 2 - 12 + 0 + 2x = 0 \qquad \therefore x = 5$

(s) $CaO\underline{C}l_2$ - Its structure is



$\therefore$ O.N. of Cl is –1 and +1.

(t) O_3 - The structure of O_3 is



$\therefore$ O.N. of O in ozone is + 1 and –1

OXIDATION NUMBER CONCEPT OF OXIDANT (OXIDISING AGENT) AND REDUCTANT (REDUCING AGENT) :

(i) Oxidising agent : A substance can act as oxidising agent if the oxidation number of one of its element is maximum eg HNO_3 (O.N. of N = 5 which is maximum value)

The more the electronegativity of element and the more is O.N., the more is the oxidising power eg $KClO_4$, $KBrO_4$. $KMnO_4$, $K_2Cr_2O_7$, $HClO_4$, HNO_3 etc. Oxyanions are stronger oxidising agents in acidic solution than in basic or neutral solution.

(ii) Reducing agent : A substance can act as reducing agent if the oxidation number of one of its element is **minimum** eg $SnCl_2$ (O.N. of Sn = 2 which is minimum value), $FeSO_4$, $Na_2S_2O_3$, H_2S, $H_2C_2O_4$ Electronegative elements I^-, Br^-, N^{3-} are powerfully reducing in nature.

(iii) Reducing as well as oxidising agent : A substance that can act as both, reducing as well as oxidising agent if O.N. of one of its element is in between the maximum and the minimum value eg HNO_2 (O.N. of N = +3 which is intermediate of +5 and 0).

OXIDATION NUMBER AND ACID STRENGTH :

The greater the O.N. of the element in oxyacids, the greater is the acid strength.

$$H\overset{+7}{Cl}O_4 > H\overset{+5}{Cl}O_3 > H\overset{+3}{Cl}O_2 > H\overset{+1}{Cl}O$$

EQUIVALENT WEIGHT OF AN OXIDISING AGENT

It can be obtained by dividing the molecular weight by the number of electrons gained represented in a chemical balanced equation

eg. $$2K\overset{+7}{Mn}O_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 3H_2O + 5O$$

Equivalent wt. of $KMnO_4$ in acid medium

$$= \frac{\text{Mol.wt of } KMnO_4}{5}$$

$$Cr_2O_7^{2-} + 14H^+ + 6\bar{e} \rightarrow 2Cr^{3+} + 7H_2O$$

$$\text{Eq. wt. of } K_2Cr_2O_7 = \frac{\text{Mol.wt of } K_2Cr_2O_7}{6}$$

EQUIVALENT WEIGHT OF REDUCING AGENT :

It can be obtained by dividing the molecular weight by the number of electrons lost as represented by a chemical balanced equation

$$\overset{+2}{H_2}\,\overset{+6}{C_2}\,\overset{-8}{O_4} + O \longrightarrow 2\,\overset{+4}{C}\,\overset{-4}{O_2} + H_2O$$

The change in O.N. of two atoms of carbon is +2. Hence

$$\text{Equivalent weight of oxalic acid } = \frac{\text{Mol.wt of Oxalic acid}}{2}$$

SOME OXIDISING AND REDUCING AGENTS

Oxidising agents

Substance	Radical	O.N. of effective element	Reduction product	New O.N.	Difference in O.N.	Gain of electrons
$K_2Cr_2O_7$	$Cr_2O_7^{2-}$	+6	Cr^{3+}	+3	3	3
$KMnO_4$ (acidic)	MnO_4^-	+7	Mn^{2+}	+2	5	5
$KMnO_4$ (alkaline)	MnO_4^-	+7	MnO_4^{2-}	+6	1	1
$KMnO_4$ (neutral)	MnO_4^-	+7	MnO_2	+4	3	3
H_2O_2	O_2	0	O^{2-}	–2	2	2
Cl_2	Cl	0	Cl^-	–1	1	1
$KClO_3$	ClO_3^-	+5	Cl^-	–1	6	6
$FeCl_3$	Fe^{3+}	+3	Fe^{2+}	+2	1	1
HNO_3	NO_3^-	+5	NO_2	+4	1	1

Reducing agents

Substance	Radical	O.N. of effective element	Oxidation product	New O.N.	Difference in O.N.	Loss of electrons
$SnCl_2$	Sn^{2+}	+2	Sn^{4+}	+4	2	2
$FeSO_4$	Fe^{2+}	+2	Fe^{3+}	+3	1	1
H_2	H	0	H^+	+1	1	1
H_2S	S^{2-}	–2	S^0	0	2	2
Mg	Mg	0	Mg^{2+}	+2	2	2
H_2SO_3	SO_3^{2-}	+4	SO_4^{2-}	+6	2	2
Na_3AsO_3	AsO_3^{3-}	+3	AsO_4^{3-}	+5	2	2
Na	Na	0	Na^+	+1	1	1
$H_2C_2O_4$	$C_2O_4^{2-}$	+3	CO_2	+4	1	1

BALANCING OF CHEMICAL EQUATIONS :

For balancing a chemical equation the two important methods are

(1) Oxidation number method - The certain rules are as follows

- (a) Assign oxidation number to the atoms showing a change in oxidation state.
- (b) Balance the total number of atoms undergoing change in oxidation state.
- (c) Balance the number of electrons gained and lost.
- (d) Balance [O] on both sides by adding H_2O.
- (e) Balance H atoms by adding H^+ ions

(f) If the reaction proceeds in basic solution add sufficient number of OH^- ions on both sides.

Example 1 :

Balance the equation involving oxidation of ammonia by copper oxide to give Cu, N_2 and H_2O

Solution - $$\underset{\underset{3\times2=6\bar{e}}{\uparrow}}{\overset{+2}{CuO}} + 2\underset{\underset{6\bar{e}}{\downarrow}}{\overset{-3}{NH_3}} \rightarrow Cu^0 + N_2^0 + H_2O$$

$$\therefore 3CuO + 2NH_3 \rightarrow 3Cu + N_2 + H_2O$$

Balance O by adding H_2O to RHS

$$3\,CuO + 2NH_3 \rightarrow 3Cu + N_2 + 3H_2O$$

Example 2 :

The reduction of permanganate ion by ferrous ion in presence of a dilute acid

$$MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$$

Solution =

$$\underset{\underset{5\bar{e}}{\uparrow}}{\overset{+7}{MnO_4^-}} + \underset{\underset{5\times1\bar{e}}{\downarrow}}{Fe^{2+}} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$$

$$MnO_4^- + 5Fe^{2+} + H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + H_2O$$

Balance O and H by adding H_2O and H^+; $3H_2O$ on RHS and $7H^+$ on LHS

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Example 3 :

The reduction of dichromate ion by an iodide in presence of a dilute acid

$$Cr_2O_7^{2-} + \bar{I} + H^+ \rightarrow Cr^{3+} + I_2 + H_2O$$

Solution - Balancing atoms

$$\overset{+12}{\underset{\underset{6\bar{e}}{\uparrow}}{Cr_2}}\,O_7^{2-} + \underset{\underset{3\times2\bar{e}}{\downarrow}}{2\bar{I}} + H^+ \rightarrow 2Cr^{3+} + I_2 + H_2O$$

$$\therefore Cr_2O_7^{2-} + 6I^- + H^+ \rightarrow 2Cr^{3+} + 3I_2 + H_2O$$

Balance O by adding $6H_2O$ on RHS and balance H^+ by adding $13H^+$ on LHS

$$\therefore Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

(2) Ion electron method - The rules are as follows:

(a) Split up the reaction into two half reactions showing oxidation and reduction separately.
(b) Balance number of atoms undergoing the change of oxidation state.
(c) Balance O on both sides by adding H_2O.
(d) Balance H atoms by adding H^+ ions.
(e) Balance charge by adding required number of electrons
(f) Make the number of electrons equal in two half reactions by multiplying with suitable coefficient.
(g) Add the two half reactions

Example 1 :

Oxidation of ferrous salt by potassium dichromate in acid solution.

$$Cr_2O_7^{2-} + Fe^{2+} + H^+ \rightarrow Cr^{3+} + Fe^{3+} + H_2O$$

Solution - (i) Reduction half reactions

$$Cr_2O_7^{2-} + H^+ \rightarrow Cr^{3+} + H_2O$$

Equalize Cr atoms

$$Cr_2O_7^{2-} + H^+ \rightarrow 2Cr^{3+} + H_2O$$

Balance O and H atoms on both sides by adding H_2O and H^+ ions.

$$Cr_2O_7^{2-} + \underset{+13H^+}{H^+} \rightarrow 2Cr^{3+} + \underset{+6H_2O}{H_2O}$$

Balance charge on both sides by adding electrons

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

(ii) Oxidation half-reaction

$$Fe^{2+} - e^- \rightarrow Fe^{3+}$$

Balance electrons of two half reactions

$$6Fe^{2+} - 6e^- \rightarrow 6Fe^{3+}$$

Adding two half reaction (electrons are cancelled)

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Example 2 :

Balance the equation

$$H_2C_2O_4 + H_2O_2 \rightarrow CO_2 + H_2O$$

Solution (i) Oxidation half - reaction

$$H_2C_2O_4 \rightarrow CO_2$$

Balance C, O, H atoms and charge

$$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^- \quad \text{..........(i)}$$

(ii) Reduction half reactions

$$H_2O_2 \rightarrow H_2O$$

Balance O, H atoms and charge

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad \text{..........(ii)}$$

Add two balanced half reactions (i) and (ii)

$$H_2C_2O_4 + H_2O_2 \rightarrow 2CO_2 + 2H_2O$$

Example 3 :

Write the complete balanced equation for the change

$CrO_4^{2-} + SO_3^{2-} \rightarrow Cr(OH)_4^- + SO_4^{2-}$ taking place in basic solution

Solution - **(i)** The equation is

$CrO_4^{2-} + SO_3^{2-} \rightarrow Cr(OH)_4^- + SO_4^{2-}$ reduction half reaction.

$$CrO_4^{2-} \rightarrow Cr(OH)_4^-$$

Balancing O, H atoms and charge on both sides

$$CrO_4^{2-} + 4H^+ + 3\bar{e} \rightarrow Cr(OH)_4^- \quad \text{(i)}$$

(ii) Oxidation half reaction

$$SO_3^{2-} \rightarrow SO_4^{2-}$$

Balancing O, H, charge and atoms on both sides

$$SO_3^{2-} + H_2O - 2\bar{e} \rightarrow SO_4^{2-} + 2H^+ \quad \text{(ii)}$$

Multiply (i) by 2 and (ii) by 3 and add

$$2CrO_4^{2-} + 8H^+ + 3SO_3^{2-} + 3H_2O \rightarrow$$

$$2Cr(OH)_4^- + 3SO_4^{2-} + 6H^+$$

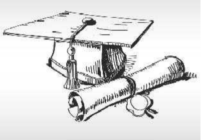
or

$$2CrO_4^{2-} + 2H^+ + 3SO_3^{2-} + 3H_2O \rightarrow 2Cr(OH)_4^- + 3SO_4^{2-}$$

Again adding $2OH^-$ on both sides.

$$2CrO_4^{2-} + 3SO_3^{2-} + 5H_2O \rightarrow 2Cr(OH)_4^- + 3SO_4^{2-} + 2OH^-$$

Exercise-1 | NCERT BASED QUESTIONS



Very Short/Short Answer Questions

1. Why is anode called oxidation electrode whereas cathode is called reduction electrode?

2. $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$. In this reaction which substance is getting oxidised and which substance is getting reduced. Name reducing agent and oxidising agent.

3. Calculate oxidation number of Cr in $K_2Cr_2O_7$ and S in $S_2O_3^{2-}$

4. Fe decomposes steam while Cu does not, why?

5. Arrange the following in order of increasing oxidation number of iodine. I_2, HI, ICl.

6. In the reaction given below which species is called a spectator ion and why?

$$Zn(s) + Cu^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) + SO_4^{2-}(aq)$$

7. Show that oxidation and reduction go side by side by taking a suitable example.

8. MnO_4^{2-} undergoes disproportionation reaction in acidic medium but MnO_4^- does not. Give reason.

9. Starting with the correct half-reaction, write the correct overall net ionic reaction in the following changes.
- (i) Chromite ion (CrO_3^-) is oxidised by H_2O_2 in strongly basic solution.
- (ii) Iodate ion (IO_3^-) oxidises the iodide I^- to I_2 in acidic solution.
- (iii) Permanganate ion $MnO^-{}_4$ oxidises the oxalate ion ($C_2O^2{}_4{}^-$) to CO_2 in acidic solution.

10. Is it possible to store:
- (i) copper sulphate solution in a zinc vessel?
- (ii) copper sulphate solution in a nickel vessel?
- (iii) copper sulphate solution in a silver vessel?
- (iv) copper sulphate solution in a gold vessel?

(Take help from electrochemical series)

11. The standard electrode potential corresponding to the reaction

$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$ is + 1.42 V.

Predict if gold can be dissolved in 1 M HCl solution and on passing H_2 gas through gold solution, metallic gold will be precipitated or not?

12. Arrange A, B, C, D, E and H in order of increasing electrode potential in the electrochemical series:

$A + H_2SO_4 \rightarrow ASO_4 + H_2$

$ACl_2 + C \rightarrow CCl_2 + A$

$ECl_2 + C \rightarrow$ No reaction

$2BCl + D \rightarrow DCl_2 + 2B$

$H_2SO_4 + D \rightarrow$ No reaction

Long Answer Questions

13. **(i)** Balance the following reaction by ion–electron method

$$K^+ MnO_4 + H^+ Cl^- \longrightarrow K^+Cl^- + Mn^{2+}(Cl^-)_2 + H_2O + Cl_2$$

(ii) Balance the following reaction by oxidation number method

$$As_2S_5 + H^+ NO_3^-(conc.) \longrightarrow H_3AsO_4 + 5H_2SO_4 + H_2O + NO_2$$

14. **(i)** Balance the following equations using the half-reaction method in the acidic medium.
- (a) $Zn + NO_3^- \longrightarrow Zn^{2+} + NH_4^+$
- (b) $MnO_4^- + H_2C_2O_4 \longrightarrow Mn^{2+} + CO_2$
- (c) $Cr_2O_7^{2-} + Cl^- \longrightarrow Cr^{3+} + Cl_2$

(ii) Balance the following redox reaction in basic medium using the half-reaction method:
- (a) $Mn^{2+} + ClO_3^- \rightarrow MnO_2 + ClO_2$
- (b) $Cl_2 \rightarrow Cl^- + ClO_3^-$

15. **(i)** What are the highest oxidation numbers of N, S and Cl?

(ii) Is $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$ a redox reaction?

(iii) Calculate oxidation number of:
- (a) Cr in CrO_5
- (b) S in H_2SO_5
- (c) Fe in Fe_3O_4.

Multiple Choice Questions

16. Which of the following is not an example of redox reaction?
- (a) $CuO + H_2 \rightarrow Cu + H_2O$
- (b) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
- (c) $2K + F_2 \rightarrow 2KF$
- (d) $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$

17. The oxidation number of an element in a compound is evaluated on the basis of certian rules. Which of the following rules is not correct in this respect?
- (a) The oxidation number of hydrogen is always + 1.
- (b) The algebraic sum of all the oxidation numbers in a compound is zero.
- (c) An element in the free or the uncombined state bears oxidation number zero.
- (d) In all its compounds, the oxidation number of fluorine is – 1.

18. Which of the following arrangements represent increasing oxidation number of the central atom?
- (a) $CrO_2^-, ClO_3^-, CrO_4^{2-}, MnO_4^-$
- (b) $ClO_3^-, CrO_4^{2-}, MnO_4^-, CrO_2^-$
- (c) $CrO_2^-, ClO_3^-, MnO_4^-, CrO_4^{2-}$
- (d) $CrO_4^{2-}, MnO_4^-, CrO_2^-, ClO_3^-$

19. Nitric oxide acts as a reducing agent in the reaction

(a) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

(b) $2NO + 3I_2 + 4H_2O \rightarrow 2NO_3^- + 6I^- + 8H^+$

(c) $2NO + H_2SO_3 \rightarrow N_2O + H_2SO_4$

(d) $2NO + H_2S \rightarrow N_2O + S + H_2O$

20. What products are expected from the disproportionation reaction of hypochlorous acid?

(a) HCl and Cl_2O (b) HCl and $HClO_3$
(c) $HClO_3$ and Cl_2O (d) $HClO_2$ and $HClO_4$

21. Thiosulphate reacts differently with iodine and bromine in the reactions given below:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

$$S_2O_3^{2-} + Br_2 + 5H_2O \rightarrow 2SO_4^{2-} + 2Br^- + 10H^+$$

Which of the following statements justifies the above dual behaviour of thiosulphate?

(a) Bromine is a stronger oxidant than iodine.
(b) Bromine is a weaker oxidant than iodine.
(c) Thiosulphate undergoes oxidation by bromine and reduction by iodine in these reactions.
(d) Bromine undergoes oxidation and iodine undergoes reduction in these reactions.

22. The more positive the value of $E^{\ominus}$, the greater is the tendency of the species to get reduced. Using the standard electrode potential of redox couples given below find out which of the following is the strongest oxidising agent.

$E^{\ominus}$ **Values :** $Fe^{3+}/Fe^{2+} = +0.77$; $I_2(s)/I^- = +0.54$;
$Cu^{2+}/Cu = +0.34$; $Ag^+/Ag = +0.80V$

(a) Fe^{3+} (b) $I_2(s)$ (c) Cu^{2+} (d) Ag^+

23. Which of the following elements does not show disproportionation tendency?

(a) Cl (b) Br (c) F (d) I

24. For the redox reaction

$$MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$$

the correct coefficients of the reactants for the balanced reaction are:

	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	2	5	16
(b)	16	5	2
(c)	5	16	2
(d)	2	16	5

25. $(x)MnO_4^- + (y)H_2O_2 \rightarrow$

$$2Mn^{+2} + 5H_2O + 13/2\,O_2 + (z)e^-$$

In this reaction, value of (x), (y) and (z) are

(a) 2, 5, 6 (b) 5, 2, 9 (c) 3, 5, 5 (d) 2, 6, 6

Exercise-2 | CONCEPTUAL MCQs

1. In the following reaction, which is the species being oxidised ?

$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$$

(a) Fe^{3+} (b) I^-
(c) I_2 (d) Fe^{2+}

2. Which of the following reactions depicts the oxidising property of SO_2 ?

(a) $SO_2 + H_2O \rightarrow H_2SO_3$

(b) $2H_2S + SO_2 \rightarrow 3S + 2H_2O$

(c) $Cl_2 + SO_2 \rightarrow SO_2Cl_2$

(d) $2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+$

3. Which of the following statements is not correct ?

(a) Potassium permanganate is a powerful oxidising substance.
(b) Potassium permanganate is a weaker oxidising agent than potassium dichromate
(c) Potassium permanganate is a stronger oxidising agent than potassium dichromate
(d) Potassium dichromate oxidises a secondary alcohol into a ketone.

4. Which substance serves as reducing agent in the following reaction?

$$14H^+ + Cr_2O_7^{2-} + 3Ni \rightarrow 2Cr^{3+} + 7H_2O + 3Ni^{2+}$$

(a) H_2O (b) Ni
(c) H^+ (d) $Cr_2O_7^{2-}$

5. In the reaction

$$3Br_2 + 6CO_3^{2-} + 3H_2O \rightarrow 5Br^- + BrO_3^- + 6HCO_3^-$$

(a) bromine is oxidised and carbonate is reduced.
(b) bromine is reduced and water is oxidised
(c) bromine is neither reduced nor oxidised
(d) bromine is both reduced and oxidised

6. Which of the following is a redox reaction ?

(a) H_2SO_4 with NaOH
(b) In atmosphere, O_3 from O_2 by lightning
(c) Nitrogen oxides from nitrogen and oxygen by lightning
(d) Evaporation of H_2O

7. For the redox reaction

$MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$

the correct coefficients of the reactants for the balanced reaction are:

	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	2	5	16
(b)	16	5	2
(c)	5	16	2
(d)	2	16	5

8. $KMnO_4$ oxidises oxalic acid in acidic medium. The number of CO_2 molecules produced as per the balanced equation is
(a) 10 (b) 8
(c) 6 (d) 3

9. Of the following reactions, only one is a redox reaction. Identify it
(a) $Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$
(b) $BaCl_2 + MgSO_4 \rightarrow BaSO_4 + MgCl_2$
(c) $2S_2O_7^{2-} + 2H_2O \rightarrow 4SO_4^{2-} + 4H^+$
(d) $Cu_2S + 2FeO \rightarrow 2Cu + 2Fe + SO_2$

10. The reaction of $KMnO_4$ and HCl results in
(a) oxidation of Mn in $KMnO_4$ and production of Cl_2
(b) reduction of Mn in $KMnO_4$ and production of H_2
(c) oxidation of Mn in $KMnO_4$ and production of H_2
(d) reduction of Mn in $KMnO_4$ and production of Cl_2

11. The reaction,

$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ is
(a) an oxidation reaction
(b) a reduction reaction
(c) a redox reaction
(d) a hydrolysis reaction

12. The chemical that undergoes self oxidation and self reduction in the same reaction is
(a) benzyl alcohol (b) acetone
(c) formaldehyde (d) acetic acid

13. In which of the following pairs, there is greatest difference in the oxidation number of the underlined elements ?
(a) $\underline{N}O_2$ and $\underline{N}_2O_4$ (b) $\underline{P}_2O_5$ and $\underline{P}_4O_{10}$
(c) $\underline{N}_2O$ and $\underline{N}O$ (d) $\underline{S}O_2$ and $\underline{S}O_3$

14. Phosphorus has the oxidation state of +3 in
(a) phosphorous acid
(b) orthophosphoric acid
(c) hypophosphorous acid
(d) metaphosphoric acid

15. In which of the compounds does 'manganese' exhibit highest oxidation number ?
(a) MnO_2 (b) Mn_3O_4
(c) K_2MnO_4 (d) $MnSO_4$

16. One of the following has both positive and negative oxidation states
(a) F (b) Cl
(c) He (d) Na

17. In which of the following compounds, the oxidation number of iodine is fractional ?
(a) IF_7 (b) I_3^-
(c) IF_5 (d) IF_3

18. In which of the following compounds, nitrogen has an oxidation state of –1 ?
(a) N_2O (b) NO_2^-
(c) NH_2OH (d) N_2H_4

19. Which of the following involves transfer of five electrons ?
(a) $MnO_4^- \rightarrow Mn^{2+}$ (b) $CrO_4^{2-} \rightarrow Cr^{3+}$
(c) $MnO_4^{2-} \rightarrow MnO_2$ (d) $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$

20. Oxidation number of nitrogen in $(NH_4)_2SO_4$ is
(a) –1/3 (b) –1
(c) +1 (d) –3

21. Oxidation number of carbon in CH_2Cl_2 is
(a) –4 (b) +4
(c) 0 (d) –2

22. Which of the following elements has least oxidation number ?
(a) $Ni(CN)_4$ (b) $Ni(CO)_4$
(c) Fe_2O_3 (d) SF_6

23. The oxidation number of cobalt in $K_3[Co(NO_2)_6]$ is
(a) 0 (b) +4
(c) +3 (d) +6

24. The brown ring complex is formulated as $[Fe(H_2O)_5NO]SO_4$. The oxidation number of iron is
(a) 1 (b) 2
(c) 3 (d) 0

25. In which of the following complexes, oxidation state of metal is zero ?
(a) $[Pt(NH_3)_2Cl_2]$ (b) $[Cr(CO)_6]$
(c) $[Cr(NH_3)_3Cl_3]$ (d) $[Cr(en)_2Cl_2]$

26. The oxidation state of chromium in potassium dichromate ($K_2Cr_2O_7$) is
(a) –5 (b) +6
(c) +2 (d) –2

27. The oxidation state of osmium (Os) in OsO_4 is
(a) +7 (b) +6
(c) +4 (d) +8

28. In H_2O_2, the oxidation state of oxygen is
(a) –2 (b) –1
(c) 0 (d) –4

29. A, B and C are three elements forming a part of compound in oxidation states of +2, +5 and –2 respectively. What could be the compound ?
(a) $A_2(BC)_2$ (b) $A_2(BC_4)_3$
(c) $A_3(BC_4)_2$ (d) ABC

30. Among the following, identify the species with an atom in +6 oxidation state
(a) MnO_4^- (b) $Cr(CN)_6^{3-}$
(c) NiF_6^{2-} (d) CrO_2Cl_2

31. On reduction of $KMnO_4$ by oxalic acid in acidic medium, the oxidation number of Mn changes. What is the magnitude of this change?
(a) From 7 to 2 (b) From 6 to 2
(c) From 5 to 2 (d) From 7 to 4

32. The oxidation number of iron in Fe_3O_4 is
(a) +2 (b) +3
(c) 8/3 (d) 2/3

33. The oxidation number of S in $H_2S_2O_8$ is
(a) +2 (b) +4
(c) +6 (d) +7

34. When $KMnO_4$ acts as an oxidising agent and ultimately forms MnO_4^{-2}, MnO_2, Mn_2O_3 and Mn^{+2}, then the number of electrons transferred in each case respectively is
(a) 4, 3, 1, 5 (b) 1, 5, 3, 7
(c) 1, 3, 4, 5 (d) 3, 5, 7, 1

35. The oxidation number of sulphur in $Na_2S_4O_6$ is
(a) 1.5 (b) 2.5
(c) 3 (d) 2

36. In which of the following reactions, there is no change in valency ?
(a) $4KClO_3 \rightarrow 3KClO_4 + KCl$
(b) $SO_2 + 2H_2S \rightarrow 2H_2O + 3S$
(c) $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$
(d) $2BaO + O_2 \rightarrow 2BaO_2$

37. What is the coefficient of oxalate ion in the following reaction ?

$$MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$$

(a) 4 (b) 2
(c) 3 (d) 5

38. The compound that can work both as an oxidising as well as a reducing agent is
(a) $KMnO_4$ (b) H_2SO_4
(c) BaO_2 (d) H_2O_2

39. When SO_2 is passed through the solution of potassium iodate, the oxidation state of iodine changes from
(a) + 5 to 0 (b) + 5 to – 1
(c) – 5 to 0 (d) – 7 to – 1

40. Which of the following behaves as both oxidising and reducing agents ?
(a) H_2SO_4 (b) SO_2
(c) H_2O (d) HNO_3

41. In the reaction

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S$$

(a) $FeCl_3$ acts as an oxidising agent
(b) Both H_2S are $FeCl_3$ are oxidised
(c) $FeCl_3$ is oxidised while H_2S is reduced
(d) H_2S acts as an oxidising agent.

42. Which of the following is not a reducing agent?
(a) SO_2 (b) H_2O_2
(c) CO_2 (d) NO_2

43. Number of moles of $K_2Cr_2O_7$ reduced by one mole of Sn^{2+} ions is
(a) 1/3 (b) 3
(c) 1/6 (d) 6

44. The reaction in which hydrogen peroxide acts as a reducing agent is
(a) $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$
(b) $2KI + H_2O_2 \rightarrow 2KOH + I_2$
(c) $2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O$
(d) $Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2$

45. HNO_3 acts as
(a) acid (b) oxidising agent
(c) reducing agent (d) Both (a) and (b)

46. When $KMnO_4$ reacts with acidified $FeSO_4$
(a) $FeSO_4$ is oxidised and $KMnO_4$ is reduced
(b) only $KMnO_4$ is oxidised
(c) only $FeSO_4$ is oxidised
(d) None of these

47. Formula weight divided by the change in oxidation number gives
(a) equivalent weight of an oxidant
(b) equivalent weight of the reductant
(c) the number of electrons gained in the reaction
(d) the equivalent weight of the oxidant or reductant

48. The equivalent weight of Mohr's salt, $FeSO_4(NH_4)_2SO_4.6H_2O$ is equal to
(a) its molecular weight
(b) its atomic weight
(c) half-its molecular weight
(d) one-third its molecular weight

49. In the reaction between SO_2 and O_3 the equivalent weight of ozone is
(a) the same as its molecular weight
(b) half of the molecular weight
(c) one-third of the molecular weight
(d) one-fourth of the molecular weight

50. Equivalent weight of iron in Fe_2O_3 would be
(a) 28 (b) 56
(c) 18.6 (d) 112

51. Atomic number of an element is 22. The highest O.S. exhibited by it in its compounds is
(a) 1 (b) 2
(c) 3 (d) 4

52. The equivalent weight of potassium permaganate in acid solution is
(a) 158 (b) 31.6
(c) 52.16 (d) 79

53. The equivalent weight of phosphoric acid (H_3PO_4) in the reaction:

$$NaOH + H_3PO_4 \rightarrow NaH_2PO_4 + H_2O$$

(a) 59 (b) 49
(c) 25 (d) 98

54. Equivalent mass of oxidising agent in the reaction, $SO_2 + 2H_2S \rightarrow 3S + 2H_2O$ is
(a) 32 (b) 64
(c) 16 (d) 8

55. In the chemical reaction,

$$K_2Cr_2O_7 + X\,H_2SO_4 + YSO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + Z\,H_2O$$

X, Y and Z are

(a) 1, 3, 1 (b) 4, 1, 4

(c) 3, 2, 3 (d) 2, 1, 2

56. Consider the following reaction

$$5H_2O_2 + XClO_2 + 2OH^- \rightarrow XCl^- + Y\,O_2 + 6H_2O$$

The reaction is balanced if

(a) $X = 5, Y = 2$ (b) $X = 2, Y = 5$

(c) $X = 4, Y = 10$ (d) $X = 5, Y = 5$

57. The set of numerical coefficients that balances the equation

$$K_2CrO_4 + HCl \rightarrow K_2Cr_2O_7 + KCl + H_2O$$

(a) 1, 1, 2, 2, 1 (b) 2, 2, 1, 1, 1

(c) 2, 1, 1, 2, 1 (d) 2, 2, 1, 2, 1

58. $(X)\,MnO_4^- + (Y)H_2O_2 \rightarrow$

$$2Mn^{+2} + 5H_2O + 9O_2 + (Z)e^-$$

In this reaction, value of (X), (Y) and (Z) are

(a) 2, 5, 6 (b) 5, 2, 9

(c) 3, 5, 5 (d) 2, 6, 6

Exercise-3 | PAST COMPETITION MCQs

1. The oxidation number of phosphorus in pyrophosphoric acid is **[CBSE-PMT 1999]**

(a) +3 (b) +1

(c) +4 (d) +5

2. The oxidation states of sulphur in the anions SO_3^{2-}, $S_2O_4^{2-}$ and $S_2O_6^{2-}$ follow the order **[CBSE-PMT 2003]**

(a) $S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$

(b) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$

(c) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$

(d) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$

3. Oxidation numbers of P in PO_4^{3-}, of S in SO_4^{2-} and that of Cr in $Cr_2O_7^{2-}$ are respectively **[CBSE-PMT 2009]**

(a) +3, +6 and +5 (b) +5, +3 and +6

(c) −3, +6 and +6 (d) +5, +6 and +6

4. When Cl_2 gas reacts with hot and concentrated sodium hydroxide solution, the oxidation number of chlorine changes from : **[CBSE-PMT 2012 S]**

(a) zero to +1 and zero to −5

(b) zero to −1 and zero to +5

(c) zero to −1 and zero to +3

(d) zero to +1 and zero to −3

5. Which of the following is a redox reaction? **[AIEEE 2002]**

(a) $NaCl + KNO_3 \rightarrow NaNO_3 + KCl$

(b) $CaC_2O_4 + 2HCl \rightarrow CaCl_2 + H_2C_2O_4$

(c) $Mg(OH)_2 + 2NH_4Cl \rightarrow MgCl_2 + 2NH_4OH$

(d) $Zn + 2AgCN \rightarrow 2Ag + Zn(CN)_2$

6. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is: **[AIEEE 2005]**

(a) +3 (b) +2

(c) +6 (d) +4

7. Which of the following chemical reactions depict the oxidising beahviour of H_2SO_4? **[AIEEE 2006]**

(a) $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

(b) $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

(c) $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$

(d) $Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$

8. What products are expected from the disproportionation reaction of hypochlorous acid? **[AIEEE 2006]**

(a) HCl and Cl_2O (b) HCl and $HClO_3$

(c) $HClO_3$ and Cl_2O (d) $HClO_2$ and $HClO_4$

9. Consider the following reaction :

$$xMNO_4^- + yC_2O_4^{2-} + zH^+ \rightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2}H_2O$$

The value's of x, y and z in the reaction are, respectively : **[JEE M 2013]**

(a) 5, 2 and 16

(b) 2, 5 and 8

(c) 2, 5 and 16

(d) 5, 2 and 8

10. The compound $YBa_2Cu_3O_7$ which shows superconductivity has copper in oxidation state .... Assume that the rare earth element Yttrium is in its usual +3 oxidation state

(a) 3/7 (b) 7/3 **[IIT 1994]**

(c) 3 (d) 7

11. For H_3PO_3 and H_3PO_4 the correct choice is **[IIT SCREENING 2003]**

(a) H_3PO_3 is dibasic and reducing

(b) H_3PO_3 is dibasic and non-reducing

(c) H_3PO_4 is tribasic and reducing

(d) H_3PO_3 is tribasic and non-reducing

Exercise-4 | Applied MCQs

1. The oxidation number of sulphur in S_8, S_2F_2, H_2S respectively, are

(a) 0, +1 and –2

(b +2, +1 and –2

(c) 0, +1 and +2

(d) –2, +1 and –2

2. When SO_2 is passed through acidified solution of potassium dichromate, then chromium sulphate is formed. The change in valency of chromium is

(a) +4 to +2 (b) +5 to +3

(c) +6 to +3 (d) +7 to +2

3. One mole of N_2H_4 loses 10 moles of electrons to form a new compound, y. Assuming that all nitrogen appear in the new compound, what is the oxidation state of nitrogen in y (There is no change in the oxidation state of hydrogen)

(a) –1 (b) –3

(c) +3 (d) +5

4. In the reaction : $C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2$

HNO_3 act as

(a) an oxidizing agent

(b) an acid

(c) an acid as well as oxidizing agent

(d) a reducing agent.

5. Which of the following reaction involves neither oxidation nor reduction

(a) $CrO_4^{2-} \rightarrow Cr_2O_7^{2-}$ (b) $Cr \rightarrow CrCl_3$

(c) $Na \rightarrow Na^+$ (d) $2S_2O_3^{2-} \rightarrow S_4O_6^{2-}$

6. A compound of Xe and F is found to have 53.5% of Xe. What is oxidation number of Xe in this compound ?

(a) –4 (b) 0

(c) +4 (d) +6

7. In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is

(a) (molecular weight)/2

(b) (molecular weight)/6

(c) (molecular weight)/3

(d) same as molecular weight

8. In the following reaction

$$4P + 3KOH + 3H_2O \longrightarrow 3KH_2PO_2 + PH_3$$

(a) only phosphorus is oxidised and reduced.

(b) only phosphorus is reduced.

(c) phosphorus is both oxidised and reduced.

(d) phosphorus is neither oxidised nor reduced.

9. The following acts as a reducing as well as oxidising agent

(a) O_3 (b) ClO_4^-

(c) F_2 (d) MnO_4^-

10. Oxidation state for nitrogen is incorrectly given for compound oxidation state

(a) $[Co(NH_3)_5Cl]Cl_2$ 0

(b) NH_2OH –1

(c) $(N_2H_5)_2SO_4$ –2

(d) Mg_3N_2 –3

11. The most powerful oxidizing agent from the following is

(a) H_3BO_3 (b) HPO_3

(c) H_3PO_4 (d) H_2SO_4

12. The species that undergoes disproportionation in an alkaline medium are

(a) Cl_2 (b) MnO_4^{2-}

(c) NO_2 (d) All of these

13. Which of the following reactions will not take place

(a) $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$

(b) $Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$

(c) $2KBr + I_2 \rightarrow 2KI + Br_2$

(d) $CuO + H_2 \rightarrow Cu + H_2O$

Hints & Solutions

EXERCISE 1

1. At anode, oxidation takes place whereas at cathode, reduction takes place.
2. Cu_2S oxidised whereas O_2 reduced.
3. $Cr = +6,\ S = +2$
4. Fe has lower reduction potential and Cu has higher reduction potential than H_2.
5. HI, I_2, ICl is order of increasing oxidation number.
6. SO_4^{2-} ion as it does not participate in the reaction.
8. In MnO_4^-, Mn is in the highest oxidation state i.e. +7.
9. (i) $2CrO_3^- + H_2O_2 \longrightarrow 2CrO_4^{-2} + H_2O$
   (ii) $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$
   (iii) $5C_2O_4^{-2} + 2MnO_4^- + 16H^+ \longrightarrow 10CO_2 + 2Mn^{+2} + 8H_2O$
10. (i) No, because $E^o_{Zn^{2+}/Zn} < E^o_{Cu^{2+}/Cu}$
    (ii) No,
    (iii) Yes, as $E^o_{Cu^{2+}/Cu} < E^o_{Ag^+/Ag}$
    (iv) Yes,
12. $E < C < A < H < D < B$.

16. **(d)** **17.** **(a)** **18.** **(a)** **19.** **(b)** **20.** **(b)**
21. **(a)** **22.** **(d)** **23.** **(c)** **24.** **(a)** **25.** **(a)**

EXERCISE 2

1. **(b)** O.N. of I^- is –1 and in I_2 O.N. is zero (loss of electrons). Hence I^- oxidised.

2. **(b)** SO_2 oxidises H_2S to S, since the O.N. of S change from –2 to 0

3. **(b)** $MnO_4^- + 8H^+ + 5\bar{e} \rightarrow Mn^{2+} + 4H_2O$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$. As the gain of electrons per mole is more in case of $Cr_2O_7^{2-}$ then MnO_4 hence it is stronger oxidising than MnO_4^-

4. **(b)** ($Ni \rightarrow Ni^{2+}$) Ni loses electrons hence act as reducing agent.

5. **(d)** $3Br_2 + 6CO_3^{2-} + 3H_2O \rightarrow 5Br^- + BrO_3^- + 6HCO_3^-$
O.N. of Br_2 changes from 0 to –1and +5 hence it is reduced as well as oxidised.

6. **(c)** $N_2 + O_2 \rightarrow 2NO$
O.N. of N changes from 0 to +2 (oxidation) and O.N. of O changes from 0 to –2 (reduction).

7. **(a)** The balanced equation is

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

8. **(a)** 10 moles of CO_2 are produced.

9. **(d)** In redox reaction oxidation and reduction take place side by side. $Cu_2S + 2FeO \rightarrow 2Cu + 2Fe + SO_2$.
O.N. of Cu changes from +1 to 0 (reduction) and O.N. of S changes from –2 to +4 (oxidation).

10. **(d)** $2K\overset{+7}{Mn}O_4 + 16HCl \rightarrow 2KCl + 2\overset{+2}{Mn}Cl_2 + 8H_2O + 5Cl_2$
Mn (O.N. changes from +7 to +2 gain of electrons) reduced and Cl_2 formed.

11. **(d)** Since there is loss of electrons, hence it is oxidation reaction.

12. **(c)** In Cannizaro's reaction
$(2HCHO + KOH \rightarrow CH_3OH + HCOOK)$
formaldehyde is reduced as well as oxidised.

13. **(d)** O.N. of N in NO_2 and N_2O_4 is +4 $\therefore$ difference is zero.
O.N. of P in P_2O_5 and P_4O_{10} is +5 $\therefore$ difference is zero
O.N. of N in N_2O is +1 and in NO is +2. The difference is 1
O.N. of S in SO_2 is +4 and in SO_3 is +6. The difference is +2.

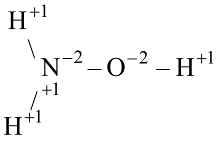
14. **(a)** H_3PO_3 phosphorous acid O.N. of P is +3. orthophosphoric acid $H_3\overset{+5}{P}O_4$, Hypophosphorous acid $H_3\overset{+1}{P}O_2$
Metaphosphoric acid $H\overset{+5}{P}O_3$

15. **(c)** O.N. of Mn in K_2MnO_4 is +6 (find O.N. of Mn in others)

16. **(b)** Cl has O. S. as –1, +1 +3 +5 and +7

17. **(b)** O.N. of iodine in I_3^- is –1/3

18. **(c)**

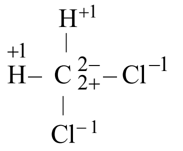


O.N. of N is NH_2OH is –1

19. **(a)** O.N. of Mn in MnO_4^- is +7 and in Mn^{2+} it is +2. The difference is of 5 electrons.

20. **(d)** $(NH_4)_2\ SO_4$ is split into ions NH_4^+. Let O.N. of N be x then, $1 \times (x) + 4x\,(+1) = 1$ $\therefore x = -3$

21. **(c)** Find O.N. by chemical bond method



O.N. of C is zero

22. (b) In metal carbonyls metal always has O.N. zero.

23. (c) $K_3[Co(NO_2)_6]$ Let O.N. of Co be x then
$3x(+1) + 1 \times (x) + 6x(-1) = 0 \quad \therefore x = +3$

24. (a) $[Fe(H_2O)_5NO]\,SO_4$ Let O.N. of Fe be x then,
$1 \times (x) + 5 \times (0) + 1 \times (+1) + 1 \times (-2) = 0 \qquad \therefore x = +1$

25. (b) $Cr(CO)_6$ is metal carbonyl, hence O.N. of chromium is zero.

26. (b) $K_2Cr_2O_7$ O.N. of Cr is +6.

27. (d) OsO_4 Let O.N. of Os be x then $1 \times (x) + 4(-2) = 0$
$\therefore x = 8$

28. (b) $H-O-O-H$. O.N. of oxygen is –1.

29. (c) Put values of O.S. of A, B and C in all the given compounds. The compound giving sum of O.S. as zero will be the real compound. For $A_3(BC_4)_2$ $= 3 \times (+2) + 2 \times (+5) + 8 \times (-2) = 0$

30. (d) MnO_4^- (O.S. of Mn +7); $Cr(CN)_6^{3-}$ (O.S. of Cr +3), NiF_6^{2-} (O.S. of Ni +4) and CrO_2Cl_2 (O.S. of Cr +6)

31. (a) In acid medium MnO_4^- changes to Mn^{2+}, hence O.N. changes from +7 to +2.

32. (c) In fact Fe_3O_4 is a mixed oxide of FeO and Fe_2O_3. O.N. of Fe in FeO is +2 and O.N. of Fe in Fe_2O_3 is +3. The average O.N. of Fe will be $3 \times (x) + 4 \times (-2) = 0$
$\therefore x = 8/3$

33. (c) O.N. of S in $H_2S_2O_8$ is + 6. See text and find O.N. by chemical bond method.

34. (c) In $KMnO_4$ the O.N. of Mn is +7, in MnO_4^{-2} +6, in MnO_2 +4 in Mn_2O_3 +3 and in Mn^{2+}, it is +2. The difference being 1, 3, 4 and 5 respectively.

35. (b) $Na_2S_4O_6$ Let O.N. of S be x then
$2 \times (+1) + 4 \times (x) + 6 \times (-2) = 0$
$\therefore x = 2.5$. By chemical bonding method the two S, atoms have O.N. + 5 and two S atoms have O.N. zero.

36. (c) In $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$ all atoms are present in the same O.S. in reactants and products.

37. (d) The balanced equation is

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Hence coefficient of oxalate ion is 5

38. (d) In H_2O_2 the O.N. of O is –1 which can be increased to 0 or decresed to –2 hence H_2O_2 can work as reducting and oxidising agent.

39. (b) O.S. of I, $3\underset{+5}{KIO_3} + 3SO_2 \rightarrow 3\underset{-1}{KI} + 3SO_3$

40. (b) In SO_2 the O.N. of S can increase and decrease. Hence can behave as reducing and oxidising agent. Oxidation state of S varies from –2 to 6.

41. (a) In $2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S$
O.N. of S changes from –2 to 0 (hence oxidised) O.N. of Fe changes from +3 to +2 hence reduced.

42. (c) In CO_2, O.N. of C is +4 which is maximum. So it can act as oxidising agent and not as reducing agent.

43. (a) $\left(Cr_2O_7^{2-} + 14H^+ + 6\bar{e} \longrightarrow 2Cr^{3+} + 7H_2O\right)\frac{1}{3}$

$Sn^{2+} - 2e^- \longrightarrow Sn^{4+}$

Hence $\frac{1}{3}Cr_2O_7^{2-} + \frac{14}{3}H^+ + Sn^{2+} \longrightarrow$

$$\frac{2}{3}Cr^{3+} + \frac{7}{3}H_2O + Sn^{4+}$$

44. (d) In Ag_2O (O.N. of Ag +1) in Ag the O.N. is 0. There is gain of electrons, hence H_2O_2 is reducing.

45. (d) In HNO_3 O.N. of N is +5 which is maximum value hence it can act as oxidising agent and as an acid only.

46. (a) $2K\overset{+7}{Mn}O_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 3H_2O + 5O$
$2\overset{+2}{Fe}SO_4 + H_2SO_4 + O \rightarrow \overset{+3}{Fe_2}(SO_4)_3 + H_2O$
O.N. of Mn changes from +7 to +2 (Reduction)
O.N. of Fe changes from +2 to +3 (Oxidation)

47. (d) $\text{Eq. wt} = \dfrac{\text{Molecular weight}}{\text{Change in O.N.}}$

48. (a) $FeSO_4$ is oxidised to $Fe_2(SO_4)_3$, change in O.N. of Fe is by 1. Hence equivalent weight of Mohr's salt is M/1 = M.

49. (b) $3SO_2 + O_3 \rightarrow 3SO_3$
O.N. of S changes from +4 to +6. Two electron change
$\therefore$ Eq. Wt = M/2.

50. (c) $Fe_2O_3 \rightarrow 2Fe$
The change in O.N. of Fe is from +3 to 0. Hence equivalent weight of iron = $\frac{1}{3} \times 56 = 18.6$

51. (d) The element is Ti (At. no. 22). Electronic configuration is $1s^2, 2s^2p^6, 3s^2p^6d^2, 4s^2$. the energy level of 3d and 4s is very close. It can have Ti^{4+} O.S.

52. (b) (158/5 = 31.6),

53. (d) $NaOH + H_3PO_4 \rightarrow NaH_2PO_4 + H_2O$
Here 1 gev. of NaOH is reacting with 1 gev of H_3PO_4 hence Eq. wt of H_3PO_4 is 98.

54. (c) $SO_2 + 2H_2S \rightarrow 3S + 2H_2O$. SO_2 is oxidising and change in O.N. of S is from +4 to zero.

$\therefore$ Eq. Wt. of $SO_2 = \frac{64}{4} = 16$

55. (a) $K_2Cr_2O_7 + \underset{X=1}{H_2SO_4} + \underset{Y=3}{3SO_2} \rightarrow$

$$K_2SO_4 + Cr_2(SO_4)_3 + \underset{Z=1}{H_2O}$$

56. (b) $5H_2O_2 + 2ClO_2 + 2OH^- \rightarrow \underset{X=2}{2Cl^-} + \underset{Y=5}{5O_2} + 6H_2O$

57. (d) $2K_2CrO_4 + 2HCl \rightarrow K_2Cr_2O_7 + 2KCl + H_2O$
Coefficients are 2, 2, 1, 2, 1

58. (a) $2MnO_4^- + 5H_2O_2 \rightarrow 2Mn^{2+} + 5H_2O + 9O_2 + 6e^-$
X = 2, Y = 5 and Z = 6

EXERCISE 3

1. **(d)** Pyrophosphoric acid $H_4P_2O_7$
Let oxidation state of phosphorus is x
$(4 \times 1 + (-2) \times 7 + 2x) = 0$
$\therefore 2x = 10$ or $x = +5$

2. **(c)** $SO_3^{2-} \rightarrow$ S is in + 4 oxidation state

$S_2O_4^{2-} \rightarrow$ S is in + 3 oxidation state

$S_2O_6^{2-} \rightarrow$ S is in + 5 oxidation state

3. **(d)** $PO_4^{3-} = x + 4(-2) = -3; x - 8 = -3; x = +5$

$SO_4^{2-} = x + 4(-2) = -2; x - 8 = -2; x = +6$

$Cr_2O_7^{2-} = 2x + 7(-2) = -2; 2x - 14 = -2;$
$2x = 12;\ x = +6$

4. **(b)** On reaction with hot and concentrated alkali a mixture of chloride and chlorate is formed

$$3Cl_2 + 3\,NaOH(excess) \xrightarrow{\text{Hot}} 5Na\overset{-1}{Cl} + Na\overset{+5}{Cl}O_3 + 3H_2O$$

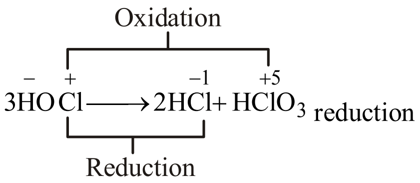
5. **(d)** The oxidation states show a change only in reaction (d).

$$\overset{0}{Zn} + 2\overset{+1}{A}gCN \xrightarrow[+2e^-]{-2e^-} 2\overset{0}{Ag} + \overset{+2}{Zn}(CN)_2$$

6. **(a)** $Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$
+ 3 oxidation state of Cr.

7. **(c)** $2HI^{-1} + H_2\overset{+6}{S}O_4 \longrightarrow \overset{0}{I_2} + \overset{+4}{S}O_2 + 2H_2O$
In this reaction O.N. of S is decreasing from + 6 to +4 hence undergoing reduction and O.N. of I is increases from –1 to 0 hence undergoing oxidation therefore H_2SO_4 is acting as oxidising agent.

8. **(b)** During disproportionation same compound undergo simultaneously oxidation and reduction.



$$3HO\overset{-\ +}{Cl} \longrightarrow 2H\overset{-1}{Cl} + H\overset{+5}{Cl}O_3$$

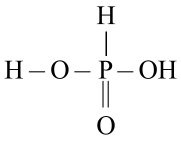
9. **(c)** On balancing the given equations, we get

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{++} + 10CO_2 + 8H_2O$$

So, $x = 2, y = 5$ & $z = 16$

10. **(b)** $YBa_2Cu_3O_7$
$3 + 2 \times 2 + 3x - (2 \times 7) = 0$
$3 + 4 + 3x - 14 = 0$
$3x = 7$
$x = \frac{7}{3}$.

11. **(a)**



$$H-O-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}-OH$$

, hence it is dibasic. It acts as reducing agent also.

EXERCISE 4

1. **(a)** ON of S in $S_8 = 0$
ON of S in $S_2F_2 = +1$
ON of S in $H_2S = -2$

2. **(c)** $K_2Cr_2O_7 + 3SO_2 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3SO_3 + 4H_2O$
O.N. of chromium changes from +6 to +3

3. **(c)** $\overset{-4}{N_2}\overset{+4}{H_4} \xrightarrow[N]{\text{loss of } 10\bar{e}} \overset{+6}{N_2}(y);$
O.N. of N changes from -2 to +3

4. **(a)** O.N. of C changes form 0 to + 4 by oxidation. Hence HNO_3 is oxidising agent.

5. **(a)** $CrO_4^{2-} \rightarrow Cr_2O_7^{2-}$ O.N of Cr does not change. It remains +6 on both sides. Hence there is no oxidation or reduction.

6. **(d)** $Xe = 53.5\,\% \therefore F = 46.5\%$
Relative number of atoms Xe

$$= \frac{53.5}{131.2} = 0.4 \text{ and } F = \frac{46.5}{19} = 2.4$$

Simple ratio Xe = 1 and F = 6 ; Molecular formula is XeF_6
O.N. of Xe is +6

7. **(b)** In iodometry, $K_2Cr_2O_7$ liberates I_2 from iodides (NaI or KI). Which is titrated with $Na_2S_2O_3$ solution.

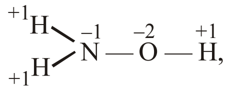
$K_2Cr_2O_7 + I^- + H^+ \longrightarrow Cr^{3+} + I_2$
Here, one mole of $K_2Cr_2O_7$ accepts 6 mole of electrons.

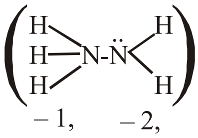
$$\therefore \text{Equivalent weight} = \frac{\text{molecular weight}}{6}$$

8. **(c)** $4P + 3KOH + 3H_2O \rightarrow KH_2PO_2 + PH_3$
O.N of P = 0, In KH_2PO_2 it is + 1, In PH_3 it is –3. Hence P is oxidised and reduced

9. **(a)** Ozone is reducing as well as oxidising is nature

10. **(a)** $[Co(\overset{-3}{N}H_3)_5Cl.]Cl_2,$





$, Mg_3\overset{-3}{N_2}$

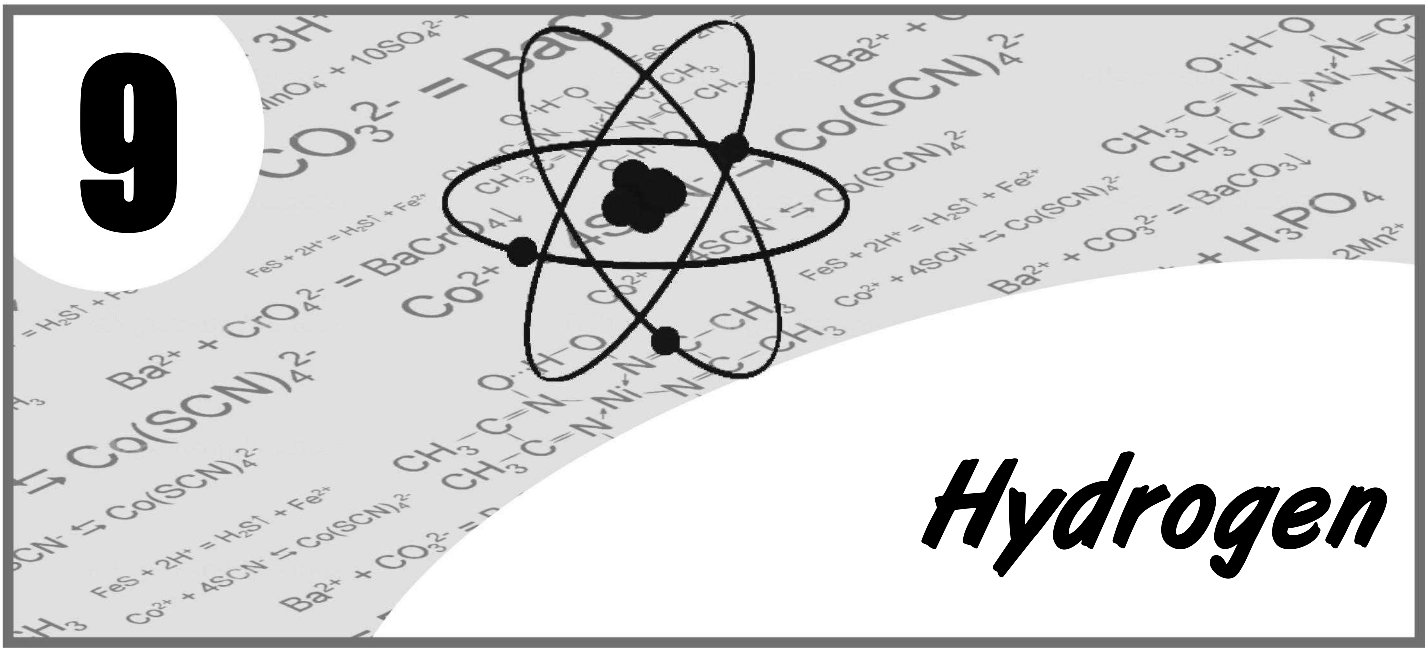
11. **(d)** In H_2SO_4, sulphur is in highest oxidation state (+6), Hence H_2SO_4 will be strongest by oxidising agent.

12. **(d)** $\overset{0}{Cl_2} + 2NaOH \rightarrow Na\overset{-1}{Cl} + Na\overset{+1}{Cl}O + H_2O$

$\overset{+6}{3MnO_4^{--}} + 2H_2O \rightarrow 2\overset{+7}{MnO_4^-} + \overset{+4}{MnO_2} + 4OH^-$

$2\overset{+4}{NO_2} + H_2O \rightarrow H\overset{+5}{NO_3} + H\overset{+3}{NO_2}$
All undergo disproportionation

13. **(c)** I_2 is less electronegative than Br_2



9

Hydrogen

GENERAL INTRODUCTION :

Symbol of hydrogen is H. Electronic Configuration $1s^1$. Hydrogen is the lightest and most abundant element in the universe. It was first prepared by **Sir Henry Cavendish** by the action of sulphuric acid on Zinc and named by **Antoine Lavoisier** since it produced water on burning.

(Greek : hydra= water, gennas = maker or producing)

PREPARATION OF DIHYDROGEN :

i) ***From cold water :*** By the action of Na, K, Ca etc.

$2Na + 2H_2O \rightarrow 2NaOH + H_2$ (highly exothermic and H_2 cathces fire)

Al-Hg and Zn-Cu couple decompose water to give nascent hydrogen

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + 2H$$

Hence Couples constitute better reducing agents

ii) ***From hot water :*** By the action of Mg, Zn, Al etc.

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$$

iii) ***From steam :*** By the action of Fe, Sn etc.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

iv) ***From water :*** By the action of metallic hydrides of alkali and alkaline earth metals.

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + H_2$$

v) ***From acids :*** By the action of dilute acids on Zn, Mg, Fe, etc. placed above hydrogen in electrochemical series.

$$Sn + 2HCl \rightarrow SnCl_2 + H_2$$

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

vi) ***From alkalies :*** By the action Zn, Al, Sn etc.

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$$

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

MANUFACTURE OF HYDROGEN :

i) ***From water gas (Bosch process) :*** By passing water gas mixed with steam over heated catalyst Fe_3O_4 and Cr_2O_3 at 450ºC.

$$H_2O(\text{Steam}) \xrightarrow[\text{Coke}]{\text{Red Hot}} \underset{\text{water gas}}{(CO + H_2)}$$

$$(CO + H_2) + H_2O \xrightarrow[450°C]{Fe_2O_3,\ Cr_2O_3} CO_2 + 2H_2$$

The CO_2 is removed by dissolving in water under high pressure.

ii) ***By Lane's process :*** The superheated steam is passed over heated iron at 600 - 800ºC

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2\uparrow$$

Iron is regenerated by passing water gas. (H_2 + CO)

$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$$

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$$

In actual practice steam is passed over hot iron for 10 - 15 minutes and then water gas is blown over heated oxide for 25 - 30 minutes.

iii) ***By electrolysis of water :*** By the electrolysis of acidified or alkaline water.

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode $2H^+ + 2e^- \rightarrow H_2$

At anode $4OH^- - 4e^- \rightarrow 4OH \rightarrow 2H_2O + O_2$

iv) ***As by product :*** When NaOH is manufactured by electrolysis of NaCl in **Nelson** or **Castner Kellner** cell hydrogen is obtained as by product.

$$2NaCl \rightarrow 2Na^+ + Cl^-$$

$$2Cl^- - 2e^- \rightarrow Cl_2 \text{ At anode}$$

$$\left.\begin{array}{l} 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \\ 2Na^+ + 2OH^- \rightarrow 2NaOH \end{array}\right\} \text{At Cathode}$$

v) ***From hydrocarbons :*** By cracking of hydrocarbons

$$C_6H_{12} \xrightarrow[10-50\text{ Atm.}]{Pt/Al_2O_3} C_6H_6 + 3H_2$$

PURE HYDROGEN METHOD OF PREPARATION :

i) ***By Uyeno's method :*** By the action of Caustic Soda on aluminium.

$$2NaOH + 2Al + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

ii) ***By the action of NaH on water***

$$NaH + H_2O \rightarrow NaOH + H_2$$

iii) ***By treating pure Mg or Al*** with chemically pure H_2SO_4 (dil) or HCl

$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$$

PHYSICAL PROPERTIES :

Hydrogen is tasteless, odourless, colourless gas. It is non poisonous but presence of AsH_3 makes it poisonous. Its critical temperature is –234.5°C which makes its liquefaction difficult. It is slightly soluble in water.

ISOTOPES OF HYDROGEN :

Hydrogen has three isotopes

Name	$_1H^1$	$_1H^2$ or D	$_1H^3$ or T
	Protium	Deuterium	Tritium
Abundance	99.985%	0.016%	Traces (10^{-15}%)

Deuterium is known as heavy hydrogen. Tritium is formed in upper atmosphere and is β-radioactive.

$$_2He^3 + {}_{-1}e^0 \rightarrow {}^3_1H \ (t_{1/2} = 12.34 \text{ year})$$

$$_7N^{14} \rightarrow {}_6C^{12} + {}_1H^3 \text{ (formation)}$$

CHEMICAL PROPERTIES :

Its chemical properties are

i) ***Reaction with non metals :***

$$H_2 + X_2 \rightarrow 2HX (X = F, Cl, Br, I)$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$3H_2 + N_2 \rightarrow 2NH_3$$

ii) ***Reaction with metals :*** $2Na + H_2 \rightarrow NaH$

$$Ca + H_2 \rightarrow CaH_2 \text{ (Hydrolith)}$$

Metals like Fe, Ni and Pd form interstitial or metallic hydrides.

iii) ***Reducing property :***

$$CuO + H_2 \rightarrow Cu + H_2O$$

$$Ag_2O + H_2 \rightarrow 2Ag + H_2O$$

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$$

iv) ***Hydrogenation :*** $C_nH_{2n} + H_2 \xrightarrow{Ni} C_nH_{2n+2}$

APPLICATIONS OF HYDROGEN :

i) ***Manufacture of methyl alcohol :***

$$CO + 2H_2 \xrightarrow[300°C,\ 200\text{ Atm}]{ZnO, Cr_2O_3} CH_3OH$$

ii) ***Manufacture of ammonia :***

$$N_2 + 3H_2 \xrightarrow[490°C, 210\text{ Atm}]{Fe/Mo} 2NH_3$$

iii) ***Synthetic petrol :*** Fisher-Tropsch process

a) $n(CO + H_2) + nH_2 \rightarrow \underset{\text{olefin}}{C_nH_{2n}} + nH_2O$

b) $nCO + (2n+1)H_2 \rightarrow \underset{\text{paraffin}}{C_nH_{2n+2}} + nH_2O$

iv) ***Manufacture of vegetable ghee :*** By hydrogenation of oils in presence of Ni.

v) ***To produce low-temperature :*** It is used as Cryogenic fluid.

vi) ***Oxy-hydrogen flame :*** It produces temperature of 2850ºC and oxy-atomic hydrogen flame produces a temperature of 4000ºC.

vii) ***Mixed with Helium*** it is used for filling balloons.

FORMS OF HYDROGEN :

i) ***Atomic Hydrogen :***

$$H_2 \xrightarrow{\text{Electric arc}} 2H \qquad \Delta H = 105.4 \text{ kcal mol}^{-1}$$

It is very reactive and its half life period is 0.33 seconds.

ii) ***Occluded Hydrogen :*** Hydrogen adsorbed by certain metals eg. Pt, Pd, Fe, Ni etc is known as occluded ***hydrogen***. One volume of finely divided metals adsorb the following volumes of hydrogen.

Palladium black 870, Platinum 49.5; Gold 46.3, Iron 15.7, Copper 4.5, Aluminium 2.7.

iii) ***Nascent hydrogen :*** Freshly prepared hydrogen is known as ***nascent hydrogen*** and is more reactive than ordinary hydrogen. It causes the reduction of certain compounds which is not possible with ordinary hydrogen.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H$$

$$FeCl_3 + H \rightarrow FeCl_2 + HCl$$

$$KClO_3 + 6H \rightarrow KCl + 3H_2O$$

iv) ***Ortho and Para hydrogen :*** The nucleus of the hydrogen atom also spins like a top. When in hydrogen molecule, the nuclear spins are in the same direction it is known as ortho hydrogen and when the nuclear spins are in the opposite direction it is known as para hydrogen. The two electrons in a hydrogen molecule always spin in opposite direction. At room temperature hydrogen consists of 75% ortho and 25% para. At low temperature more para is present.

Ortho-hydrogen (Parallel nuclear spin) Para-hydrogen (Anti parallel nuclear spin)

$$\text{Nuclear spin} = \frac{1}{2}+\frac{1}{2}=1 \qquad \text{(For ortho-hydrogen)}$$

$$\text{Nuclear spin} = \frac{1}{2}+\left(-\frac{1}{2}\right)=0 \qquad \text{(For para-hydrogen)}$$

v) ***Transportation of hydrogen :*** It is transported in the form of **Hydrolith** (CaH_2) or **ammonia** (NH_3). Ammonia is cracked by passing over heated catalysts yielding a mixture of hydrogen (75%) and N_2 (25%).

$$2NH_3 \rightarrow 3H_2 + N_2$$

HYDRIDES :

Binary compounds of hydrogen and other elements are called hydrides. Hydrides are classified into the following four classes.

1) Saline or ionic hydrides.
2) Molecular or covalent hydrides.
3) Metallic or intertitial hydrides.
4) Polymeric hydrides.

1. ***Saline or ionic hydrides :*** These are formed by elements of group 1, 2 (Except Be and Mg) and lanthanides by heating the metal in hydrogen.

These are white colourless solids (crystalline) having high mpt. and bpt. easily decomposed by water, alcohol, CO_2 or SO_2.

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$$

$$CaH_2 + 2C_2H_5OH \rightarrow Ca(OC_2H_5)_2 + 2H_2$$

$$CaH_2 + 2CO_2 \rightarrow (HCOO)_2Ca$$

They are strong reducing agents. Alkali metal hydrides are used for making $LiAlH_4$, $NaBH_4$ etc and for removing last traces of water from organic compound.

2) ***Molecular or covalent hydrides :*** These are formed by 4th, 5th, 6th, 7th group elements and boron by sharing electrons with hydrogen atoms. eg.: NH_3, HCl, B_2H_6, AsH_3 . These are non electrolytes and are usually gases or liquids.

3) ***Metallic or interstitial hydrides :*** The transition elements and rare earth metals combine with hydrogen to give interstitial hydrides. They exhibit metallic properties and are powerful reducing agents. They are non stoichiometric compounds and their composition varies with temperature and pressure. eg. $LaH_{2.76}$, $TiH_{1.73}$

4) ***Polymeric hydrides :*** These are solids containing molecules, linked together in two or three dimensions by hydrogen bridge bonds. e.g.: $(BeH_2)_n$, $(MgH_2)_n$ and $(AlH_3)_n$

HYDROGEN PEROXIDE :

Discovery : French chemist Thenard 1818.

Occurrence : Traces in air, rain and plants.

PREPARATION :

i) ***Lab method :*** From true peroxide by the action of ice cold dil. H_2SO_4.

$$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$$

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$$

(HNO_3 is not used since it will oxidise H_2O_2).

ii) ***Merck process :*** By passing CO_2 through a suspension of BaO_2 in ice cold water.

$$BaO_2 + H_2O + CO_2 \rightarrow BaCO_3 + H_2O_2$$

Manufacture :

1) ***By electrolysis of 50% ice cold H_2SO_4***

$$2H_2SO_4 \rightleftharpoons H_2 + \underset{\substack{\text{Persulphuric acid}\\ \text{(Marshall's acid)}}}{H_2S_2O_8}$$

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_4 + \underset{\substack{\text{Permonosulphuric acid}\\ \text{(Caro's Acid)}}}{H_2SO_5}$$

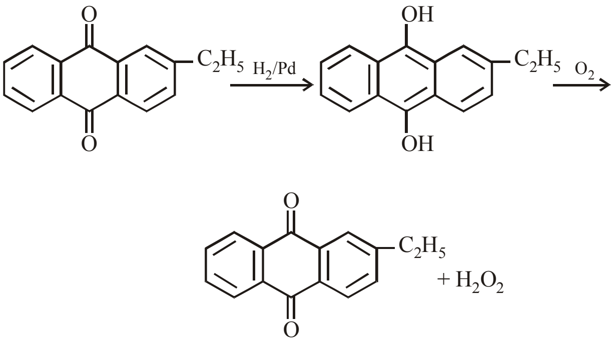
$$H_2SO_5 + H_2O \rightarrow H_2SO_4 + H_2O_2$$

<u>Mechanism</u> : $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

At anode : $2HSO_4^- \rightarrow H_2S_2O_8 + 2e^-$

At cathode : $2H^+ + 2e^- \rightarrow H_2$

2) ***Auto oxidation :*** Most recent method used in America. In this method the anthraquinone is reduced to anthraquinol by dissolving in an organic solvent and passing hydrogen in presence of Pd. On frothing, the anthraquinol derivative with air, 20% solution of H_2O_2 is obtained and anthraquinone is regenerated.



3) ***By electrolysis of ammonium sulphate solution and sulphuric acid.*** When aqueous solution of ammonium sulphate and sulphuric acid in equimolar proportion is electrolysed at low temperature ammonium persulphate is formed. The latter on distillation with sulphuric acid gives 30% solution of hydrogen peroxide.

$$(NH_4)_2SO_4 + H_2SO_4 \rightarrow 2NH_4.HSO_4$$

$$NH_4HSO_4 \rightleftharpoons NH_4SO_4^- + H^+$$

At anode :

$$2\ NH_4SO_4^- \rightarrow (NH_4)_2S_2O_8 + 2e^-$$

At cathode :

$$2\ H^+ + 2e^- \rightarrow H_2(g)$$

$$(NH_4)_2S_2O_8 + 2H_2O \rightarrow 2\ NH_4HSO_4 + H_2O_2$$

CONCENTRATION OF HYDROGEN PEROXIDE :

It is very carefully concentrated since it decomposes on heating or on standing.

$2H_2O_2 \rightarrow 2H_2O + O_2$ (auto-oxidation)

Decomposition is catalysed by Cu, Ag, Pt, Co, Fe, MnO_2 etc.

The methods employed for concentration are

i) ***Evaporation :*** By careful evaporation of solution on a water bath (50% H_2O_2 is obtained).

ii) ***Dehydration in vacuum desicator :*** The 50% H_2O_2 is dehydrated in a vacuum desicator in presence of conc. H_2SO_4 when 90% H_2O_2 is obtained.

iii) ***Vacuum distillation :*** The 90% H_2O_2 obtained in step (ii) is distilled under reduced pressure to get 100% H_2O_2

iv) ***Cooling :*** The traces of water left are removed by freezing in a freezing mixture when crystals of hydrogen peroxide separate out.

STRENGTH OF HYDROGEN PEROXIDE :

The strength of hydrogen peroxide is indicated in terms of the volume of oxygen at NTP that 1 volume of H_2O_2 gives on heating. For example "20 volume H_2O_2 means 1 volume of H_2O_2 at NTP will give 20 volume of oxygen. The normality and percentage strength of H_2O_2 can be calculated as follows

$2H_2O_2 \rightarrow 2H_2O + O_2$

$2 \times 34 = 68$ g $\quad$ 1 mole O_2 = 22.4 litres of O_2 at NTP

22.4 litres of O_2 at NTP are evolved from 68g of H_2O_2

x litres of O_2 at NTP would be evolved from $\frac{68}{22.4} \times x$ g of H_2O_2

where x is volume strength of H_2O_2

$\therefore$ Hence strength of x volume of $H_2O_2 = \frac{68 \times x}{22.4}$ g / litre

Again **Strength (g/ℓ) = Equivalent weight × Normality**

$$\therefore \frac{68 \times x}{22.4} = 17 \times N$$

where 17 is the equivalent weight of H_2O_2

STORAGE OF HYDROGEN PEROXIDE :

It is stored in presence of traces of alcohol, acetanilide or sodium pyrophosphate which slow down the rate of decomposition of hydrogen peroxide.

CHEMICAL PROPERTIES :

i) ***Acidic nature :*** It is weakly acidic in nature and pure hydrogen peroxide turns blue litmus into red. ($K_a = 1.57 \times 10^{-12}$ at 293 K). It ionises in two steps

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$

$$HO_2^- \rightleftharpoons H^+ + O_2^{2-}$$

Hence it forms two series of salts eg. $NaHO_2$ sodium hydroperoxide and Na_2O_2 (Sodium peroxide)

ii) ***Oxidising agent :*** It is strong oxidising agent in acidic as well as in basic medium.

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E^o = 1.77\text{ V}$$

$$H_2O_2 + OH^- + 2e^- \rightarrow 3OH^- \qquad E^o = 0.88\text{ V}$$

or $\quad H_2O_2 \rightarrow H_2O + O$

$$PbS + 4O \rightarrow PbSO_4$$

$$2KI + H_2O + O \rightarrow 2KOH + I_2$$

$$2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O$$

$$2K_4[Fe(CN)_6] + H_2O + O \rightarrow 2K_3[Fe(CN)_6] + 2KOH$$

$$\underset{\text{Chromic acid}}{H_2Cr_2O_7} + 4O \rightarrow \underset{\text{Blue peroxide of chromium}}{2CrO_5} + H_2O$$

$$C_6H_6 + O \rightarrow C_6H_5OH$$

In basic medium

$$2Cr^{3+} + 3H_2O_2 + 10OH^- \rightarrow 2CrO_4^{2-} + 8H_2O$$

$$Mn^{2+} + H_2O_2 + 2OH^- \rightarrow MnO_2 + 2H_2O$$

iii) ***Reducing agent :***

a) In acidic medium

$$\underset{\text{Pink}}{2MnO_4^-} + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

$$Cr_2O_7^{2-} + 8H^+ + 3H_2O_2 \rightarrow 2Cr^{3+} + 7H_2O + 3O_2$$

b) In basic medium

$$2K_3[Fe(CN)_6] + 2KOH + H_2O_2 \rightarrow 2K_4[Fe(CN)_6] + 2H_2O + O_2$$

iv) ***Bleaching properties :*** Its bleaching action is due to oxidation reaction.

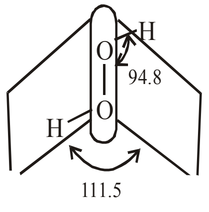
$H_2O_2 \rightarrow H_2O + O$

dye + O → dye is oxidised and bleached

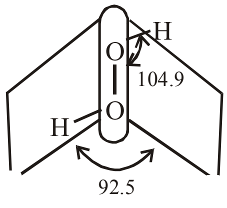
STRUCTURE :

It is represented as follows

In liquid and gas form



In solid form



TEST :

i) It liberates I_2 from acidified KI

$$2KI + H_2O_2 \rightarrow 2KOH + I_2$$

ii) **Perchromic acid :**

$$H_2Cr_2O_7 + 4H_2O_2 \rightarrow \underset{\substack{\text{Blue colour}\\ \text{(chromium peroxide)}}}{2CrO_5} + 5H_2O$$

(acidified H_2O_2 + amyl alcohol + $K_2Cr_2O_7$) → blue colour

iii) With titanic sulphate it gives orange red pertitanic acid

$$Ti(SO_4)_2 + H_2O_2 + 2H_2O \rightarrow 2H_2SO_4 + H_2TiO_4$$

iv) Black lead sulphide turned white

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

USES :

It is used as a bleaching agent, disinfectant, source of power (90% H_2O_2 as fuel in submarines, rockets and helicopters), in restoration of old paintings in which lead oxide is used as white paint.

WATER :

Water is one of the most abundant substances in nature. The 4/5th of the earth surface is covered with water.

Sources of water : The sources of water are

i) ***Surface water :***
- a) Flowing water eg.: streams and rivers
- b) Still water eg.: ponds, lakes and reservoirs

ii) ***Underground water :*** water from wells

iii) **Rain water**

iv) **Sea water**

TYPES OF IMPURITIES PRESENT IN WATER :

They are

i) ***Dissolved impurities***
- a) Inorganic salts eg. : Ca^{2+}, Mg^{2+}, Fe^{2+}, Al^{3+}, Na^+, K^+ traces of Zn^{2+} and Cu^{2+} (cations) and Cl^-, SO_4^{2-}, NO_3^-, F^- or HCO_3^- etc. (anions)
- b) Gases eg.: CO_2, N_2, O_2, oxides of nitrogen, H_2S etc.
- c) Organic salts

ii) ***Suspended impurities :***
- a) **Inorganic** : eg.: sand and clay
- b) **organic** : eg.: animal matter, vegetable etc.

iii) ***Colloidal impurities :*** Finely divided clay, $Al(OH)_3$, $Fe(OH)_3$ colouring matter etc.

iv) ***Bacterial impurities :*** Micro-organisms and bacteria

Effect of impurities : The impurities effect the followings

a) Colour
b) Taste
c) Hardness
d) alkalinity
e) Turbidity
f) odour etc

SOFT AND HARD WATER :

The water which produces large amount of lather with soap is known as soft water and which forms a scum with soap is known as hard water.

TYPES OF HARDNESS OF WATER :

It is of two kinds

i) ***Temporary hardness :*** It is due to the presence of bicarbonates of calcium or magnesium or both.

ii) ***Permanent hardness :*** It is due to the presence of chlorides and sulphates of calcium and magnesium.

REMOVAL OF TEMPORARY HARDNESS :

It can be achieved by following methods

i) ***By boiling :*** The soluble bicarbonates are converted into insoluble carbonates.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

$$Mg(HCO_3)_2 \rightarrow MgCO_3 \downarrow + H_2O + CO_2 \uparrow$$

ii) ***By Clark's process :*** By adding lime water or milk of lime

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$$

REMOVAL OF PERMANENT HARDNESS :

i) ***By adding washing soda :*** The calcium or magnesium salts are precipitated as carbonates

$$Mg(HCO_3)_2 + Na_2CO_3 \rightarrow MgCO_3 \downarrow + 2NaHCO_3$$

$$MgCl_2 + Na_2CO_3 \rightarrow MgCO_3 \downarrow + 2NaCl$$

$$Ca(HCO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaHCO_3$$

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl$$

ii) ***By adding Caustic Soda :*** The temporary and permanent hardness can be removed by adding caustic soda

$$Ca(HCO_3)_2 + 2NaOH \rightarrow Ca(OH)_2 \downarrow + 2NaHCO_3$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2NaOH \rightarrow Mg(OH)_2 \downarrow + 2NaHCO_3$$

$$CaCl_2 + 2NaOH \rightarrow Ca(OH)_2 \downarrow + 2NaCl$$

$$CaSO_4 + 2NaOH \rightarrow Ca(OH)_2 \downarrow + Na_2SO_4$$

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 \downarrow + 2NaCl$$

$$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 \downarrow + Na_2SO_4$$

iii) ***By adding Sodium phosphate (Na_3PO_4) :*** The phosphates of calcium and magnesium are precipited

$$3Ca(HCO_3)_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 \downarrow + 6NaHCO_3$$

$$3CaCl_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 \downarrow + 6NaCl$$

$$3CaSO_4 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 \downarrow + 3Na_2SO_4$$

$$3Mg(HCO_3) + 2Na_3PO_4 \longrightarrow Mg_3(PO_4)_3 \downarrow + 6NaHCO_3$$

$$3MgCl_2 + 2Na_3PO_4 \longrightarrow Mg_3(PO_4)_2 \downarrow + 6NaCl$$

$$3MgSO_4 + 2Na_3PO_4 \longrightarrow Mg_3(PO_4)_2 \downarrow + 3Na_2SO_4$$

iv) ***Calgon process :*** Calgon is sodium hexa metaphosphate. The water is passed through the bed of calgon the Ca^{2+} and Mg^{2+} form soluble complex.

$$2CaSO_4 + Na_2[Na_4(PO_3)_6] \rightarrow 2Na_2SO_4 + Na_2[Ca_2(PO_3)_6]$$

$$2MgSO_4 + Na_2[Na_4(PO_3)_6] \rightarrow 2Na_2SO_4 + Na_2[Mg_2(PO_3)_6]$$

Water becomes free from Ca^{++} and Mg^{++} ions.

v) ***Permutit process :*** Permutit is hydrated Sodium aluminium silicate $Na_2\ Al_2\ Si_2\ O_8.xH_2O$. It exchanges its sodium ions for divalent ions such as Ca^{2+} and Mg^{2+}.

$$Na_2Al_2Si_2O_8 + CaCl_2 \rightarrow CaAl_2Si_2O_8 + 2NaCl$$

$$Na_2Al_2Si_2O_8 + MgSO_4 \rightarrow MgAl_2Si_2O_8 + Na_2SO_4$$

Permutit when fully exhausted can be regenerated by treating with 10% solution of sodium chloride

$$Ca - \text{permutit} + 2NaCl \rightarrow 2Na - \text{permutit} + CaCl_2$$

$$Mg - \text{permutit} + 2NaCl \rightarrow 2Na - \text{permutit} + MgCl_2$$

It is most efficient method to get water with zero degree hardness.

vi) ***By synthetic resins :*** They are of two types :

a) ***Cation exchange resins*** *:* These are giant molecules containing sulphonic acid group ($-SO_3H$). It is first changed into sodium salt and has the general fomula

R^-Na^+ The hard water is passed through it when Ca^{2+} and Mg^{2+} are exchanged and removed.

$$2R^-Na^+ + Ca^{2+} \rightarrow R_2Ca + 2Na^+$$

$$2R^-Na^+ + Mg^{2+} \rightarrow R_2Mg + 2Na^+$$

The resins like permutit can be regenerated with a solution of common salt.

$$R_2Ca + 2NaCl \rightarrow 2RNa + CaCl_2$$

b) ***Anion exchange resins*** *:* These are also giant molecules and can exchange anions. They contain an amino group.

$$RNH_2 + H_2O \rightarrow R\overset{+}{N}H_3OH^-$$

$$2RNH_3^+OH^- + CO_3^{2-} \rightleftharpoons (RNH_3^+)_2CO_3^{--} + 2OH^-$$

$$RNH_3^+OH^- + Cl^- \rightleftharpoons RNH_3^+Cl^- + OH$$

Anion exchange resin   Exhausted anion exchange resin.

The water is first passed through cation resins and then through anion resins and pure distilled water is obtained.

DEGREE OF HARDNESS :

The hardness of water is expressed in terms of ppm of calcium carbonates.

$$\underset{100\text{ ppm}}{1\ CaCO_3} \equiv \underset{95\text{ ppm}}{1\ MgCl_2} \equiv \underset{120\text{ ppm}}{1\ MgSO_4} \equiv \underset{111\text{ ppm}}{1\ CaCl_2} \equiv \underset{136\text{ ppm}}{1\ CaSO_4}$$

Ex. A water sample contains 204 mg of $CaSO_4$ per litre. Calculate the hardness in terms of $CaCO_3$ equivalent.

Sol. $\underset{136\ g\,mol^{-1}}{CaSO_4} \equiv \underset{100\ g\,mol^{-1}}{CaCO_3}$

$$136\ mg/L\ of\ CaSO_4 \equiv 100\ mg/L\ of\ CaCO_3\ eq.$$

$$204\ mg/L\ of\ CaSO_4 \equiv \frac{100\ mg/L\ of\ CaCO_3 \times 204}{136}$$

$= 150\ mg/L$ of $CaCO_3$

Hence hardness = 150 mg/L or ppm.

Ex. A sample of water on analysis was found to contain the following impurities expressed in mg/litre.

Impurity	$Ca(HCO_3)_2$	$Mg(HCO_3)_2$	$CaSO_4$	$MgSO_4$
Quantity	10.0	8.5	12.0	14.0
Mol. wt.	162	146	136	120

Calculate the temporary, permanent and total hardness of water in mg/litre.

Sol. Conversion into $CaCO_3$ equivalents

Impurity	***Amount***	***Multiplication factor***	***$CaCO_3$ equivalt.***
$Ca(HCO_3)_2$	10.0 mg/L	100/162	$10.0 \times 100/162$ $= 6.17$ mg/L
$Mg(HCO_3)_2$	8.5 mg/L	100/146	$8.5 \times 100/146$ $= 5.82$ mg/L
$CaSO_4$	12.0 mg/L	100/136	$12.0 \times 100/136$ $= 8.82$ mg/L
$MgSO_4$	14.0 mg/L	100/120	$14.0 \times 100/120$ $= 11.67$ mg/L

Temporary hardness due to $Ca(HCO_3)_2 + Mg(HCO_3)_2$

$= (6.17 + 5.82) = 11.99$ mg/L

Permanent hardnesss due to $CaSO_4 + MgSO_4$

$= (8.82 + 11.67) = 20.49$ mg/L

Total hardness $(11.99 + 20.49) = 32.48$ mg/L

HYDRATES :

The substances (salts) containing water molecules are called hydrates. These are of three types:

1) Cationic hydrates : When water molecules are held by cations by coordinate bonds, the hydrates are known as Cationic hydrates. eg. : $MgCl_2.6H_2O$, $CaCl_2.6H_2O$, etc.

2) Anionic hydrates : In this case the water molecules are held by anions as well as cations by coordinate bonds. eg. : $MgSO_4.7H_2O$, $CuSO_4.5H_2O$.

3) Lattice hydrates : The water molecules occupy the lattice sites e.g. : $Na_2CO_3.10H_2O$, $K_2SO_4.\ Al_2(SO_4)_3.\ 24H_2O$. On heating the water molecules are lost and substances change to powder form.

HEAVY WATER/DEUTERIUM OXIDE (D_2O) :

It was discovered by Urey, who showed that ordinary water contains one part of heavy water in 6,000 parts of it.

PREPARATION :

It is prepared by exhaustive electrolysis of water containing alkali with nickel electrodes. About 20 litres of ordinary water gives 0.5 ml of heavy water.

PROPERTIES :

Heavy water is a colourless, odourless, tasteless mobile liquid. Its physical properties in comparision to ordinary water are as follows :

Physical constants :	*D_2O*	*H_2O*
Melting point	276.8K	273K
Boiling point	374.4K	373K
Sp. gravity at 20° C	1.106	0.998
Temperature of max. density	284.6K	277K
Specific heat at 20° C	1.018	1.000
Viscosity at 293 K	14.2	10.87
Surface tension	67.8	72.8
Latent heat of vaporisation	2330kJkg^{-1}	2255 kJkg^{-1}
Dielectric Constant	82	80.5
Solubility of NaCl at 20°C	30.5%	35.9%
Refractive index	1.328	1.33

CHEMICAL PROPERTIES :

i) ***Electrolysis :***

$$2D_2O \rightleftarrows 2D_2 + O_2$$

ii) ***Reaction with Na :***

$$2Na + D_2O \rightarrow 2NaOD + D_2$$

iii) ***with acid oxides :***

$$P_2O_5 + 3D_2O \rightarrow \underset{\text{Heavy phosphoric acid}}{2D_3PO_4}$$

$$SO_3 + D_2O \rightarrow \underset{\text{Heavy sulphuric acid}}{D_2SO_4}$$

iv) ***with metallic carbides :***

$$Al_4C_3 + 12D_2O \rightarrow 4Al(OD)_3 + 3CD_4$$

$$CaC_2 + 2D_2O \rightarrow Ca(OD)_2 + C_2D_2$$

v) ***Deuterolysis :*** $AlCl_3 + 3D_2O \rightarrow Al(OD)_3 + 3DCl$

vi) ***As water of crystallisation :*** It gives deuterohydrates $CuSO_4.5D_2O$, $MgSO_4.7D_2O$, etc.

Theoretically six different types of heavy water are possible

eg. : $H-\overset{16}{O}-D,\ H-\overset{17}{O}-D,\ H-\overset{18}{O}-D,$

$D-\overset{16}{O}-D,\ D-\overset{17}{O}-D,\ \&\ D-\overset{18}{O}-D$

BIOLOGICAL AND PHYSIOLOGICAL EFFECTS :

It does not support life, and is injurious to living organism. It checks the growth of plants and animals.

USES :

(i) As a tracer compound
(ii) For production of heavy hydrogen.
(iii) As moderator in nuclear reactors.

Exercise-1 | NCERT BASED QUESTIONS

Very Short/ Short Answer Questions

1. Why is 2-ethylanthraquinol preferred in the commercial production of H_2O_2?

2. Give an example to show that ionic hydrides forms complexes.

3. Which gas is evolved when Mg_3N_2 (Magnesium nitride) is treated with H_2O? Give chemical reaction.

4. How would you prepare a sample of ND_3?

5. How does heavy water react with Al_4C_3?

6. Arrange H_2, D_2 and T_2 in the decreasing order of their boiling points.

7. Conc. H_2SO_4 cannot be used for drying H_2, why?

8. Why ice is less dense than water ?

9. Statues coated with white lead on long exposure to atmosphere turn black and original colour can be restored on treatment with H_2O_2. Why?

10. How will you show that H_2O_2 will act like oxidizing agent in acidic as well as basic medium?

11. Why hard water is not used in industrial boilers for producing steam?

12. Hydrogen forms compounds with elements having atomic number 9, 11, 12 and 17. What are their chemical formulae? Compare their chemical behaviour.

13. What happens when–

(i) Water reacts with cyanamide of calcium

(ii) Peroxosulphuric acid is hydrolysed.

(iii) Moist silver oxide reacts with H_2O_2

14. Describe the industrial application of H_2 dependent on

(i) the heat liberated when its atoms are made to combine on the surface of a metal

(ii) its effect on unsaturated organic system is presence of catalyst

(iii) its ability to combine with N_2 under specific conditions

15. A mixture of hydrazine and H_2O_2 with Cu (II) catalyst is used as a rocket propellant. Why?

Long Answer Questions

16. (i) What are the ways in which water molecules are bound to an anhydrous salt to form hydrate?

(ii) Why water is an excellent solvent?

17. How does dihydrogen react with

(i) O_2 (ii) C

(iii) N_2 (iv) F_2

(v) Cl_2?

18. Complete the following reactions :

(i) $P_4O_{10} + H_2O \rightarrow$ (ii) $AlCl_3 + H_2O \rightarrow$

(iii) $SiCl_4 + H_2O \rightarrow$ (iv) $Ca_3P_2 + H_2O \rightarrow$

(v) $NaH + H_2O \rightarrow$

Multiple Choice Questions

19. Hydrogen resembles halogens in many respects for which several factors are responsible. Of the following factors which one is most important in this respect?

(a) Its tendency to lose an electron to form a cation.

(b) Its tendency to gain a single electron in its valence shell to attain stable electronic configuration.

(c) Its low negative electron gain enthalpy value.

(d) Its small size.

20. Which of the following reactions increases production of dihydrogen from synthesis gas?

(a) $CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270K} CO(g) + 3H_2(g)$

(b) $C(s) + H_2O(g) \xrightarrow{1270K} CO(g) + H_2(g)$

(c) $CO(g) + H_2O(g) \xrightarrow[\text{Catalyst}]{673K} CO_2(g) + H_2(g)$

(d) $C_2H_6 + 2H_2O \xrightarrow[Ni]{1270K} 2CO + 5H_2$

21. Which of the following reactions is an example of use of water gas in the synthesis of other compounds?

(a) $CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270K} CO(g) + H_2(g)$

(b) $CO(g) + H_2O(g) \xrightarrow[\text{Catalyst}]{673K} CO_2(g) + H_2(g)$

(c) $C_nH_{2n+2} + nH_2O\,(g) \xrightarrow[Ni]{1270K} nCO + (2n+1)H_2$

(d) $CO(g) + 2H_2(g) \xrightarrow[\text{Catalyst}]{\text{Cobalt}} CH_3OH(l)$

22. Consider the following statements :

1. Atomic hydrogen is obtained by passing hydrogen through an electric arc.
2. Hydrogen gas will not reduce heated aluminium oxide.
3. Finely divided palladium absorbs large volume of hydrogen gas.
4. Pure nascent hydrogen is best obtained by reacting Na with C_2H_5OH.

Which of the above statements is/are correct ?

(a) 1 alone (b) 2 alone

(c) 1, 2 and 3 (d) 2, 3 and 4

23. Elements of which of the following group(s) of periodic table do not form hydrides.
(a) Groups 7, 8, 9 (b) Group 13
(c) Groups 15, 16, 17 (d) Group 14

24. Water contracts on heating
(a) to 100 °C (b) from 0°C to 4°C
(c) to 273 K (d) from 10°C to 20°C

25. Match list I with list II and select the correct answer using the codes given below the lists :

	List I		**List II**
1.	Heavy water	A.	Bicarbonates of Mg and Ca in water
2.	Temporary hard water	B.	No foreign ions in water
3.	Soft water	C.	D_2O
4.	Permanent hard water	D.	Sulphates & chlorides of Mg & Ca in water

Codes
(a) 1–C, 2–D, 3–B, 4–A
(b) 1–B, 2–A, 3–C, 4–D
(c) 1–B, 2–D, 3–C, 4–A
(d) 1–C, 2–A, 3–B, 4–D

26. Consider the reactions
(A) $H_2O_2 + 2HI \rightarrow I_2 + 2H_2O$
(B) $HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$
Which of the following statements is correct about H_2O_2 with reference to these reactions? Hydrogen peroxide is ______ .
(a) an oxidising agent in both (A) and (B)
(b) an oxidising agent in (A) and reducing agent in (B)
(c) a reducing agent in (A) and oxidising agent in (B)
(d) a reducing agent in both (A) and (B)

Exercise-2 | CONCEPTUAL MCQs

1. Which of the following metal evolves hydrogen on reaction with cold dilute HNO_3 ?
(a) Mg (b) Al
(c) Fe (d) Cu

2. The metal which gives hydrogen on treatment with acid as well as sodium hydroxide is
(a) Fe (b) Zn
(c) Cu (d) None of these

3. The metal that cannot displace hydrogen from dil HCl is
(a) Al (b) Fe
(c) Cu (d) Zn

4. Action of water or dilute mineral acids on active metals can give
(a) monohydrogen (b) tritium
(c) dihydrogen (d) trihydrogen

5. The property of hydrogen which distinguishes it from other alkali metals is
(a) its electropositive character
(b) its affinity for non-metals
(c) its reducing character
(d) its non-metallic character

6. 2 g of aluminium is treated separately with excess of dilute H_2SO_4 and excess of NaOH. The ratio of the volumes of hydrogen evolved is
(a) 2 : 3 (b) 1 : 1
(c) 2 : 1 (d) 1 : 2

7. Which of the following statements is correct ?
(a) Hydrogen has same IP as alkali metals
(b) Hydrogen has same electronegativity as halogens
(c) It has oxidation number of –1 and +1
(d) It will not be liberated at anode.

8. Which one of the following pairs of substances on reaction will not evolve H_2 gas ?
(a) Iron and H_2SO_4 (aq)
(b) Iron and steam
(c) Copper and HCl (aq)
(d) Sodium and ethanol

9. Which of the following will not displace hydrogen
(a) Ba (b) Pb
(c) Hg (d) Sn

10. The adsorption of hydrogen by palladium is called
(a) hydration
(b) reduction
(c) occlusion
(d) hydrogenation

11. Reaction of potassium with water is
(a) exothermic (b) endothermic
(c) hydrolysis (d) absorption

12. Consider the following statements :
1. Atomic hydrogen is obtained by passing hydrogen through an electric arc.
2. Hydrogen gas will not reduce heated aluminium oxide.
3. Finely divided palladium adsorbs large volume of hydrogen gas
4. Pure nascent hydrogen is best obtained by reacting Na with C_2H_5OH

Which of the above statements is/are correct ?
(a) 1 alone (b) 2 alone
(c) 1, 2 and 3 (d) 2, 3 and 4

13. Metal hydride on treatment with water gives
(a) H_2O_2 (b) H_2O
(c) acid (d) hydrogen

14. H_2O_2 is commonly prepared in lab. by the reaction of
(a) $PbO_2 + H_2SO_4$ (b) $MnO_2 + H_2SO_4$
(c) $BaO_2 + H_2O + CO_2$ (d) $Na_2O_2 + H_2O$

15. Calculate the normality of 10 volume H_2O_2 ?
(a) 1.7 N (b) 12 N
(c) 30.3 N (d) 0.0303 N

16. Commercial 10 volume H_2O_2 is a solution with a strength of approximately
(a) 30% (b) 3%
(c) 1% (d) 10%

17. A, 6 volume sample of H_2O_2
(a) will contain 6% V/V of H_2O_2
(b) will contain 6% W/V of H_2O_2
(c) would give 6 volumes of oxygen per unit volume of H_2O_2 sample at STP
(d) would give 6 volumes of oxygen per unit weight of H_2O_2 sample at STP

18. The structure of H_2O_2 is
(a) planar (b) non planar
(c) spherical (d) linear

19. In which of the following reactions, H_2O_2 is acting as a reducing agent
(a) $H_2O_2 + SO_2 \rightarrow H_2SO_4$
(b) $2KI + H_2O_2 \rightarrow 2KOH + I_2$
(c) $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$
(d) $Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2$

20. Which of the following is formed by the action of water on sodium peroxide
(a) H_2 (b) N_2
(c) O_2 (d) CO_2

21. The percentage by weight of hydrogen in H_2O_2 is
(a) 5.88 (b) 6.25
(c) 25 (d) 50

22. In which of the following reactions, H_2O_2 acts as a reducing agent?
(a) $PbO_2(s) + H_2O_2(aq) \rightarrow PbO(s) + H_2O(l) + O_2(g)$
(b) $Na_2SO_3(aq) + H_2O_2(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$
(c) $2KI(aq) + H_2O_2(aq) \rightarrow 2KOH(aq) + I_2(s)$
(d) $KNO_2(aq) + H_2O_2(aq) \rightarrow KNO_3(aq) + H_2O(l)$

23. The low density of ice compared to water is due to
(a) hydrogen bonding interactions
(b) dipole – dipole interactions
(c) dipole – induced dipole interactions
(d) induced dipole – induced dipole interactions

24. The alum used for purifying water is
(a) Ferric alum (b) Chrome alum
(c) Potash alum (d) Ammonium alum

25. The boiling point of water is exceptionally high because
(a) there is covalent bond between H and O
(b) water molecule is linear
(c) water molecules associate due to hydrogen bonding
(d) water molecule is not linear

26. The H–O–H angle in water molecule is about
(a) 90° (b) 180°
(c) 102° (d) 105°

27. When two ice cubes are pressed over each other, they unite to form one cube. Which of the following forces is responsible to hold them together ?
(a) Hydrogen bond formation
(b) van der Waals forces
(c) Covalent attraction
(d) Ionic interaction

28. The process used for the removal of hardness of water is
(a) Calgon (b) Baeyer
(c) Serpeck (d) Hoope

29. Pure water can be obtained from sea water by
(a) centrifugation (b) plasmolysis
(c) reverse osmosis (d) sedimentation

30. Polyphosphates are used as water softening agents because they
(a) form soluble complexes with anionic species
(b) precipitate anionic species
(c) form soluble complexes with cationic species
(d) precipitate cationic species

31. What is heavy water ?
(a) H_2O^{18} (b) H_2O^{16}
(c) H_2O_3 (d) D_2O

32. D_2O is used in
(a) industry (b) nuclear reactor
(c) medicine (d) insecticide

33. Match list I with list II and select the correct answer using the codes given below the lists :

	List I		List II
1.	Heavy water	A.	Bicarbonates of Mg and Ca in water
2.	Temporary hard water	B.	No foreign ions in water
3.	Soft water	C.	D_2O
4.	Permanent hard water	D.	Sulphates & chlorides of Mg & Ca in water

Codes
(a) 1–C, 2–D, 3–B, 4–A (b) 1–B, 2–A, 3–C, 4–D
(c) 1–B, 2–D, 3–C, 4–A (d) 1–C, 2–A, 3–B, 4–D

34. What is formed when calcium carbide reacts with heavy water?
(a) C_2D_2 (b) CaD_2
(c) Ca_2D_2O (d) CD_2

35. The correct order of the O–O bond length in O_2, H_2O_2 and O_3 is
(a) $O_2 > O_3 > H_2O_2$ (b) $O_3 > H_2O_2 > O_2$
(c) $H_2O_2 > O_3 > O_2$ (d) $O_2 > H_2O_2 > O_3$

36. The hydride ion H^- is stronger base than its hydroxide ion OH^-. Which of the following reactions will occur if sodium hydride (NaH) is dissolved in water ?
(a) $H^-(aq) + H_2O \rightarrow H_3O^-$
(b) $H^-(aq) + H_2O(l) \rightarrow OH^- + H_2$
(c) $H^- + H_2O \rightarrow$ No reaction
(d) None of these

37. The component present in greater proportion in Coal gas is
(a) CH_4 (b) CO_2
(c) CO (d) H_2

Exercise-3 | PAST COMPETITION MCQs

1. The O – O – H bond angle in H_2O_2 is **[CBSE-PMT 1994]**
(a) 106° (b) 109°28'
(c) 120° (d) 94.8°

2. When H_2O_2 is oxidised the product is **[CBSE-PMT 1999]**
(a) OH^- (b) O_2
(c) O^{2-} (d) HO_2^-

3. Some statements about heavy water are given below:
(A) Heavy water is used as a moderator in nuclear reactors.
(B) Heavy water is more associated than ordinary water.
(C) Heavy water is more effective solvent than ordinary water.
Which of the above statements are correct? **[CBSE-PMT 2010]**
(a) (A) and (C) (b) (A) and (B)
(c) (A), (B) and (C) (d) (B) and (C)

4. Which one of the following processes will produce hard water ? **[AIEEE 2003]**
(a) Saturation of water with $MgCO_3$
(b) Saturation of water with $CaSO_4$
(c) Addition of Na_2SO_4 to water
(d) Saturation of water with $CaCO_3$

5. Which of the following species is diamagnetic in nature? **[AIEEE 2005]**
(a) H_2^- (b) H_2^+
(c) H_2 (d) He_2^+

6. Which of the following statements in relation to the hydrogen atom is correct ? **[AIEEE 2005]**
(a) 3s, 3p and 3d orbitals all have the same energy
(b) 3s and 3p orbitals are of lower energy than 3d orbital
(c) 3p orbital is lower in energy than 3d orbital
(d) 3s orbital is lower in energy than 3p orbital

7. In context with the industrial preparation of hydrogen from water gas (CO + H_2), which of the following is the correct statement? **[AIEEE 2008]**
(a) CO and H_2, are fractionally separated using differences in their densities
(b) CO is removed by absorption in aqueous Cu_2Cl_2 solution
(c) H_2 is removed through occlusion with Pd
(d) CO is oxidised to CO_2 with steam in the presence of a catalyst followed by absorption of of CO_2 in alkali

8. The critical temperature of water is higher than that of O_2 because H_2O molecule has **[IIT 1997]**
(a) fewer electrons than oxygen
(b) two covalent bonds
(c) v-shape
(d) dipole moment

Exercise-4 | Applied MCQs

1. Hydrogen is not obtained when Zn reacts with
(a) cold water (b) dil H_2SO_4
(c) dil. HCl (d) 20% NaOH

2. True peroxide is
(a) BaO_2 (b) MnO_2
(c) PbO_2 (d) NO_2

3. An inorganic compound gives off O_2 when heated, turns an acidic solution of KI violet and reduces acidified $KMnO_4$. The compound is
(a) SO_3 (b) KNO_3
(c) H_2O_2 (d) All of these

4. Acidified solution of chromic acid on treatment with H_2O_2 yields
(a) $CrO_3 + H_2O + O_2$ (b) $Cr_2O_2 + H_2O + O_2$
(c) $CrO_5 + H_2O + K_2SO_4$ (d) $H_2Cr_2O_7 + H_2O + O_2$

5. The m.pt. of most of the solid substances increase with an increase of pressure. However ice melts at a temperature lower than its usual melting point when pressure is increased. This is because
(a) ice is less denser than H_2O
(b) pressure generates heat
(c) the chemical bonds break under pressure
(d) ice is not a true solid

6. Acidified $K_2Cr_2O_7$ on oxidation by H_2O_2 gives
(a) Blue solution (b) CrO_5
(c) Chromium peroxide (d) All of these

7. Which reaction shows oxidising nature of H_2O_2
(a) $H_2O_2 + 2KI \longrightarrow 2KOH + I_2$
(b) $Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$
(c) $H_2O_2 + Ag_2O \longrightarrow 2Ag + H_2O + O_2$
(d) $NaClO + H_2O_2 \longrightarrow NaCl + H_2O + O_2$

8. The volume strength of 0.5 N H_2O_2 solution is

(a) 4.8 (b) 8.4

(c) 3.0 (d) 8.0

9. Calgon is an industrial name given to

(a) normal sodium phosphate

(b) sodium meta aluminate

(c) sodium hexametaphosphate

(d) hydrated sodium aluminium silicate

10. When zeolite (hydrated sodium aluminium silicate) is treated with hard water the sodium ions are exchanged with

(a) H^+ ions (b) Ca^{2+} ions

(c) SO_4^{2-} ions (d) OH^- ions

11. The species that does not contain peroxide ions

(a) PbO_2 (b) H_2O_2

(c) SrO_2 (d) BaO_2

12. Hydrogen peroxide does not

(a) liberate iodide from KI

(b) turn titanium salt yellow

(c) gives silver peroxide with moist silver oxide

(d) turn mixture of aniline, $KClO_3$ and dil. H_2SO_4 violet

13. 30 volume hydrogen peroxide means

(a) 30% of H_2O_2 solution

(b) 30 cm^3 solution contains 1g of H_2O_2

(c) 1 cm^3 of solution liberates 30 cm^3 of O_2 at STP

(d) 30 cm^3 of solution contains 1 mole of H_2O_2

14. The molarity of a 100 ml solution containing 5.1 g of hydrogen peroxide is

(a) 0.15 M (b) 1.5 M

(c) 3.0 M (d) 50.0 M

15. The oxidation states of most electronegative element in the products of reaction BaO_2 with dil. H_2SO_4 are

(a) 0 and – 1 (b) –1 and – 2

(c) – 2 and 0 (d) – 2 and + 1

16. Permanent hardness of water can be removed by adding Calgon $(NaPO_3)_n$. This is an example of

(a) adsorption (b) exchange of ion

(c) precipitation (d) None of these.

17. Water contracts on heating

(a) to 100 °C (b) from 0°C to 4°C

(c) to 273 K (d) from 10°C to 20°C

18. 1000g aqueous solution of $CaCO_3$ contains 10g of calcium carbonate . Hardness of solution is

(a) 10 ppm (b) 100 ppm

(c) 1000 ppm (d) 10000 ppm

19. Which statement is wrong?

(a) Ordinary hydrogen is an equilibrium mixture of ortho and para hydrogen

(b) In ortho hydrogen spin of two nuclei is in same direction

(c) Ortho and para forms do not resemble in their chemical properties

(d) In para hydrogen spin of two nuclei is in opposite direction.

20. Decomposition of H_2O_2 is retarded by :

(a) H_3PO_4 (b) alcohol

(c) acetanilide (d) All of these

21. Hydrogen can be placed in halogens group because :

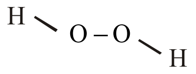
(a) H is light

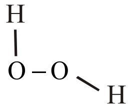
(b) it has isotopes D and T

(c) it forms hydrides like halides

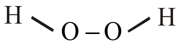
(d) H contains one electron only

22. The structure of H_2O_2 is :

(a) 

(b) 

(c) H – O – O – H

(d) 

23. Which is true peroxide :

(a) MnO_2 (b) KO_2

(c) PbO_2 (d) K_2O_2

24 In the hydrogen peroxide molecule :

(a) O – H bonds are polar but molecule is non polar.

(b) the four atoms are arranged in a non linear and non planar manner.

(c) all the four atoms are in same plane.

(d) two hydrogen atoms are connected to one of the oxygen.

25. The oxide that gives H_2O_2 on treatment with a dil. acid is

(a) Na_2O_2 (b) PbO_2

(c) TiO_2 (d) MnO_2

26. The metal that does not displace hydrogen from an acid is

(a) Al (b) Ca

(c) Hg (d) Zn

27. Nascent hydrogen consists of

(a) solvated protons

(b) hydrogen molecules with excess energy

(c) hydrogen ions in excited state

(d) hydrogen atoms with excess energy

28. Which hydride is an ionic hydride :

(a) H_2S (b) $TiH_{1.73}$

(c) NH_3 (d) NaH

29. The reaction,

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

shows that H_2O_2 :

(a) acts as reducing agent

(b) acts as oxidising agent

(c) is decomposed

(d) None of these

Hints & Solutions

EXERCISE 1

1. Because it gets regenerated during the reaction
2. $8LiH + Al_2Cl_6 \longrightarrow 2LiAlH_4 + 6LiCl$.
3. $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$.
4. $Mg_3N_2 + \underset{\text{Heavy water}}{6D_2O} \rightarrow 3Mg(OD)_2 + \underset{\text{Deutero ammonia}}{2ND_3}$
5. $Al_4C_3 + 12D_2O \rightarrow 4Al(OD)_3 + 3CD_4$
6. $T_2 > D_2 > H_2$.
7. Conc. H_2SO_4 on absorbing water from moist hydrogen produces so much heat that hydrogen catches fire.
9. $PbO + H_2S \longrightarrow \underset{\text{(black)}}{PbS} + H_2O$

   $PbS + 4H_2O_2 \longrightarrow \underset{\text{(white)}}{PbSO_4} + 4H_2O$
10. **Acidic :**

    $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$

    Basic :

    $H_2O_2(aq) + OH^-(aq) + 2e^- \rightarrow 3OH^-(aq)$
12. Compounds are : HF, NaH, MgH_2 and HCl
13. (i) $CaCN_2 + 4H_2O \rightarrow CaCO_3 + NH_4OH$.
    (ii) $H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$
    (iii) $H_2O_2 + Ag_2O \rightarrow 2Ag + H_2O + O_2$
14. (i) Atomic hydrogen torch is used industrially to melt refractory materials like tungstun, tantalum, etc.
    (ii) $Oil + H_2 \xrightarrow[450K/5atm]{Ni}$ saturated vanaspati ghee
    (iii) $N_2(g) + 3H_2(g) \xrightarrow[Fe/Mo]{400°C/200atm} 2NH_3(g)$

19. **(b)** **20.** **(c)** **21.** **(d)** **22.** **(c)** **23.** **(a)**
24. **(b)** **25.** **(d)** **26.** **(b)**

EXERCISE 2

1. **(a)** $Mg + 2HNO_3(dil.) \rightarrow Mg(NO_3)_2 + H_2$
   (Mg and Mn give H_2 with dil HNO_3)
2. **(b)** Zn is amphoteric, it reacts with acids and alkali to give hydrogen.

   $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

   $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$
3. **(c)** Cu is below hydrogen in E.C.S. hence cannot evolve H_2 with acids.
4. **(c)** Active metals can react with water and dil acids to give H_2.
5. **(d)** Hydrogen is non metallic in nature.
6. **(b)** $2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2$

   $2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$

   The ratio of volumes of hydrogen evolved is 1:1.
7. **(c)** In metal hydrides the O.S. of hydrogen –1 otherwise it is +1.
8. **(c)**
9. **(c)** Hg will not displace hydrogen since it is present below hydrogen in ECS.
10. **(c)** Adsorption of gas by solid is called Occlusion (see text)
11. **(a)** $2K + 2H_2O \rightarrow 2KOH + H_2$. It is exothermic in nature. H_2 catches fire.
12. **(c)** Pure hydrogen is evolved by reacting absolute alcohol and Na

    $C_2H_5OH + Na \rightarrow C_2H_5ONa + ½H_2$

    other statements are correct. See text.
13. **(d)** Metal hydride + $H_2O \rightarrow$ Metal hydroxide + H_2
14. **(c)** $BaO_2 + H_2O + CO_2 \rightarrow BaCO_3 + H_2O_2$ (Merck process)
15. **(a)** Normality of 10V of H_2O_2

    $\frac{68 \times 10}{22.4} = 17 \times N \quad \therefore N = 1.78$
16. **(b)** Strength of 10V $H_2O_2 = \frac{68 \times 10}{22.4} g/l = 3.035\%$
17. **(c)** 6 volume H_2O_2 would give 6 volumes of O_2 per unit volume of H_2O_2
18. **(b)** See text. Structure of H_2O_2 is nonplanar
19. **(d)** SO_2 changes to H_2SO_4 (O.N. changes from +4 to +6 oxidation)

    $2KI \rightarrow I_2$ (O.S. changes from –1 to 0 oxidation)

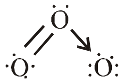
    $PbS \rightarrow PbSO_4$ (O.S. changes from –2 to +6 oxidation)

    $Ag_2O \rightarrow 2Ag$ (O.S. changes from +1 to 0 Reduction)
20. **(c)** $Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$

    $2H_2O_2 \rightarrow 2H_2O + O_2$
21. **(a)** % hydrogen in $H_2O_2 = \frac{2}{34} \times 100 = 5.88\%$
22. **(a)** $PbO_2 \rightarrow PbO$ (change in O.S. is +4 to +2 hence reduction)
23. **(a)** It is due to hydrogen bonding when H_2O forms a cage like structure in solid ice and density is reduced.
24. **(c)** Potash alum is used for purifying water.
25. **(c)** The high boiling point of water is due to H-bonding.
26. **(d)** The hybridisation in water is sp^3 and bond angle 105°
27. **(a)** Two ice cubes stick to each other due to H-bonding
28. **(a)** Calgon process is used to remove permanent hardness of water
29. **(c)** Sea water is purified by reverse osmosis.
30. **(c)** Polyphosphates form soluble complexes with Ca^{2+} and Mg^{2+} and are removed.
31. **(d)** D_2O is heavy water
32. **(b)** D_2O is used in nuclear reactors as moderators.
33. **(d)** Heavy water is D_2O (1–C); Temporary hard water contains the bi-carbonates of Mg and Ca (2–A); Soft water contains no foreign ions (3–B); Permanent hard water contains the sulphates and chlorides of Mg and Ca (4–D) therefore the answer is D.

34. (a) $CaC_2 + 2D_2O \rightarrow C_2D_2 + Ca(OD)_2$

35. (c) $H-\ddot{\underset{\cdot\cdot}{O}}-\ddot{\underset{\cdot\cdot}{O}}-H, \ddot{\underset{\cdot\cdot}{O}}=\ddot{\underset{\cdot\cdot}{O}}$



Hence O–O bond length follows the order $H_2O_2 > O_3 > O_2$

36. (b) $H^-(aq) + H_2O(l) \rightarrow OH^- + H_2$. Since H^- is a strong base it will abstract H^+ to form H_2O.

37. (d) Composition of Coal gas is 45%, H_2, 35%, CH_4, 8%, CO, 4% gaseous hydrocarbons and 8% N_2, O_2 CO_2.

EXERCISE 3

1. **(d)** $O-O-H$ bond angle in H_2O_2 is 94.8°.

2. **(b)** $H_2O_2 + [O] \xrightarrow{\text{Oxidation}} H_2O + O_2 \uparrow$

3. **(b)** ∴ **Correct choice : (b)**

4. **(b)** Permanent hardness of water is due to chlorides and sulphates of calcium and magnesium i.e $CaCl_2$, $CaSO_4$, $MgCl_2$ and $MgSO_4$.

5. **(c)** A diamagnetic substance contains no unpaired electron.

H_2 is diamagnetic as it contains all paired electrons

$$\underset{\text{(diamagnetic)}}{H_2 = \sigma_b^2}\ ,\quad \underset{\text{(paramagnetic)}}{H_2^+ = \sigma_b^1},\quad \underset{\text{(paramagnetic)}}{H_2^- = \sigma_b^2},\ \sigma_a^{*1}$$

$$\underset{\text{(paramagnetic)}}{He_2^+} \quad = \quad \underset{\text{(paramagnetic)}}{\sigma_b^2, \sigma_a^{*1}}$$

6. **(a)** In one electron species, such as H-atom, the energy of orbital depends only on the principal quantum number, n.

Hence answer (d)

i.e., $1s < 2s = 2p < 3s = 3p = 3d <$
$4s = 4p \Rightarrow 4d = 4g$

7. **(d)** On the industrial scale hydrogen is prepared from water gas according to following reaction sequence

$$\underbrace{CO + H_2}_{\text{water gas}} + \underbrace{H_2O}_{\text{(steam)}} \xrightarrow{\text{catalyst}} CO_2 + 2H_2$$

$$\xrightarrow[\text{(alkali)}]{2NaOH} Na_2CO_3 + H_2O$$

From the above it is clear that CO is first oxidised to CO_2 which is then absorbed in NaOH.

8. **(d)** Critical temperature of water is more than O_2 due to its dipole moment (Dipole moment of water = 1.84 D; Dipole moment of O_2 = zero).

EXERCISE 4

1. **(a)** Only elements having reduction potential less than - 0.41V liberate hydrogen with cold water.

2. **(a)** True peroxide contains O-O linkage and O_2^{2-} ion. They give hydrogen peroxide with dil H_2SO_4.

$BaO_2 + H_2SO_4(\text{dil.}) \rightarrow BaSO_4 + H_2O_2$

3. **(c)** $2H_2O_2 \xrightarrow{\Delta} 2H_2O + O_2$

$2KI + H_2O_2 \rightarrow 2KOH + I_2$

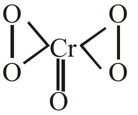
$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow$
$K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

4. **(c)** $K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + H_2Cr_2O_7$

$H_2Cr_2O_7 + 4H_2O_2 \rightarrow 2CrO_5 + 5H_2O$

5. **(a)** Ice occupy more volume than liquid water (Ice $\rightleftharpoons$ water). Increase of pressure favours forward reaction (Le-Chatelier's principle).

6. **(b)** CrO_5 is blue peroxide of chromium and has butterfly structure



7. **(a)** $H_2O_2 + 2KI \rightarrow 2KOH + I_2$, O.S of $I^-(-1)$ changes to I_2 (Zero) There is loss of electrons, hence oxidation.

8. **(b)** Use the formula $\frac{68}{22.4}$, volume strength = N × E

∴ volume strength $= \frac{1.5 \times 17 \times 22.4}{68} = 8.4$

9. **(c)** Sodium hexametaphosphate $(Na_6P_6O_{18})$ is calgon, it is used to remove permanent hardness of water.

10. **(b)** Na_2 zeolite + $CaCl_2 \rightarrow$ Ca zeolite + 2NaCl

11. **(a)** PbO_2 is lead dioxide and does not contain O - O bonds and O_2^{2-} ions.

12. **(c)** No such reaction is known (c).

13. **(c)** 30 vol of H_2O_2 means one volume of H_2O_2 on decomposition will give 30 volume of oxygen.

14. **(b)** $M = \frac{5.1 \times 1000}{34 \times 100} = 1.5$

15. **(b)** $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$.

oxygen has common O.S. as –2 and in peroxides as –1.

16. **(b)** There is exchange of ions

17. **(b)** When water is heated from 0°C to 4°C , its density. increases and volume decreases. $\left(d = \frac{m}{V}\right)$

18. **(d)** Amount of $CaCO_3$ in ppm is $= \frac{10 \times 10^6}{1000} = 10^4$ ppm.

19. **(c)** Ortho and para forms of hydrogen resemble in their chemical properties.

20. **(d)** Acetanilide, alcohol and H_3PO_4 are negative catalyst and retard decomposition of H_2O_2.

21. **(c)** Hydrogen forms hydrides like halides e.g. NaH, NaCl.

22. **(a)** The structure given (a) is correct.

23. **(d)** True peroxides contain O_2^{2-} and $O-O$ linkage.

24. **(b)** Statement (b) is correct. See structure of H_2O_2.

25. **(a)** $Na_2O_2 + 2HCl \rightarrow 2NaCl + H_2O_2$

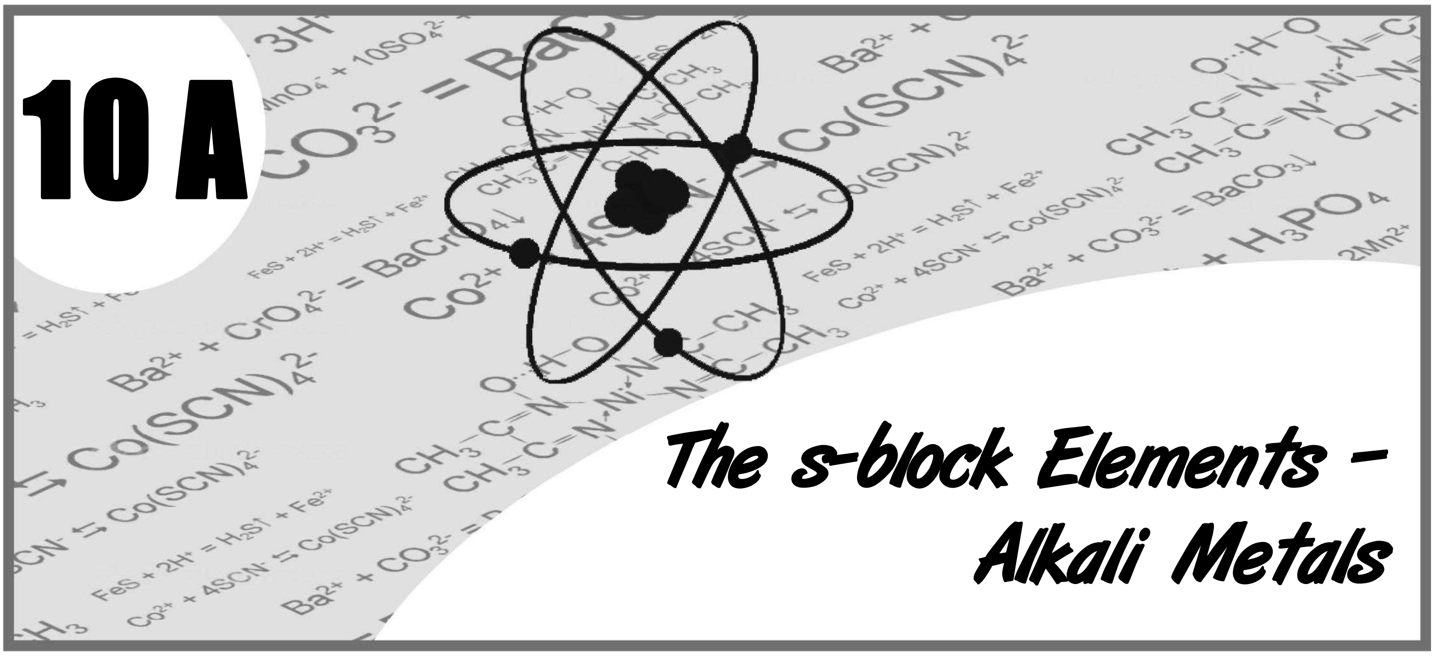
26. **(c)** The metals present below hydrogen in electrochemical series can not displace hydrogen from acids.

27. **(d)** Statement (d) is correct.

28. **(d)** All metal hydrides are ionic in nature.

29. **(c)** $2H_2O_2 \rightarrow 2H_2O + O_2$

The reaction is decomposition of H_2O_2.



10 A

The s-block Elements - Alkali Metals

THE ELEMENTS OF GROUP I ARE:

Li - Lithium	Na - Sodium	K - Potassium
Rb - Rubidium	Cs - Caesium	Fr - Francium

These elements are known as alkali metals.

Lithium is known as a bridge element and was discovered by Arfwedson.

Sodium and potassium were discovered by Davy, rubidium and caesium by Bunsen and Kirchoff while francium by Perey.

These do not occur in the native state (i.e.,do not occur free in nature).

GENERAL CHARACTERISTICS

Physical properties of alkali metals are

(i) Electronic configuration :- These are s-block elements and have one electron in the valence shell in s-orbital. In general their electronic configuration may be represented as [noble gas] ns^1 where 'n' represents the valence shell.

Element	Atomic no.	Electronic configuration	Valence shell configuration
Li	3	[He] $2s^1$	$2s^1$
Na	11	[Ne] $3s^1$	$3s^1$
K	19	[Ar] $4s^1$	$4s^1$
Rb	37	[Kr] $5s^1$	$5s^1$
Cs	55	[Xe] $6s^1$	$6s^1$
Fr	87	[Rn] $7s^1$	$7s^1$

(ii) Size of the atoms **- Atomic radii.**

(a) The alkali metals atoms have the largest atomic radii in their respective periods.

(b) Atomic radii increases as we move down the group from Li to Cs due to the additon of a new shell at each step.

(iii) Size of the ion **- Ionic radii -**

(a) The ions of the alkali metals are much smaller than their corresponding atomic radii due to lesser number of shells and contractive effect of the increased nuclear charge.

(b) The ionic radii like atomic radii of all these alkali metal ions goes on increasing on moving down the group because of the same reason.

(iv) Density -

(a) These are light metals having low densities. Lithium is the lightest known metal.

(b) On moving down the group, both the atomic size and atomic mass increases and since the increase in latter is not compensated by increase in former,consequently density increases from Li to Cs.

(c) The density of potassium is lesser than that of sodium because of the abnormal increase in size on moving from Na to K.

(v) Melting and Boiling points :-

(a) The melting and boiling points of alkali metals are quite low and decreases down the group due to weakening of metallic bond.

(b) Fr is a liquid at room temperature.

(vi) Softness - These are soft,malleable and ductile solids which can be cut with knife. They possess metallic lustre when freshly cut due to oscillation of electrons.

(vii) Atomic volume- Atomic volume of alkali metals is the highest in each period and goes on increasing down the group

Element	**Li**	**Na**	**K**	**Rb**	**Cs**
Gram atomic volume in cm^3	13	24	46	56	71

(viii)Ionisation energy:-

(a) The first ionisation energy of alkali metals is the lowest amongst the elements in their respective periods and decreases on moving down the group.

Element	**Li**	**Na**	**K**	**Rb**	**Cs**	**Fr**
IE, (kJ mol^{-1})	520	496	419	403	376	---

(b) The second ionisation energies of all the alkali metals are very large because on releasing an electron from the elements, the resulting ions acquire noble gas (stable) configurations.

(ix) Electropositive character :- Because of their low ionisation energies, alkali metals are strongly electropositive or metallic in nature and this character increases from Li to Cs.

(x) Crystal structure :- All alkali metals possess body centred cubic structures with co-oridination number 8

(xi) Oxidation state :-

(a) The alkali metal atoms show only +1 oxidation state, because their unipositive ions have the stable gas electronic configuration $(ns^2 \text{or } ns^2p^6)$ in the valence shell.

(b) Since the alkali metal ions have noble gas configuration with no unpaired electrons, they are diamagnetic and colourless but their permanganates and dichromates compounds are coloured.

(xii) Hydration of ions :-

(a) All alkali metal salts are ionic (except Lithium) and soluble in water due to the fact that cations get hydrated by water molecules. The degree of hydration depends upon the size of the cation. Smaller the size of a cation, greater is its hydration energy.

Relative ionic radii :

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$

Relative ionic radii in water or relative degree of hydration : $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

(b) The alkali metal ions exist as hydrated ions $M^+(H_2O)_x$ in the aqueous solution.

(c) Since the degree of hydration of M^+ions decreases as we go down the group, the hydration energy of alkali metal ions decreases from Li^+ to Cs^+.

(xiii) Flame colouration :-

(a) All alkali metals and their salts impart characteristic colours to the flame because of the bonding of the outermost electron.The outer eletrons of these atoms are excited to higher energy levels. On returning to the original state they give out visible light of characteristic wavelength. This gives a characteristic colour to the flame.

(b) On moving down the group, the ionisation energy goes on decreasing and hence the energy or the frequency of emitted light goes on increasing in the order Li < Na < K < Rb < Cs. As a result, the colour shows following trend

Li	**Na**	**K**	**Rb**	**Cs**
crimson red	golden yellow	pale violet	purple (violet)	sky blue

(xiv)Photoelectric effect :- Due to low I.E., alkali metals especially K and Cs show photoelectric effect (i.e. eject electrons when exposed to light) and hence are used in photelectric cells.

(xv) Electrical conductivity :- Due to the presence of loosely held valence electrons which are free to move throughout the metal structure, the alkali metals are good conductors of heat and electricity. Electrical conductivity increases from top to bottom in the order

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$

(xvi) Reducing character :-

(a) All the alkali metals are good reducing agents and it is due to their low ionisation energies. Their reducing character, follows the order

$Na < K < Rb < Cs < Li$

(b) Among the alkali metals Li has the highest negative electrode potential, which depends upon its (i) **heat of vaporisation** (ii) **ionisation energy** and (iii)**heat of hydration** and hence Li is the strongest reducing agent.

Elements	**Li**	**Na**	**K**	**Rb**	**Cs**	**Fr**
E^o (V)at at 298 K	–3.05	–2.71	–2.93	–2.99	–2.99	—

CHEMICAL PROPERTIES :

(i) Alkali metals form ionic compounds (Lithium can form covalent compounds because of its high ionisation energy) and others form ionic compounds because of their large atomic size and low I.E.

(ii) Due to low I.E. and high electropositive character the alkali metals are chemically very reactive.

(iii) Action of Air :- On exposure to moist air, their surface is tarnished due to the formation of their oxides, hydroxides and carbonates at the surface.

$$\underset{\text{Sodium}}{4Na(s)} + O_2(g) \longrightarrow \underset{\text{Sodium oxide}}{2Na_2O(s)}$$

$$Na_2O(s) + H_2O(l) \longrightarrow \underset{\text{sodium hydroxide}}{2NaOH(s)}$$

$$2NaOH(s) + CO_2(g) \longrightarrow \underset{\text{sodium carbonate}}{Na_2CO_3(s)} + H_2O(\ell)$$

Hence they are kept under inert liquid kerosene oil but lithium is kept wrapped in paraffin wax because it floats on the surface of kerosene oil due to its very low density.

(iv) Action of oxygen :-

(a) All the alkali metals when heated with oxygen form different types of oxides for example, lithium forms lithium oxide (Li_2O), sodium forms sodium peroxide (Na_2O_2), while K, Rb and Cs form their respective superoxides (MO_2 where M=K, Rb or Cs). The increasing stability of peroxides and superoxides of alkali metals from Li to Cs is due to stabilisation of larger anions by larger cations through lattice energy.

(b) Superoxides are coloured and paramagnetic as these possess three electron bond $(:O\overset{\cdots}{-}O:)^{-}$ where one unpaired electron is present.Sodium peroxide acquires yellow colour due to the presence of traces of superoxide as an impurity. KO_2 is orange, RbO_2 is brown and CsO_2 is orange in colour.

(c) All oxides, peroxides and superoxides are basic in nature.

(d) The solubility and basic strength of oxides increase in the order $Li_2O < Na_2O < K_2O < Cs_2O$

(e) The stability of peroxides and superoxides increases in the order

$$Na_2O_2 < K_2O_2 < Rb_2O_2 < Cs_2O_2 \text{ and}$$

$$NaO_2 < KO_2 < RbO_2 < CsO_2$$

(v) Action with water and other compounds containing acidic hydrogen :

(a) All the alkali metals readily react with water evolving hydrogen.

$$2M + 2H_2O \rightarrow 2MOH + H_2$$

(where M=Li, Na, K, Rb or Cs)

The reactivity with water increases on descending the group from Li to Cs as $Li < Na < K < Rb < Cs$ due to increase in electropositive character in the same order.

(b) Alkali metals also react with alcohols and acetylene and liberate H_2 e.g.

$$2Li + \underset{\text{Ethyl alcohol}}{2C_2H_5OH} \rightarrow \underset{\text{Lithium ethoxide}}{2C_2H_5OLi} + H_2$$

$$2M + HC \equiv CH \rightarrow \underset{\text{Alkali metal acetylide}}{M - C \equiv C - M} + H_2$$

(vi) Action of hydrogen :- Alkali metals combine with hydrogen to form ionic hydrides M^+H^-

$2M + H_2 \rightarrow 2MH$ (where $M = Li, Na, K$ etc.)

The reactivity of alkali metals towards hydrogen decreases as we move down the group i.e. $Li > Na > K > Rb > Cs$, due to the decreasing lattice energy of these hydrides with the increasing size of the metal cation. Thus the stability of hydrides follows the order

$$LiH > NaH > KH > RbH > CsH$$

(vii) Reaction with halogens :-

(a) Alkali metals combine readily with halogens to form ionic halides M^+X^-

$$2M + X_2 \rightarrow 2M^+X^-$$

[where M= Li,Na, K etc. and X = F,Cl, Br,I]

(b) The reactivity of alkali metals towards a particular halogen increases in the order :

$Li < Na < K < Rb < Cs$

while that of halogen towards a particular alkali metal decreases in the order :

$F_2 > Cl_2 > Br_2 > I_2$

(c) All alkali halides except LiF are freely soluble in water (LiF is soluble in non-polar solvents.Since it has strong covalent bond.)

(d) The power of the cation to polarise the anion is known as the **polarising power** while the tendency of the anion to get polarised is known as its **polarisability**. The polarising power of cation and polarisability of anion depends on the following factors (which are collectively referred to as Fajan's rules)

- ***Size of the cation*** :- Smaller the size of cation greater is its polarising power. So LiCl is more covalent than KCl.
- ***Size of the anion***:-Bigger the anion, larger is its polarisability. Hence the covalent character of lithium halides is in the order -
  $LiI > LiBr > LiCl > LiF$
- ***Charge of the ion and electronic configuration*** -Larger the charge on the cation,greater is its polarising power Thus the covalent character of various halides is in the order

$$Na^+Cl^- < Mg^{2+}Cl_2^- < Al^{3+}Cl_3^-$$

when two cations have same charge and size, the one having 18 electrons in their outermost shell will have larger polarising power than a cation having 8 electrons in the outermost shell.For example CuCl is more covalent then NaCl.

Above rules help to predict the ionic /covalent character of metal halides.

(viii)Melting points of alkali metal halides -

(a) For the same alkali metal, the melting points decrease in the order with the increase in the size of halides ion. Fluorides > chlorides > bromides > iodides

Thus

	NaF	NaCl	NaBr	NaI
Melting point	1268K	1081K	1028K	934K

(b) For the same halide ion, melting points decreases with the increasing size of the metal but lithium halides being covalent have lower melting point than corresponding sodium halides. Thus

	LiCl	NaCl	KCl	RbCl	CsCl
Melting point	883K	1081K	1045K	990K	918K

(ix) Reaction with nitrogen :- Only lithium reacts with nitrogen and forms lithium nitride (Li_3N)

$$6Li + N_2 \xrightarrow{\Delta} 2Li_3N$$

(x) Reaction with sulphur and phosphorus :- Alkali metals react with sulphur and phosphorus on heating and form respective sulphides and phosphides.

$$16M + S_8 \xrightarrow{\Delta} \underset{\text{metal sulphide}}{8M_2S} \;;\; 12M + P_4 \xrightarrow{\Delta} \underset{\text{metal phosphide}}{4M_3P}$$

(xi) Solubility in liquid ammonia:- All alkali metals dissolve in liquid ammonia giving deep blue solution, which has some characteristic properties given below due to formation of ammoniated metal cations and ammoniated electrons in the solution.

$$M \rightarrow M^+ + e^-$$

$$M^+ + xNH_3 \rightarrow [M(NH_3)_x]^+$$

$$e^- + yNH_3 \rightarrow [e(NH_3)_y]^-$$

$$M + (x+y)NH_3 \rightarrow \underset{\text{Ammoniated cation}}{[M(NH_3)_x]^+} + \underset{\text{Ammoniated electron}}{[e(NH_3)_y]^-}$$

(a) ***Colour*** -The blue colour is due to the excitation of ammoniated electron to higher energy levels and the absorption of photons occurs in the red region of the spectrum.Thus the solution appears blue.But at very high concentration the solution attains the colour like that of metallic copper.

(b) ***Conductivity*** :- It is highly conducting because of the presence of ammoniated electrons and ammoniated cations.However, on cooling,the conductivity increases further.

(c) ***Paramagnetism*** :- It is paramagnetic due to the presence of an unpaired electrons and ammoniated cations.However the paramagnetism decreases with increasing concentration due to the association of ammoniated electrons to yield diamagnetic species containing electron pairs.

$$2[e^-(NH_3)_y] \rightarrow [e^-(NH_3)_y]_2$$

(d) ***Reducing property*** :- Due to the presence of ammoniated electrons, solution is a very powerful reducing agent and used in organic chemistry under the name ***Birch reduction.***

(xii)Complex formation :- Alkali metals have a weak tendency to form complexes but polydentate ligands such as crown ethers and cryptands form highly stable complexes collectively called as **Wrap Around Complexes.** Cryptands are macrocyclic molecules with N and O atoms and their complexes are called **cryptates.** The name cryptate came from the fact that metal ion is hidden in the structure.

(xiii)Nature of hydroxides :- Alkali metals hydroxides are very strong bases, highly soluble in water and are not decomposed on heating.However, LiOH decomposes on heating to give Li_2O because latter is more stable than former.

$$2LiOH \rightarrow Li_2O + H_2O$$

Their basic strength increases from LiOH to CsOH due to a corresponding decresae in the I.E., of the metal in a group,i.e., the order:-

$$LiOH < NaOH < KOH < RbOH < CsOH$$

(xiv)Nature of carbonates and bicarbonates :-

(a) Li_2CO_3 is unstable towards heat and decomposes to give Li_2O and CO_2.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

The thermal stability of carbonates increases with the increasing basic strength of metal hydroxides on moving down the group.Thus the order is

$$Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$$

(b) The bicarbonates of all the alkali metals are known. All the bicarbonates (except *$LiHCO_3$* which exits in solution) exist as solids and on heating form carbonates.

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

(c) *The solubility of the carbonates* and bicarbonates increases on moving down the group due to lower lattice energies. Thus order is

$$LiHCO_3 < NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3.$$

(xv)Nature of Nitrates:- $LiNO_3$ on heating decomposes to give NO_2 and O_2 while the nitrates of the other alkali metals decompose on heating to form nitrites and O_2 .

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$$

All nitrates are soluble in water.

(xvi)Nature of sulphates :-

(a) Li_2SO_4 is insoluble in water whereas the other sulphates i.e, Na_2SO_4, K_2SO_4 are soluble in water.

(b) Lithium sulphate does not form alums and is also not amorphous with other sulphates.

ANOMALOUS BEHAVIOUR OF LITHIUM :

Lithium, the first member of the alkali metal family shows an anomalous behaviour because of the following main reasons:-

(a) It has the smallest size in the group

(b) It has very high ionization energy and highest electronegativity in the group.

(c) It has no vacant d-orbital in the valence shell.

As a result, it differs from the other member of the alkali metal family in following respects:

(i) Lithium is harder than other alkali metals, due to strong metallic bond.

(ii) Lithium combines with O_2 to form lithium monoxide, Li_2O, whereas other alkali metals form Peroxides, M_2O_2 and superoxides MO_2 .

(iii) Lithium, unlike the other alkali metals, reacts with nitrogen to form the nitride.

$$6Li + N_2 \rightarrow \underset{\text{Lithium nitride}}{2Li_3N}$$

(iv) LiOH is a weak base and decomposes to give the corresponding oxide while the hydroxides of alkali metals are stable to heat and sublime as such.

$$2LiOH \xrightarrow{900°C} Li_2O + H_2O$$

(v) Li_2CO_3, LiF and lithium phosphate are insoluble in water while the corresponding salts of other alkali metals are soluble in water.

(vi) LiH is the stablest among all the alkali metal hydrides.

(vii) Li_2CO_3 decomposes on heating to evolve CO_2 whereas other alkali metal carbonates do not.

(viii) Lithium nitrate on heating evolves O_2 and NO_2 and forms Li_2O while other alkali metal nitrates on heating evolve O_2 and form their respective nitrites.

(ix) Lithium when heated with ammonia forms lithium imide (Li_2NH) while other alkali metals form amides of the general formula (MNH_2 where M=Na,K, Rb and S).

(x) Only lithium combines directly with carbon to form lithium carbide, Li_2C_2, while other alkali metals react with ethyne to form the corresponding metal carbides.

DIAGONAL RELATIONSHIP :

Lithium shows diagonal relationship with magnesium, the element of group 2 and this resemblance is due to polarising power, i.e,

$\left[\frac{\text{Ionic charge}}{(\text{Ionic radius})^2}\right]$ is similar for both of these elements.

Lithium resembles magnesium in the following respects:

(i) The atomic radius of Lithium is $1.31Å$ while that of magnesium is $1.36Å$.

(ii) The ionic radius of Li^+ion is(0.60Å) which is very close to that of Mg^{2+} ion (0.65Å).

(iii) Lithium (1.0) and magnesium (1.2) have almost similar electronegativities.

(iv) Both Li and Mg are hard metals.

(v) LiF is partially soluble in water like MgF_2.

(vi) Both decompose water only on heating.

(vii) Alkyls of lithium and magesium are soluble in organic solvents.

(viii) Both combine with O_2 to form monoxides,e.g., Li_2O and MgO.

(ix) Both LiOH and $Mg(OH)_2$ are weak bases.

(x) Both LiCl and $MgCl_2$ are predominantly covalent.

(xi) Both Li and Mg combine with N_2 to form their respective nitrides, Li_3N and Mg_3N_2.

(xii) The hydroxides and carbonates of both Li and Mg decompose on heating and form their respective oxides.

(xiii) Both lithium and magnesium nitrates on heating evolve NO_2 and O_2 leaving behind their oxides.

Fire caused by burning of alkali metals is extinguished by sprinkling CCl_4.

A mixture of Na_2O_2 and dil.HCl is commercially called **Oxone** and is used for bleaching delicate fibres.

METALLURGY OF SODIUM

OCCURRENCE AND MINERALS :

(i) Sodium does not occur in the free state because of its high reactivity.

(ii) ***Important minerals of sodium are -***

- (a) Common salt or rock salt,NaCl
- (b) Chile saltpetre, $NaNO_3$
- (c) Sodium carbonate, Na_2CO_3
- (d) Sodium sulphate or Glauber's salt $Na_2SO_4.10H_2O$
- (e) Cryolite, Na_3AlF_6
- (f) Borax, $Na_2B_4O_7.10H_2O$

EXTRACTION OF SODIUM :

(a) Sodium metal is extracted by electrolysis of fused NaCl containing a little $CaCl_2$ and KF at 873 K. This process is known as ***Down process.***

(b) ***Reactions during electrolysis*** -

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$\text{At Cathode: } Na^+ + e^- \rightarrow Na$$
$$\text{At Anode : } Cl^- \rightarrow Cl + e^- \text{ ; } Cl + Cl \rightarrow Cl_2$$

(c) ***Difficulties during the process :-***

- (i) Sodium cannot be extracted from aqueous NaCl because the metal liberated at the cathode reacts with H_2O to form metal hydroxide and H_2.
- (ii) NaCl melts at 800º C and it is difficult to attain and maintain this high temperature.
- (iii) Molten Na forms a metallic fog (colloidal solution) with fused NaCl.

  Above difficulties were removed by adding $CaCl_2$ and KF to fused NaCl which themselves do not undergo decomposition at the voltage employed and lower the melting point of NaCl to about 600°C.

(d) The electrodes are separated by a wire gauze to prevent the reaction between Na and Cl_2.

METALLURGY OF POTASSIUM

OCCURRENCE AND MINERALS :

(i) Potassium also does not occur in free state.

(ii) Important minerals of potassium are :-

- (a) Sylvine, KCl
- (b) Carnallite, $KCl.MgCl_2.6H_2O$

(c) Feldspar, $K_2O.Al_2O_3.6SiO_2$

(d) Kainite, $KCl.MgSO_4.3H_2O$

EXTRACTION OF POTASSIUM :

Potassium is not obtained by the electrolysis of fused KCl because K has lower boiling point (1039 K) than the melting point of KCl (1063K) and hence it get vaporises. Therefore, K metal is extracted by the following methods :-

(i) By the electrolysis of fused KOH:- The reaction involved are

$$KOH \rightarrow K^+ + OH^-$$

At Cathode : $K^+ + e^- \rightarrow K$

At Anode : $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

(ii) Modern method :- By the reduction of molten KCl with metallic sodium in stainless steel vessel at 1120-1150 K.

$$KCl(l) + Na(g) \xrightarrow{1120-1150\,K} NaCl + K(g)$$

COMPOUNDS OF SODIUM

SODIUM CHLORIDE, COMMON SALT OR TABLE SALT, NaCl :

(i) It is obtained by evaporation of sea water in sun but due to presence of impurities like $CaSO_4, CaCl_2$ and $MgCl_2$ it is deliquescent It is purified by passing HCl gas through the impure saturated solution of NaCl and due to common ion effect, pure NaCl gets precipitated.

(ii) 28% NaCl solution is called **Brine**.

SODIUM HYDROXIDE, CAUSTIC SODA, NaOH :

Preparation:-

(i) **Causticizing process (Gossage process):-** A 10% solution of Na_2CO_3 is treated with milk of lime, $Ca(OH)_2$.

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + 2NaOH$$

(ii) Electrolytic process :- In this process a concentrated solution of sodium chloride is electrolysed where Cl_2 is evolved at the anode and H_2 at the cathode. However Cl_2 gas reacts with NaOH forming NaCl and sodium hypochlorite.

Mercury cathode process (Castner - Kellner cell):- This process is used to avoid reaction between NaOH and Cl_2. NaOH is obtained by the electrolysis of (aqueous) solution of brine. The cell has three compartments and involves following reactions :-

In outer compartment -
Anode - Graphite rods
Cathode - Mercury
Electrolyte -Brine solution
Reaction - At Anode :

$$Cl^- \rightarrow Cl + e^-;$$

$$Cl + Cl \rightarrow Cl_2 \uparrow$$

At Cathode : $Na^+ + e^- \rightarrow Na$; $Na + Hg \rightarrow Na/Hg$

In central compartment -
Anode - Mercury
Cathode - Iron rods
Electrolyte - dil. solution of NaOH
Reaction - At Anode :

$$OH^- \rightarrow OH + e^-;$$

$$Na/Hg + OH \rightarrow NaOH + Hg$$

At Cathode : $H^+ + e^- \rightarrow H; H + H \rightarrow H_2 \uparrow$

(iii) Lowing's Process

$$Na_2CO_3 + Fe_2O_3 \rightarrow \underset{\text{Sod.ferrite}}{2NaFeO_2} + CO_2$$

$$2NaFeO_2 + H_2O \rightarrow 2NaOH + Fe_2O_3$$

(iv) Pure Sodium Hydroxide

Commercial NaOH + Alcohol →

Impurities and Na_2CO_3 are insoluble.

The filtration on evaporation give pure NaOH

PROPERTIES :

(i) It is a hygroscopic, deliquescent white solid, absorbs CO_2 and moisture from the atmosphere.

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

(ii) ***Reaction with salts:-*** It reacts with metallic salts to form hydroxides out of which some are unstable and decompose to insoluble oxides,

(a) ***Formation of insoluble hydroxides***, e.g.

$$FeCl_3 + 3NaOH \rightarrow Fe(OH)_3 \downarrow + 3NaCl$$

(b) ***Formation of unstable hydroxides***, e.g.

$$2AgNO_3 + 2NaOH \rightarrow 2NaNO_3 + 2AgOH$$

$$2AgOH \rightarrow \underset{\text{Brown}}{Ag_2O} \downarrow + H_2O$$

(c) ***Formation of insoluble hydroxides*** which dissolve in excess of NaOH e.g. Zn, Al, Sb, Pb, Sn and As.

$$ZnSO_4 + 2NaOH \rightarrow Zn(OH)_2 \downarrow + Na_2SO_4$$

$$Zn(OH)_2 + 2NaOH \rightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + 2H_2O$$

(d) ***Formation of ammonia from ammonium salts :-***

$$NH_4Cl + NaOH \xrightarrow{\Delta} NaCl + NH_3 \uparrow + H_2O$$

(iii) ***Reaction with halogens:-***

$$X_2 + 2NaOH(cold) \rightarrow NaX + \underset{\text{Sodium hypohalite}}{NaXO} + H_2O$$

$$3X_2 + 6NaOH(hot) \rightarrow 5NaX + \underset{\text{Sodium halate}}{NaXO_3} + 3H_2O$$

(where X= Cl,Br or I)

(iv) ***Reaction with metals :-*** Less electropositive metals like Zn, Al and Sn etc. give H_2 gas with NaOH.

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$$

(v) ***Reaction with sand****:-*

$$2NaOH + SiO_2 \rightarrow \underset{\substack{\text{sodium silicate}\\ \text{(glass)}}}{Na_2SiO_3} + H_2O$$

(vi) ***Reaction with CO*** *:-*

$$NaOH + CO \xrightarrow[5-10\text{ atm.}]{150°-200°C} \underset{\text{sodium formate}}{HCOONa}$$

*(vii)****Reaction with non-metals*** e.g.with P, Si, S, F, etc.

$$Si + 4NaOH \xrightarrow{\Delta} Na_4SiO_4 + 2H_2 \uparrow$$

$$P_4 + 3NaOH + 3H_2O \xrightarrow{\Delta} PH_3 + \underset{\text{sodium hypophosphite}}{3NaH_2PO_2}$$

$$S_8 + 12NaOH \xrightarrow{\Delta} \underset{\text{sodium sulphide}}{4Na_2S} + \underset{\text{sodium thiosulphate}}{2Na_2S_2O_3} + 6H_2O$$

(viii) It breaks down the proteins of the skin flesh to a pasty mass and hence it is commonly known as caustic soda.

SODIUM CARBONATE OR WASHING SODA $Na_2CO_3.10H_2O$:

PREPARATION :

It is obtained by the following process -

(i) Solvay or ammonia - soda process :- In this process,NaCl (brine), ammonia and CO_2 are taken as raw materials. The involving reactions are

$$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \xrightarrow{30^\circ C} \underset{\text{Sodium bicarbonate}}{NaHCO_3} \downarrow + NH_4Cl$$

$$\underset{\text{Sodium bicarbonate}}{2NaHCO_3} \xrightarrow{250^\circ C} Na_2CO_3 + H_2O + CO_2$$

$$\underset{\text{Amm. chloride}}{2NH_4Cl} + \underset{\text{Slaked lime}}{Ca(OH)_2} \longrightarrow \underset{\substack{\text{Cal. Chloride}\\ \text{(by product)}}}{CaCl_2} + 2H_2O + 2NH_3$$

(ii) Electrolytic Process :- In this Nelson cell is used for the manufacture of NaOH, CO_2 under pressure is blown with steam

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

(iii) Leblance Process:-This is now an absolute method.

Properties :-

(i) Sodium Carbonate crystallizes from water as decahydrate which effloresces on exposure to dry air forming monohyrate which on heating change to anhydrous salt (soda-ash).

$$Na_2CO_3.10H_2O \xrightarrow{\text{dry air}} Na_2CO_3.H_2O + 9H_2O$$

$$Na_2CO_3.H_2O \xrightarrow{\Delta} \underset{\text{soda ash}}{Na_2CO_3} + H_2O$$

(ii) On hydrolysis it forms an alkaline solution

$$Na_2CO_3 + 2H_2O \rightarrow \underset{\text{(weak acid)}}{H_2CO_3} + \underset{\text{(strongbase)}}{2NaOH}$$

(iii) Aqueous sodium carbonate solution react with CO_2 gas and forms sodium bicarbonate.

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

(iv) It is used as fusion mixture $(Na_2CO_3 + K_2CO_3)$ and black ash $(Na_2CO_3 + CaS)$

SODIUM BICARBONATE, BAKING SODA, $NaHCO_3$:-

Preparation :- It is obtained as an intermediate product in Solvay ammonia process.

Properties :-

(i) ***Heating effect :-*** It gives CO_2 and Na_2CO_3.

$$2NaHCO_3 \xrightarrow{373K} Na_2CO_3 + CO_2 + H_2O$$

(ii) In aqueous medium it is alkaline due to hydrolysis:

$$NaHCO_3 + H_2O \rightarrow NaOH + H_2CO_3$$

(iii) It is used as a constituent of baking powder and in medicine to remove acidity of the stomach (as antacid).

(iv) It is present in Selidlitz powder.

(v) Baking powder is a mixture of starch, sodium bicarbonate and potassium hydrogen tartarate.

(vi) Fire extinguishers contain $H_2SO_4 + Na_2CO_3 + NaHCO_3$

(vii) $Na_2SO_4.10H_2O$ is called **Glauber's salt**, anhydrous Na_2SO_4 is called **salt cake**, $NaNO_3$ is called **chile salt-petre**, $NaHSO_4$ is called **nitre cake**, mixture of Na_2O_2 and dil. HCl is called **oxone**.

(viii)When common salt is fused with a little Na_2CO_3 ,5% to 10% Na_2SO_4 and some sugar, it acquires a dark purple colour and has a characteristic saline taste. It is used in medicine and is useful for digestion.It is called ***kala namak*** or black salt or ***sulemani namak***.

COMPOUNDS OF POTASSIUM

POTASSIUM HYDROXIDE,CAUSTIC POTASH, KOH

PREPARATION :

(i) It is prepared in a cell similar to that used for NaOH.In this cell electrolysis of an aqueous solution of KCl takes place.

(ii) It is also prepared by the action of soda lime $(NaOH + CaO)$ on potassium carbonate.

POTASSIUM CARBONATE, POTASH, PEARL ASH, K_2CO_3:

Preparation :- It is prepared by following two methods-

(i) By Leblanc process

(ii) By Precht process (magnesia process)

POTASSIUM CYNAIDE, KCN:

Preparation :-

(i) By heating potassium ferrocyanide with metallic potassium

$$K_4[Fe(CN)_6] + 2K \xrightarrow{\Delta} 6KCN + Fe$$

(ii) It is used in electroplating and due to the formation of soluble complexes with gold and silver, it is used in extraction of these metals.

POTASSIUM CHLORATE, $KClO_3$:

(i) Preparation :-

(a) By passing Cl_2 through boiling concentrated KOH solution.

$$6KOH + 3Cl_2 \rightarrow 5KCl + KClO_3 + 3H_2O$$

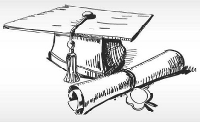
(b) By the action of KCl on $NaClO_3$ (obtained by electrolysis of NaCl at 345-350K).

$$NaClO_3 + KCl \rightarrow KClO_3 + NaCl$$

(ii) It used as an oxidising agent and in the laboratory and preparation of O_2 .

KNO_3 is called Indian salt petre or nitre.

Exercise-1 | NCERT BASED QUESTIONS



Very Short/Short Answer Questions

1. Why are alkali metals used in photoelectric cells?

2. Why is second ionisation energy of alkali metals higher than alkaline earth metals?

3. Give two uses of sodium carbonate.

4. Name the alkali metal which shows diagonal relationship with magnesium?

5. What happen when crystals of washing soda ($Na_2CO_3.10H_2O$) are exposed to air?

6. Why is the solution of alkali metals in liquid ammonia conducting in nature?

7. Sodium peroxide forms a white compound when it comes into contact with moist air. Explain.

8. Give Reasons
- (i) Li & Mg show similar properties.
- (ii) Alkali metals show +1 oxidation state.
- (iii) Alkali metals have largest size in their period

9. Mention a few difficulties involved in the extraction of sodium from fused sodium chloride.

10. How $LiNO_3$ and $NaNO_3$ differ from each other on the action of water?

11. Explain why a pellet of sodium is covered with sodium carbonate layer when exposed to atmosphere?

12. Alkali metals are paramagnetic but their salts are diamagnetic. Explain.

Long Answer Questions

13. Give Reasons
- (i) Alkali metals are good reducing agents.
- (ii) Alkali metals can be obtained only by electrolysis of their fused salts.
- (iii) Hydrogen is obtained on electrolysis of aqueous solution of salts of alkali metals.
- (iv) Alkali metals dissolve in liquid ammonia to give blue solutions.
- (v) The blue colour of metal–ammonia solution disappears on standing.

14. Give Reasons
- (i) Unlike alkali metal compounds , compounds of Li are much less soluble in water.
- (ii) Although Li has highest I.E. in group –1 but it is the best reducing agent.
- (iii) Li differs from other members of its group.
- (iv) LiOH, $LiNO_3$, Li_2CO_3 decompose readily on heating, whereas the other alkali metal hydroxides & carbonates not decompose readily on heating.
- (v) Alkali & some alkaline earth metals impart colour to bunsen flame.

15. (a) Sodium fire in the laboratory should not be extinguished by pouring water. Why?
(b) Why does table salt get wet in rainy season?

Multiple Choice Questions

16. The alkali metals have low melting point. Which of the following alkali metal is expected to melt if the room temperature rises to 30°C?
(a) Na (b) K
(c) Rb (d) Cs

17. Lithium is strongest reducing agent among alkali metals due to which of the following factor?
(a) Ionization energy (b) Electron affinity
(c) Hydration energy (d) Lattice energy

18. The solubility of metal halides depends on their nature, lattice enthalpy and hydration enthalpy of the individual ions. Amongst fluorides of alkali metals, the lowest solubility of LiF in water is due to
(a) ionic nature of lithium fluoride
(b) high lattice enthalpy
(c) high hydration enthalpy for lithium ion.
(d) low ionisation enthalpy of lithium atom

19. Which of the following alkali metal ions has lowest ionic mobility in aqueous solution ?
(a) Rb^+ (b) Cs^+
(c) Li^+ (d) Na^+

20. Which statement is false for alkali metals?
(a) Lithium is the strongest reducing agent
(b) Sodium is amphoteric in nature
(c) Li^+ is exceptionally small
(d) All alkali metals give blue solution in liquid ammonia

21. Which of the following bicarbonates does not exist as solid?
(a) $KHCO_3$ (b) $NaHCO_3$
(c) $CsHCO_3$ (d) $LiHCO_3$

22. On heating sodium metal in a current of dry ammonia gas the compound formed is
(a) sodium nitrate (b) sodium hydride
(c) sodium amide (d) sodium azide

23. In the synthesis of sodium carbonate, the recovery of ammonia is done by treating NH_4Cl with $Ca(OH)_2$. The by-product obtained in this process is
(a) $CaCl_2$ (b) NaCl
(c) NaOH (d) $NaHCO_3$

24. The formula of soda ash is
(a) $Na_2CO_3.10H_2O$ (b) $Na_2CO_3.2H_2O$
(c) $Na_2CO_3.H_2O$ (d) Na_2CO_3

25. Sodium cannot be extracted by the electrolysis of brine solution because :
(a) electrolysis cannot take place with brine solution.
(b) sodium reacts with water to produce NaOH + H_2
(c) sodium being more electropositive than hydrogen, H_2 is liberated at cathode not sodium.
(d) None of these

Exercise-2 | CONCEPTUAL MCQs

1. Which of the following is a man made element?
(a) Ra (b) Fr (c) Rn (d) Lr

2. Which one of these is most reactive ?
(a) Na (b) K (c) Pb (d) Mg

3. Alkali metals are generally extracted by
(a) reduction methods
(b) double decomposition methods
(c) displacement methods
(d) electrolytic methods

4. The alkali metal which is a liquid at room temperature is
(a) Fr (b) Cs (c) Rb (d) Na

5. The alkali metal which can emit its outermost electron under the influence of even candle light is
(a) Na (b) Rb (c) K (d) Cs

6. Francium was discoverd by
(a) Arfwedson (b) Davy
(c) Perey (d) Bunsen & Kirchoff

7. Sodium is usually kept under
(a) alcohol (b) kerosene oil
(c) ammonia (d) water

8. Sodium metal cannot be stored under
(a) benzene (b) kerosene oil
(c) alcohol (d) toluene

9. Among KO_2, AlO_2^-, BaO_2 and NO_2^+, unpaired electron is present in
(a) NO_2^+ and BaO_2 (b) KO_2 and AlO_2^-
(c) KO_2 only (d) BaO_2 only

10. The one with the largest size is
(a) Na (b) Na^+ (c) K (d) K^+

11. The increasing order of atomic radius for the elements Na, Rb, K and Mg is
(a) Na < K < Mg < Rb (b) K < Na < Mg < Rb
(c) Na < Mg < K < Rb (d) Rb < K < Mg < Na

12. Smallest among these species is
(a) hydrogen (b) helium
(c) lithium (d) lithium ion

13. Which of the following has largest size ?
(a) Na (b) Na^+ (c) Na^- (d) None of these

14. Which of the following alkali metal ions has the lowest mobility in aqueous solution ?
(a) Li^+ (b) Na^+ (c) K^+ (d) Cs^+

15. Which of the following has the least ionization potential?
(a) Li (b) He (c) N (d) Zn

16. In view of their low ionization energies, the alkali metals are
(a) weak oxidising agents (b) strong reducing agents
(c) strong oxidising agents (d) weak reducing agents

17. Which one of the following has highest electropositive character?
(a) Cu (b) Cs (c) Ba (d) Cr

18. Which of the following has the highest conductivity ?
(a) Li^+ (b) Cs^+ (c) Na^+ (d) K^+

19. The metal that dissolves in liquid ammonia, giving a dark blue coloured solution is
(a) tin (b) lead
(c) sodium (d) silver

20. Highly pure dil. solution of Na in liquid ammonia
(a) shows blue colour
(b) exhibits electrical conductivity
(c) produces sodium amides
(d) produces hydrogen gas

21. Which of the following alkali metal form complex hydrides
(a) Li (b) Na (c) K (d) Rb

22. Which of the following has the highest melting point?
(a) NaCl (b) NaF (c) NaBr (d) NaI

23. Which of the following has lowest melting point?
(a) Li (b) Na (c) K (d) Cs

24. With the increase in atomic weights melting points of the alkali metals
(a) increase
(b) decrease
(c) remain constant
(d) do not show definite trend

25. Lithium shows diagonal relationship with
(a) magnesium (b) beryllium
(c) aluminium (d) boron

26. The electronic configuration of metal M is $1s^2, 2s^2 2p^6, 3s^1$. The formula of its oxide would be
(a) MO (b) M_2O (c) M_2O_3 (d) MO_2

27. Which of the following electronic configurations corresponds to an element with the lowest ionization energy ?
(a) $1s^2 2s^2 2p^3$ (b) $1s^2 2s^2 2p^5$
(c) $1s^2 2s^2 2p^6$ (d) $1s^2 2s^2 2p^6 3s^1$

28. Solution of sodium metal in liquid ammonia is strongly reducing due to the presence of the following in solution
(a) sodium hydride (b) sodium amide
(c) sodium atoms (d) solvated electrons

29. Lithium is strongest reducing agent among alkali metals due to which of the following factor?
(a) Ionization energy (b) Electron affinity
(c) Hydration energy (d) Lattice energy

30. Microcosmic salt is :

(a) $Na_2HPO_4.2H_2O$ (b) $(NH_4)_2HPO_4.2H_2O$

(c) $Na(NH_4)HPO_4.4H_2O$ (d) None of these

31. Which of the following has lowest thermal stability ?

(a) Li_2CO_3 (b) Na_2CO_3 (c) K_2CO_3 (d) Rb_2CO_3

32. Which one of these is basic ?

(a) CO_2 (b) SiO_2 (c) Na_2O (d) SO_2

33. Sodium nitrate decomposes above 800°C to give

(a) N_2 (b) O_2 (c) NO_2 (d) Na_2O

34. Fires , that result from the combustion of alkali metals can be extinguished by

(a) CCl_4 (b) sand

(c) water (d) kerosene

35. The alkali metal that reacts with nitrogen directly to from nitride is

(a) Li (b) Na (c) K (d) Rb

36. Which of the following bicarbonates does not exist as solid?

(a) $KHCO_3$ (b) $NaHCO_3$

(c) $CsHCO_3$ (d) $LiHCO_3$

37. Which of the following is most stable?

(a) Na_3N (b) Li_3N (c) K_3N (d) Rb_3N

38. $LiNO_3$ on heating gives

(a) O_2 (b) NO_2

(c) $O_2 + NO_2$ (d) None of these

39. Which of the following does not form an oxide on heating ?

(a) $ZnCO_3$ (b) $CaCO_3$

(c) Li_2CO_3 (d) Na_2CO_3

40. Alkali metal hydrides react with H_2O to give

(a) basic solution (b) acidic solution

(c) neutral solution (d) hydrogen gas

41. The stability of the following alkali metal chlorides follows the order

(a) LiCl > KCl > NaCl > CsCl

(b) CsCl > KCl > NaCl > LiCl

(c) NaCl > KCl > LiCl > CsCl

(d) KCl > CsCl > NaCl > LiCl

42. The order of solubility of lithium halides in non polar solvents follows the order :

(a) LiI > LiBr > LiCl > LiF

(b) LiF > LiI > LiBr > LiCl

(c) LiCl > LiF > LiI > LiBr

(d) LiBr > LiCl > LiF > LiI

43. Which among the following is most soluble in water?

(a) $CsClO_4$ (b) $NaClO_4$

(c) $LiClO_4$ (d) $KClO_4$

44. When sodium is treated with sufficient oxygen/air the product obtained is

(a) Na_2O (b) Na_2O_2 (c) NaO_2 (d) NaO

45. Choose the compound which does not possess a peroxide group

(a) Na_2O_2 (b) CrO_5

(c) Fe_2O_3 (d) BaO_2

46. Which of the following alkali metals burns in air to form only monoxide ?

(a) Na (b) Li (c) K (d) Cs

47. Alkali metals form peroxides and superoxides except

(a) Na (b) Rb (c) Li (d) Cs

48. Which is the most basic of the following?

(a) Na_2O (b) BaO

(c) As_2O_3 (d) Al_2O_3

49. Which of the following is used as a source of oxygen in space capsules, submarines and breathing masks ?

(a) Li_2O (b) Na_2O_2 (c) KO_2 (d) K_2O_2

50. Which of the following oxides of potassium is not known ?

(a) K_2O (b) K_2O_4 (c) KO_3 (d) K_2O_3

51. Nitrogen dioxide cannot be prepared by heating

(a) KNO_3 (b) $Pb(NO_3)_2$

(c) $Cu(NO_3)_2$ (d) $AgNO_3$

52. When NaCl is dissolved in water, the Na^+ ions are

(a) hydrated (b) hydrolysed

(c) oxidised (d) reduced

Exercise-3 | PAST COMPETITION MCQs

1. Which one of the following properties of alkali metals increases in magnitude as the atomic number rises ?

[CBSE-PMT 1989]

(a) Ionic radius (b) Melting point

(c) Electronegativity (d) First ionization energy

2. Which of the following is known as fusion mixture?

[CBSE-PMT 1994]

(a) Mixture of $Na_2CO_3 + NaHCO_3$

(b) $Na_2CO_3.10H_2O$

(c) Mixture of $K_2CO_3 + Na_2CO_3$

(d) $NaHCO_3$

3. Sodium is made by the electrolysis of a molten mixture of about 40% NaCl and 60% $CaCl_2$ because **[CBSE-PMT 1995]**

(a) Ca^{++} can reduce NaCl to Na

(b) Ca^{++} can displace Na from NaCl

(c) $CaCl_2$ helps in conduction of electricity

(d) this mixture has a lower melting point than NaCl

4. Aqueous solution of sodium carbonate absorbs NO and NO_2 to give **[CBSE-PMT 1996]**

(a) $CO_2 + NaNO_3$ (b) $CO_2 + NaNO_2$

(c) $NaNO_2 + CO$ (d) $NaNO_3 + CO$

5. In crystals of which one of the following ionic compounds would you expect maximum distance between centres of cations and anions? **[CBSE-PMT 1998]**

(a) LiF (b) CsF

(c) CsI (d) LiI

6. In which of the following processes, fused sodium hydroxide is electrolysed at a 330ºC temperature for extraction of sodium? **[CBSE-PMT 2000]**

(a) Castner's process (b) Down's process

(c) Cyanide process (d) Both (b) and (c)

7. The sequence of ionic mobility in aqueous solution is : **[CBSE-PMT 2008]**

(a) $K^+ > Na^+ > Rb^+ > Cs^+$

(b) $Cs^+ > Rb^+ > K^+ > Na^+$

(c) $Rb^+ > K^+ > Cs^+ > Na^+$

(d) $Na^+ > K^+ > Rb^+ > Cs^+$

8. The alkali metals form salt-like hydrides by the direct synthesis at elevated temperature. The thermal stability of these hydrides decreases in which of the following orders ? **[CBSE-PMT 2008]**

(a) CsH > RbH > KH > NaH > LiH

(b) KH > NaH > LiH > CsH > RbH

(c) NaH > LiH > KH > RbH > CsH

(d) LiH > NaH > KH > RbH > CsH

9. Which of the following statements is **incorrect**? **[CBSE-PMT 2011M]**

(a) Pure sodium metal dissolves in liquid ammonia to give blue solution.

(b) NaOH reacts with glass to give sodium silicate

(c) Aluminium reacts with excess NaOH to give $Al(OH)_3$

(d) $NaHCO_3$ on heating gives Na_2CO_3

10. The ease of adsorption of the hydrated alkali metal ions on an ion-exchange resins follows the order :

(a) $Li^+ < K^+ < Na^+ < Rb^+$ **[CBSE-PMT 2012S]**

(b) $Rb^+ < K^+ < Na^+ < Li^+$

(c) $K^+ < Na^+ < Rb^+ < Li^+$

(d) $Na^+ < Li^+ < K^+ < Rb^+$

11. KO_2 (potassium super oxide) is used in oxygen cylinders in space and submarines because it **[AIEEE 2002]**

(a) absorbs CO_2 and increases O_2 content

(b) eliminates moisture

(c) absorbs CO_2

(d) produces ozone.

12. The ionic mobility of alkali metal ions in aqueous solution is maximum for **[AIEEE 2006]**

(a) Li^+ (b) Na^+

(c) K^+ (d) Rb^+

13. The products obtained on heating $LiNO_2$ will be : **[AIEEE 2011RS]**

(a) $Li_2O + NO_2 + O_2$ (b) $Li_3N + O_2$

(c) $Li_2O + NO + O_2$ (d) $LiNO_3 + O_2$

14. What is the best description of the change that occurs when $Na_2O(s)$ is dissolved in water ? **[AIEEE 2011RS]**

(a) Oxide ion accepts sharing in a pair of electrons

(b) Oxide ion donates a pair of electrons

(c) Oxidation number of oxygen increases

(d) Oxidation number of sodium decreases

Exercise-4 | Applied MCQs

1. On heating sodium metal in a current of dry ammonia gas the compound formed is

(a) sodium nitrate (b) sodium hydride

(c) sodium amide (d) sodium azide

2. The pair of compounds which cannot exits together in solution is

(a) $NaHCO_3$ and NaOH (b) Na_2CO_3 and $NaHCO_3$

(c) Na_2CO_3+ NaOH (d) $NaHCO_3$ and NaCl

3. Gun powder is

(a) KNO_3+ Charcoal + S (b) $NaNO_3 + KNO_3 + S$

(c) $NaNO_3 + S$ (d) None of these

4. Sodium carbonate is manufactured by Solvay process. The products which can be recycled are

(a) CO_2 and NH_3 (b) CO_2 and NH_4Cl

(c) NaCl and CaO (d) $CaCl_2$ and CaO.

5. Which of the following statements is false for alkali metals?
(a) Lithium is the strongest reducing agent
(b) Sodium is amphoteric in nature
(c) Li^+ is exceptionally small
(d) All alkali metals give blue solution in liquid ammonia

6. Fusion of AgCl with Na_2CO_3 gives
(a) Ag_2CO_3 (b) silver carbide
(c) Ag (d) Ag_2O

7. A mixture of $Al(OH)_3$ and $Fe(OH)_3$ can be separated easily by treating it with :
(a) HCl (b) NH_4OH
(c) HNO_3 (d) NaOH

8. When sulphur is heated with NaOH (aq). The compounds formed are
(a) $Na_2S + H_2O$
(b) $Na_2SO_3 + H_2O$
(c) $Na_2S + Na_2S_2O_3 + H_2O$
(d) $Na_2S_2O_3 + H_2O$

9. Identify the correct statement
(a) Elemental sodium can be prepared and isolated by electrolysing an aqueous solution of sodium chloride
(b) Elemental sodium is a strong oxidising agent
(c) Elemental sodium is insoluble in ammonia
(d) Elemental sodium is easily oxidised

10. Sodium sulphate is soluble in water whereas barium sulphate is sparingly soluble because
(a) the hydration energy of sodium sulphate is more than its lattice energy
(b) the lattice energy of sodium sulphate is equal to its hydration energy
(c) the hydration energy of sodium sulphate is less than its lattice energy
(d) None of these

11. Acidified solution of sodium thiosulphate is unstable because in thiosulphate
(a) the sulphur atoms are at unstable oxidation state of + 2
(b) the two sulphur atoms are at different oxidation states of + 6 and – 2
(c) the S-S bond are unstable bonds.
(d) sulphur is in zero oxidation state.

12. Common table salt becomes moist and does not pour easily in rainy season because
(a) it contains magnesium chloride
(b) it contains magnesium carbonate
(c) it melts slightly in rainy season
(d) sodium chloride is hygroscopic

13. Sodium chloride imparts a golden yellow colour to the bunsen flame . This can be interpreted due to
(a) low ionization potential of sodium
(b) photosensitivity of sodium
(c) sublimation of metallic sodium to give yellow vapours
(d) emission of excess of energy absorbed as a radiation in the visible region.

14. Sodium thiosulphate, $Na_2S_2O_3 . 5H_2O$ is used in photography to
(a) reduce the silver bromide grains to metallic silver
(b) convert the metallic silver to silver salt
(c) remove undecomposed AgBr as soluble silver thiosulphate complex.
(d) remove reduced silver

15. The salt on heating does not give brown coloured gas is
(a) $LiNO_3$ (b) KNO_3
(c) $Pb(NO_3)_2$ (d) $AgNO_3$

16. Sodium carbonate solution in water is alkaline due to
(a) hydrolysis of Na^+
(b) hydrolysis of CO_3^{2-}
(c) hydrolysis of both Na^+ and CO_3^{2-} ions
(d) None of these

17. A white solid reacts with dil.HCl to give colourless gas that decolourises aqueous bromine. The solid is most likely to be
(a) sodium carbonate (b) sodium chloride
(c) sodium acetate (d) sodium thiosulphate

18. The chloride that can be extracted with ether is
(a) NaCl (b) LiCl
(c) $BaCl_2$ (d) $CaCl_2$

19. Sodium thiosulphate is formed when
(a) NaOH is neutralized by H_2SO_4
(b) Na_2S is boiled with S
(c) Na_2SO_3 is boiled with Na_2S and I_2
(d) Na_2SO_4 is boiled with Na_2S

20. Which one of the following is formed on dissolving I_2 in aqueous solution of KI?
(a) KIO_4 (b) KIO
(c) KI_3 (d) KIO_3

21. Which of the following statements is correct for $CsBr_3$?
(a) It is a covalent compound.
(b) It contains Cs^{3+} and Br^- ions.
(c) It contains Cs^+ and Br_3^- ions
(d) It contains Cs^+, and Br^- and lattice Br_2 molecule.

22. When a crystal of caustic soda is exposed to air, a liquid layer is deposited because :
(a) crystal loses water
(b) crystal absorbs moisture and CO_2
(c) crystal melts
(d) crystal sublimes

23. Sodium reacts with water less vigorously than potassium because :
(a) it is more electronegative.
(b) it is a metal.
(c) it has higher atomic weight.
(d) it is less electropositive.

24. If NaOH is added to an aqueous solution of Zn^{2+} ions, a white precipitate appears and on adding excess NaOH, the precipitate dissolves. In this solution zinc exists in the :

(a) both in cationic and anionic parts

(b) there is no zinc left in the solution

(c) cationic part

(d) anionic part.

25. Sodium cannot be extracted by the electrolysis of brine solution because

(a) electrolysis cannot take place with brine solution.

(b) sodium reacts with water to produce NaOH + H_2

(c) sodium being more electropositive than hydrogen, H_2 is liberated at cathode and not sodium.

(d) None of these

26. The raw materials in Solvay Process are :

(a) $Na_2CO_3, CaCO_3$ and NH_3

(b) $Na_2SO_4, CaCO_3$ and NH_3

(c) NaCl, NH_3 and $CaCO_3$.

(d) NaOH, CaO and NH_3.

27. Na_2SO_3 and $NaHCO_3$ may be distinguished by treating their aqueous solution with :

(a) MgO (b) $MgSO_4$

(c) litmus solution. (d) dil. acid

28. Which hydride is most stable :

(a) NaH (b) KH

(c) CsH (d) LiH

29. A and B are two salts. A with dil. HCl and A & B with conc. H_2SO_4 react to give reddish brown vapours, hence A & B respectively are :

(a) $NaNO_3$, NaBr (b) NaBr, $NaNO_3$

(c) NaBr, $NaNO_2$ (d) $NaNO_2$, NaBr

30. When CO_2 is bubbled into an aqueous solution of Na_2CO_3 the following is formed :

(a) $NaHCO_3$ (b) H_2O

(c) NaOH (d) OH^-.

31. Sodium peroxide in contact with moist air turns white due to formation of :

(a) Na_2CO_3 (b) Na_2O

(c) NaOH (d) $NaHCO_3$

Hints & Solutions

EXERCISE 1

1. Because they have low ionisation energy and can lose electrons when light falls on them.
2. Alkali metals acquire, noble gas configuration after losing 1 electron.
3. (i) As washing soda in laundry.
   (ii) For softening of hard water.
4. Li.
5. Monohydrate (Na_2CO_3. H_2O) is formed as a result of efflorescence.
6. Due to ammoniated electrons and cations.
7. It turns white due to formation of NaOH and Na_2CO_3.
10. $NaNO_3$ is very readily soluble in water because it is ionic in nature while $LiNO_3$ is not readily soluble in water because it is covalent in nature.
12. Alkali metals contain unpaired electrons and hence are paramagnetic. But in the salts of alkali metals there are alkali metal cations which don't have unpaired electrons. Hence these are diamagnetic.

16. (d) **17.** (c) **18.** (b) **19.** (c) **20.** (b)

21. (d) **22.** (c) **23.** (a) **24.** (d) **25.** (c)

EXERCISE 2

1. (d) Lr. all transuranics $\left({}_{93}Np - {}_{103}Lr\right)$ are man-made elements.

2. (b)

3. (d) Alkali metals are highly electropositive and thus highly reducing .Therefore reduction , double decomposition and displacement methods for their extraction are not suitable .Only electrolytic methods are useful for their extraction.

4. (a)

5. (d) Cs, because of its low I.E. emits electron under the influence of even candle light.

6. (c)

7. (b) Alcohols , NH_3 and H_2O all react with sodium

$$2ROH + 2Na \rightarrow 2RONa + H_2 ;$$

$$Na(s) + NH_3(x+y) \rightarrow Na^+(NH_3)_x + e^-(NH_3)_y$$

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

Only kerosene does not react .

8. (c)

9. (c) In NO_2^+ odd (unpaired) electron is removed. In peroxides (O_2^{2-}) no unpaired electrons are present as the antibonding pi M.O.'s acquired one more electron each for pairing. AlO_2^- containing Al^{3+} ($2s^22p^6$ configuration) and 2 oxide (O^{2-}) ions each of which does not contain unpaired electron. Superoxide O_2^- has one unpaired electron in pi antibonding M.O.

10. (c) The size increases down the group.

11. (c) **12. (d)** **13. (c)**

14. (a) Li^+ is most highly hydrated $[Li^+(H_2O)_6]^+$. Therefore its effective size becomes greater than any other hydrated alkali metal cation and hence has the lowest mobility .

15. (a)

16. (b) Alkali metals are strong reducing agents and have less value for I.P.

17. (b) Alkali metals are more electropositive and this character increases down the group.

18. (b) Cs^+ due to its very high ionic mobility has the highest conductivity.

19. (c)

20. (b) Dilute solution of Na in liquid NH_3 will not produce sodium amide and hydrogen gas instantaneously. These are metastable and when catalysed give hydrogen and amide.

21. (a) Li forms $LiAlH_4$ and Na forms $NaBH_4$ as the complex hydrides besides simple hydrides of MH type.

22. (b) NaF due to its largest lattice energy has the highest melting point.

23. (d) Melting point of alkali metals decreases with increase in size.

24. (b)

25. (a)

26. (b) Electronic configuration indicates that the metal is univalent (alkali metal). Its oxide will be M_2O.

27. (d) Electronic configuration of the alkali metals correspond to lowest I.E.

28. (d)

29. (c) Li due to highest hydration energy among the alkali metals is the strongest reducing agent.

30. (c)

31. (a) The weaker the base, the less stable is its carbonate. Since LiOH is the weakest base, hence Li_2CO_3 has the lowest thermal stability.

32. (c)

33. (b) $2NaNO_3 \xrightarrow[\text{above } 800°C]{\Delta} 2NaNO_2 + O_2$

34. (a) In contrast, CCl_4 is a low boiling highly non inflammable heavy liquid . Its vapours surround the fire thereby cutting off air supply.

35. (a)

36. (d) $LiHCO_3$ is unstable and exists only in solution .

37. (b) Only Li_3N is stable ,others are not formed at all .

38. (c) $LiNO_3$ like alkaline earth metal and heavy metal nitrates undergo decomposition as

$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$

39. (d) Na_2CO_3 does not decompose to form Na_2O.

40. (d)

41. (d) Stability of a compound depends upon its enthalpy of formation ΔH_f. The more negative value of ΔH_f shows more stability of a compound. Thus KCl is more stable than LiCl ,

ΔH_f for LiCl $= -408$ kJ/mol

ΔH_f for KCl $= -436$ kJ/mol

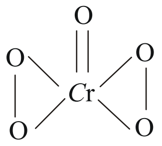
42. (a) As the size of the anion increases from F^- to I^-, the covalent character increase and hence the solubility in non -polar solvent increases

$$LiI > LiBr > LiCl > LiF$$

43. (a) The high solubility of $LiClO_4$is mainly due to high heat of hydration of Li^+ ion.

44. (b) Na in excess of O_2 forms Na_2O_2.

45. (c) Na_2O_2 is $Na^+ O^- – O^- Na^+$; Cr_2O_5 is



BaO_2 is $Ba^{2+}\left(^-O-O^-\right)$ while Fe_2O_3 consists of only $Fe^{3+}$and O^{2-}ions. Thus Fe_2O_3 does not contain a peroxide $^-O-O^-$ linkage.

46. (b)

47. (c) Li^+ does not allow its O^{2-} ion to combine with other O atom(s) to form peroxides and superoxides .

48. (a)

49. (c) Because KO_2 not only provides O_2 but also removes CO_2 as follows

$4KO_2 + 2CO_2 \rightarrow 2K_2CO_3 + 3O_2$

$4KO_2 + 4CO_2 + 2H_2O \rightarrow KHCO_3 + 3O_2$

50. (b) O_4^{2-} ion is not possible and K_2O_4 is unknown .

51. (a) Only nitrates of heavy metals and lithium decompose on heating to produece NO_2.

52. (a)

EXERCISE 3

1. (a) Within a group, ionic radius increases with increase in atomic number. The melting points decrease down the group due to weakning of metallic bond. The electronegativity and the 1st ionization energy also decreases down the group.

2. (c) Mixture of K_2CO_3 and Na_2CO_3 is called fusion mixture

3. (d) Sodium is obtained by electrolytic reduction of its chloride. Melting point of chloride of sodium is high (803°C) so in order to lower its melting point(600°C), calcium chloride is added to it.

4. (c) $2Na_2CO_3 + NO + 3NO_2 \rightarrow 4NaNO_2 + CO$

5. (c) As Cs^+ ion has larger size than Li^+ and I^- has larger size than F^-, therefore maximum distance between centres of cations and anions is in CsI.

6. (a) In Castner process, for production of (Na) Sodium metal, Sodium hydroxide (NaOH) is electrolysed at temperature 330ºC.

7. (b) Smaller the ion more is its ionic mobility in aqueous solution. Ionic radii of the given alkali metals is in the order $Na^+ < K^+ < Rb^+ < Cs^+$ and thus expected ionic mobility will be in the order $Cs^+ < Rb^+ < K^+ < Na^+$. However due to high degree of solvation (or hydration) because of lower size or high charge density, the hydrated ion size follows the order $Cs^+ < Rb^+ < K^+ < Na^+$ and thus conductivity order is $Cs^+ > Rb^+ > K^+ > Na^+$ i.e. option (b) is correct answer.

8. (d) The stability of alkali metal hydrides decreases from Li to Cs. It is due to the fact that M–H bonds become weaker with increase in size of alkali metals as we move down the group from Li to Cs. Thus the order of stability of hydrides is

$LiH > NaH > KH > RbH > CsH$

i.e. option (d) is correct answer.

9. (c) $2Al(s) + 2NaOH(aq) + 2H_2O(l) \longrightarrow \underset{\text{sod. meta aluminate}}{2NaAlO_2} + 3H_2$

10. (b) All alkali metal salts are ionic (except Lithium) and soluble in water due to the fact that cations get hydrated by water molecules. The degree of hydration depends upon the size of the cation. Smaller the size of a cation, greater is its hydration energy.

Relative ionic radii :

$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$

Relative degree of hydration:

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

11. (a) $4KO_2 + 2CO_2 \rightarrow 2K_2CO_3 + 3O_2$.

KO_2 is used as an oxidising agent. It is used as air purifier in space capsules. Submarines and breathing masks as it **produces oxygen** and **remove carbon dioxide**.

12. (d) Smaller the size of cation higher is its hydration energy and greater is its ionic mobility hence the correct order is $Li^+ < Na^+ < K^+ < Rb^+$

13. (a) $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$

14. (b)

EXERCISE 4

1. (a) $Na + NH_3 \rightarrow \underset{\text{Sodium amide}}{NaNH_2} + 1/2\ H_2$

2. (a) $NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$

   ($NaHCO_3$ is an acidic salt)

3. (a) Mixture of KNO_3 + Charcoal + S is gun powder. It is an explosive

4. (a) CO_2 and NH_3 formed are reused (See Solvay process)

5. (b) Na is basic in nature

6. (c) $2AgCl + Na_2CO_3 \rightarrow Ag_2CO_3 + 2\ NaCl.$

   $Ag_2CO_3 \xrightarrow{\Delta} 2Ag + CO_2 + 1/2\ O_2$

7. (d) $Al(OH)_3$ is soluble in NaOH and $Fe(OH)_3$ is insoluble. Hence it can be separated by NaOH

8. (c) $4S + 6NaOH \rightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$

9. (d) Elemental sodium is easily oxidised (has low I.P.) and acts as reductant.

10. (a) If lattice energy is less than hydration energy, the ionic compound will be soluble in water

11. (b) $Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S + H_2O$ (Disproportionation)

12. (a) The table salt contains the impurity of $MgCl_2$ which is hygroscopic in nature. Pure NaCl never moists

13. (d) The electrons are excited to higher energy level and on return to original state they give out visible light

14. (c) The unreacted AgBr is removed by soluble complex formation

    $AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

15. (b) Potassium nitrate gives oxygen on decomposition

    $2KNO_3 \rightarrow 2KNO_2 + O_2$

    All other nitrates give NO_2 (brown vapours) and oxygen

16. (b) Due to anionic hydrolysis

    $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + {}^-OH$

17. (d) It must be sodium thiosulphate

    $Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S + H_2O$

    $SO_2 + Br_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr$

18. (b) LiCl is covalent in nature . It is, thus soluble in polar solvents.

19. (c) $Na_2S + I_2 + Na_2SO_3 \rightarrow Na_2S_2O_3 + 2\ NaI$

20. (c) Iodine is soluble in water in presence of KI forming a complex $I_2 + KI \rightarrow KI_3$

21. (c) $CsBr_3$ may be represented as $Cs^+Br_3^-$

22. (b) It is hygroscopic and deliquescent. It absorbs moisture and CO_2 to form Na_2CO_3

    $2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

23. (d) Electropositive character and reactivity increases down the group.

24. (d) $Zn^{++} + 2NaOH \longrightarrow Zn(OH)_2 + 2Na^+$

    $Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$

    $Na_2ZnO_2 \longrightarrow 2Na^+ + (ZnO_2)^{2-}$

25. (c) The statement c is correct.

26. (c) NaCl (brine), NH_3 and CO_2 are raw materials. $CaCO_3$ is source of CO_2.

27. (b) $2MgSO_4 + 2Na_2CO_3 + H_2O \longrightarrow$

    $MgCO_3.Mg(OH)_2 + 2Na_2SO_4 + CO_2$

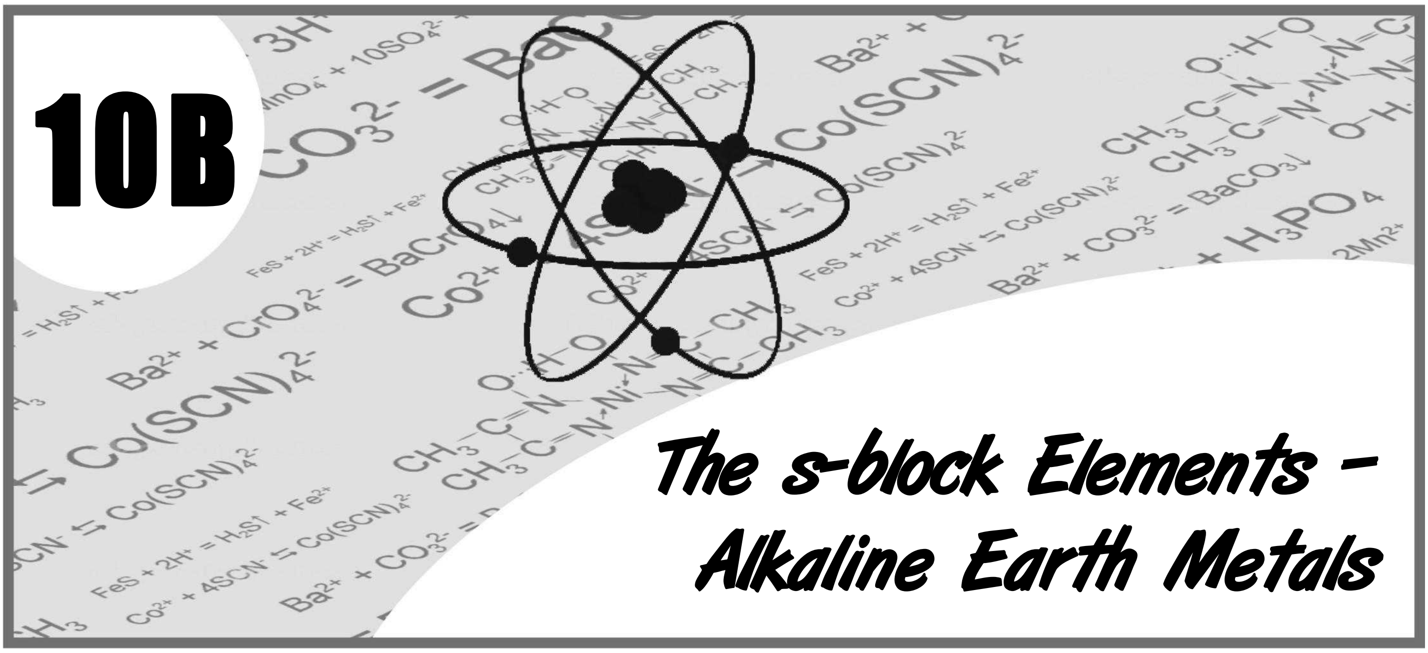
    Basic magnesium carbonate

28. (d) The basic character and stability of hydrides decrease down the group.

29. (d) Nitrites gives NO_2 (brown) with dil. acids. The nitrites and bromides give brown vapours of NO_2 and Br_2 with conc. acids.

30. (a) $Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$

31. (c) $Na_2O_2 + H_2O \longrightarrow 2NaOH + \frac{1}{2}O_2$



10B

The s-block Elements - Alkaline Earth Metals

The elements of group 2 are

Be - Beryllium	Mg - Magnesium	Ca - Calcium
Sr - Strontium	Ba - Barium	Ra - Radium (Radioactive)

These metals are known as alkaline earth metals as their oxides are alkaline and occur in earth crust.

Radium was discovered from the ore Pitch blende by Madam Curie. It is used in the treatment of cancer.

These metals do not occur in the native form (i.e., do not ocur in free state).

GENERAL CHARACTERISTICS (i.e., PHYSICAL PROPERTIES) OF ALKALINE EARTH METALS:

(i) ***Electronic configuration:*** Like alkali metals, these are s-block elements, and have two electrons in the valence shell in s-orbital. Hence their electronic configuration may be represented as [noble gas] ns^2 where 'n' represents the valence shell.

Element	*Atomic No.*	*Electronic Configuration*	*Valence Shell configuration*
Be	4	[He] $2s^2$	$2s^2$
Mg	12	[Ne] $3s^2$	$3s^2$
Ca	20	[Ar] $4s^2$	$4s^2$
Sr	38	[Kr] $5s^2$	$5s^2$
Ba	56	[Xe] $6s^2$	$6s^2$
Ra	88	[Rn] $7s^2$	$7s^2$

(ii) ***Size of the atoms and ions (Atomic radii and ionic radii):***

(a) The atomic radii of these elements are quite large but smaller than those of the corresponding elements of group 1, due to increased nuclear charge of these elements which tends to draw the orbital electrons inwards.

(b) The ionic radii are also large but smaller than those of the alkali metals.

(c) The atomic as well as ionic radii go on increasing down the group due to the gradual addition of extra energy level and also because of the screening effect.

(iii) ***Density:***

(a) These are much denser than alkali metals because of their smaller size and greater nuclear charge.

(b) The density, however, first decreases from Be to Ca and then steadily increases from Ca to Ra due to difference in crystal structure

Element	**Be**	**Mg**	**Ca**	**Sr**	**Ba**	**Ra**
Density (g cm^{-3})	1.84	1.74	1.55	2.54	3.75	6.00

(iv) ***Melting and Boiling points:***

(a) These have higher melting and boiling points than those of alkali metals because the number of bonding electrons in alkaline earth metals is two.

(b) The melting and boiling points decrease down the group with the exception of magnesium.

(c) Melting points of halides decrease as the size of the halogen increases. The correct order is

$$MF_2 > MCl_2 > MBr_2 > MI_2$$

(v) ***Metallic properties:*** They are silvery white metals, soft in nature but harder than alkali metals due to stronger metallic bonding.

(vi) ***Atomic volume:*** Atomic volume of these metals increases considerably on moving from Be to Ra as the atomic radius increases.

(vii) ***Ionization Energy:***

(a) The first I.E. of alkaline earth metals are higher than those of the corresponding alkali metals due to smaller size and higher nuclear charge.

(b) The second I.E. values are higher than their first I.E. values but much lower than the second I.E. values of alkali metals.

(c) On moving down the group due to increase in atomic size the magnitude of I.E. decreases.

(d) The ionization potential of radium is higher than that of barium.

(viii) Electropositive character:

(a) These are strong electropositive elements due to their large size and comparatively low ionisation energies.

(b) On moving down the group, the electropositive character increases due to increase in atomic radii.

(ix) Oxidation state:

(a) Alkaline earth metals uniformly show an oxidation state of +2 despite the presence of high ionisation energy because

⇒ In the solid state, the dipositive ions M^{2+} form strong lattices due to their small size and high charge (i.e., high lattice energy).

⇒ In the aqueous solution, the M^{2+} cations are strongly hydrated due to their small size and high charge. The hydration energy released by the M^{2+} cation is very large.

(b) The divalent ions are diamagnetic and colourless due to the absence of upaired electron.

(x) Conductivity: These are good conductors of heat and electricity due to the presence of two loosely held valence electrons.

(xi) Flame colouration:

(a) Like alkali metal salts, alkaline earth metal salts also impart characteristic flame colouration.

(b) As we move down the group from Ca to Ba, the ionisation energy decreases, hence the energy or the frequency of the emitted light increases. Thus,

Ca	Sr	Ba	Ra
Brick red	Crimson red	Apple green	Crimson

(c) Be and Mg because of their high ionization energies, however, do not impart any characteristic colour to the bunsen flame.

CHEMICAL PROPERTIES:

(a) Alkaline earth elements are quite reactive due to their low ionisation energies but are found to be less reactive than alkali metals because the alkaline earth metals have comparatively higher ionisation energy.

(b) Reactivity of the group 2 elements increases on moving down the group because their ionisation energy decreases.

(i) Reaction with water:

(a) Group 2 elements are less reactive with water as compared to alkali metals. They react with H_2O evolving H_2 gas.

$$M + 2H_2O \longrightarrow M(OH)_2 + H_2$$

where $M = Mg, Ca, Sr$ or Ba

(b) The chemical reactivity of the metal with H_2O, however increases as we move from Mg to Ba, i.e., Be does not react even with boiling water and Ba react vigorously even with cold water. Thus, increasing order of reactivity with water is

$$Mg < Ca < Sr < Ba$$

(ii) Reaction with oxygen:

The affinity for oxygen increases down the group. Thus, Be, Mg and Ca when heated with O_2 form monoxides while Sr, Ba and Ra form peroxides.

$$2M + O_2 \xrightarrow{\Delta} \underset{\text{Metal oxide}}{2MO} \quad (M = \text{Be, Mg or Ca})$$

$$M + O_2 \xrightarrow{\Delta} \underset{\text{Metal peroxide}}{MO_2} \quad (M = \text{Ba, Sr or Ra})$$

(iii) Reaction with acids:

(a) Alkaline earth metals except Be, displace H_2 from acids.

$$M + H_2SO_4 \longrightarrow MSO_4 + H_2$$

(where M = Mg, Ca, Sr or Ba)

(b) Reactivity, however, increases down the group from Mg to Ba i.e.,

$$Mg < Ca < Sr < Ba$$

(c) Only Mg displaces H_2 from a very dilute HNO_3.

(iv) Reaction with hydrogen:

(a) Except Be, all other elements combine with hydrogen on heating to form hydride (MH_2).

$$M + H_2 \longrightarrow MH_2 \quad (\text{where } M = \text{Mg, Ca, Sr or Ba})$$

(b) The hydride of beryllium can be prepared indirectly by reducing beryllium chloride with lithium aluminium hydride.

$$2BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$$

(c) BeH_2 and MgH_2 are covalent and polymeric whereas the hydrides of Ca, Sr and Ba are ionic and monomeric in nature.

(d) CaH_2 is also called **hydrolith**.

(e) All the hydrides react with water to evolve H_2 and thus behave as strong reducing agents.

$$MH_2 + 2H_2O \longrightarrow M(OH)_2 + 2H_2$$

(v) Reaction with halogens:

(a) All the elements of group 2 combine with halogens at high temperature and form their halides (MX_2).

$$M + X_2 \xrightarrow{\Delta} MX_2$$

(b) Beryllium halides (BeF_2, $BeCl_2$ etc.) are covalent, hygroscopic and fume in air due to hydrolysis. The halides of other alkaline earth metals are fairly ionic and this character increases as the size of the metal increases.

(c) The halides are soluble in water and their solubility decreases in the order:

$$MgX_2 > CaX_2 > SrX_2 > BaX_2$$

(d) BeF_2 is very soluble in water due to the high solvation energy of Be^{2+} in forming $[Be(H_2O)_4]^{2+}$ but the fluorides of other alkaline earth metals have high melting point and they are insoluble in water.

(e) $BeCl_2$ has a polymeric structure in the solid state but exists as a dimer in the vapour state and as a monomer at 1200 K.

(vi) Reaction with nitrogen: These metals burn in nitrogen to form nitrides of the types M_3N_2 which are hydrolysed with water to evolve NH_3.

$$3M + N_2 \longrightarrow M_3N_2$$

$$M_3N_2 + 6H_2O \longrightarrow 3M(OH)_2 + NH_3$$

(a) The ease of formation of nitrides increases from Be to Ba. (Be_3N_2) is volatile in nature.

(b) Anhydrous $CaCl_2$ is a good drying agent due to hygroscopic nature ($CaCl_2.2H_2O$) and cannot be used to dry alcohol or ammonia as it forms addition products with them.

(vii) Reaction with Carbon:

(a) When heated with carbon, these form their respective carbides of the general formula MC_2 (except Be) and are called acetylides containing the discrete C_2^{2-} anion.

$$M + 2C \xrightarrow{\Delta} MC_2$$

(where M = Mg, Ca, Sr or Ba)

(b) Under these conditions beryllium, however, forms Be_2C called methanide containing the discrete C^{4-} anion.

(c) All these carbides are ionic in nature and react with H_2O to form acetylene (except Be_2C which gives methane).

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + HC \equiv CH$$

$$Be_2C + 2H_2O \longrightarrow 2BeO + CH_4$$

or $$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

(d) On heating MgC_2 gives Mg_2C_3 called allylide which contains the disrete C_3^{4-} anion and gives allylene (methyl acetylene) on hydrolysis.

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + C_3H_4$$

(viii) Reducing character:

(a) All the alkaline earth metals, because of their low electrode potentials, are strong reducing agents but these are weaker than the corresponding alkali metals.

(b) As we move down the group from Be to Ra, the reducing character increases due to decreasing I.E. from Be to Ra.

(ix) Solubility in liquid ammonia:

(a) Like alkali metals, these dissolve in liquid ammonia giving coloured solutions.

(b) The tendency to form ammoniates decreases with increase in size of the metal atom (i.e., on moving down the group).

(x) Complex formation:

(a) Complex formation is favoured in case of alkaline earth metals because of their small sizes as compared to the alkali metals.

(b) Both Mg^{2+} and Ca^{2+} form six coordinate complexes with EDTA (ethylenedi-aminetetracetic acid) which are used to determine the hardness of water.

(c) Beryllium due to small size forms complexes of type $[BeF_3]^-$, $[BeF_4]^{-2}$ $[Be(H_2O)_4]^{2+}$.

(d) Mg exists as a natural complex, chlorophyll where it is complexed with pyrole rings of porphyrin.

(xi) Basic strength of oxides and hydroxides:

(a) BeO and $Be(OH)_2$ are amphoteric while the oxides and hydroxides of other alkaline earth metals are basic. The basic strength, however, increases from Be to Ba as the ionisation energy of metal decreases down the group thus the order:

$$BeO < MgO < CaO < SrO < BaO \text{ and}$$

$$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$$

(b) The basic character of hydroxides of group-2 elements is lesser than those of group-1 hydroxides because of the larger size elements of latter than former group.

(c) Aq. $Ba(OH)_2$ is known as **baryta water**.

(xii) Thermal stabilities and Nature of Bicarbonates and Carbonates:

(a) Bicarbonates of these metals do not exist in solid state but are known in solution only, when these solutions are heated, these get decomposed to evolve CO_2.

$$M(HCO_3)_2 \xrightarrow{\Delta} MCO_3 + CO_2 + H_2O$$

(b) The carbonates of alkaline earth metals can be regarded as salts of weak carbonic acid (H_2CO_3) and metal hydroxide, $M(OH)_2$. The carbonates decompose on heating form metal oxide and CO_2.

$$MCO_3 \xrightarrow{\Delta} MO + CO_2$$

(c) The stability of carbonates and bicarbonates increases down the group.

$$BaCO_3 > SrCO_3 > MgCO_3 > BeCO_3$$

(d) Carbonates and sulphates of Ca and Mg are responsible for permanent hardness of water while their bicarbonates cause temporary hardness.

(xiii) Solubility of the salts: The solubility of a salt in water depends upon two factors.

(1) ***Lattice energy****:* Higher the magnitude of lattice energy, lesser will be the solubility of the salt in the given solvent.

(2) ***Hydration energy****:* Higher the magnitude of hydration energy, higher will be the solubility of the salt in water (solvent).

(a) ***Solubility of hydroxides****:* As the ionic size of group 2 metals increases from Be to Ba, the lattice energy decreases from Be to Ba, as follows:

$$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$$

(b) ***Solubility of sulphates****:* The solubility of sulphates of alkaline earth metals decreases as we move down the group from Be to Ba due to the reason that ionic size

increases down the group. The lattice energy remains constant because sulphate ion is so large, so that small change in cationic sizes do not make any difference. Thus the order:

$$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$$

The negligible solubility of $BaSO_4$ in water is used in both qualitative and quantitative analysis.

(c) ***Solubility of carbonates**:* The solubility of the carbonates in water decreases down the group due to the decrease in the magnitude of hydration energy. However these insoluble metal carbonates are dissolved in water having CO_2 as shown:

$$\underset{\text{Insoluble}}{MgCO_3(s)} + CO_2(g) + H_2O \longrightarrow \underset{\substack{\text{Magnesium bicarbonate}\\ \text{(Soluble)}}}{Mg(HCO_3)_2}$$

$$Mg(HCO_3)_2 \rightleftharpoons Mg^{2+}(aq) + 2HCO_3^-(aq.)$$

The order of solubility of carbonates:

$$BeCO_3 > MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$$

ANOMALOUS BEHAVIOUR OF BERYLLIUM :

Beryllium, the first member of group 2 differs from the rest of the members of its group due to the following reasons:

(i) It has a small atomic size as well as small ionic size.
(ii) It has no vacant d-orbitals in valence shell.
(iii) It has high electronegativity value.
(iv) It has a high charge density.
(v) Its hydration energy is high.

Some points of difference are:

(i) Be is harder and denser than other members of the group.
(ii) The m.p., b.p., and ionisation energy of Be are the highest of all the alkaline earth metals.
(iii) Be does not react with water even at higher temperature where as other metals do.
(iv) BeO and $Be(OH)_2$ are amphoteric in character whereas oxides and hydroxides of the group 2 metals are basic.
(v) Be is least metallic of all the alkaline earth metals and forms covalent compounds.
(vi) Be forms nitride Be_3N_2 with nitrogen which is volatile while nitrides of others are non-volatile.
(vii) Be does not liberate H_2 from acids (HCl, H_2SO_4) where as other metals do.
(viii) Be forms Be_2C with carbon while the other members of the group form ionic carbide MC_2.

DIAGONAL RELATIONSHIP OR RESEMBLANCE BETWEEN Be AND Al :

The first member of group-2, Beryllium, shows similarities in the properties with its diagonally opposite member aluminium of the next group 13 of the next higher period, due to the similar polarizing power. i.e., ionic charge/(ionic radius)^2 of Be and Al.

(i) Both the metals are stable in air.
(ii) Both have a strong tendency to form covalent compounds.
(iii) Both form fluoro complex anions BeF_4^{2-} and AlF_6^{3-} in solution.
(iv) With conc. HNO_3, both are rendered passive due to the formation of a thin film of their respective oxides on the metal surface.
(v) Both react with conc. NaOH liberating H_2.

$$Be + 2NaOH \longrightarrow \underset{\text{Sodium berylate}}{Na_2BeO_2} + H_2$$

$$2Al + 2NaOH + 2H_2O \longrightarrow \underset{\text{Sodium metaaluminate}}{2NaAlO_2} + 3H_2$$

(vi) Oxides and hydroxides of both are amphoteric in nature.
(vii) Carbides of both liberate methane on hydrolysis.

$$Be_2C + 4H_2O \longrightarrow CH_4 + 2Be(OH)_2$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

(viii) Anyhydrous chlorides of both i.e., $BeCl_2$ and $AlCl_3$ act as Lewis acids and dissolve in organic solvents.
(ix) Both do not impart any colour to the flame.

Magnesium along with $KClO_3$ or BaO_2 is used in photography flash blubs, fire works and as a deoxidiser in metallurgical process.

$MgCl_2.5MgO\ xH_2O$ is called ***Sorel's cement*** or ***Magnesia cement*** and used to fill the cavities of teeth.

$Mg(OH)_2$ in water is used in medicine as an antacid under the name ***'Milk of Magnesia'***, while 12 gm of $MgCO_3$ per 100 c.c. of H_2O containing CO_2 is known as ***'Fluid Magnesia'.***

The finely divided $BaSO_4$ is called ***Blanc fire*** and used in paints.

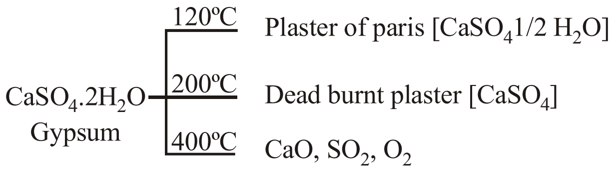
Suspension of slaked lime in water is called *white wash* (milk of lime).

A solution of $MgCl_2 + NH_4Cl$ in ammonia is known as ***Magnesia Mixture.***

Plaster of paris $CaSO_4.1/2\ H_2O$ is used in surgery for setting broken bones.

Pure $Ca(H_2PO_4)_2$ is used as ***American baking powder***.

Gypsum gives different products on heating as



Most abundant alkaline earth metal in the earth's crust is Ca.

Be and Mg crystallize in hcp, Ca and Sr in ccp and Ba in bcc structures.

Because of comparatively higher electronegativity both Be and Mg form a large number of organometallic compounds.

$CaCl_2.6H_2O$ is widely used for melting ice on roads, particularly in very cold countries, because a 30% eutectic mixture of $CaCl_2/H_2O$ freezes at –55ºC as compared with $NaCl/H_2O$ at –18ºC.

Magnesium perchlorate, $Mg(ClO_4)_2$ is known as ***anyhydrone*** and used as drying agent.

Mostly kidney stones containing calcium oxalate, $CaC_2O_4.H_2O$ which dissolves in dil. strong acids but remains insoluble in bases.

METALLURGY OF MAGNESIUM

OCCURRENCE AND IMPORTANT MINERALS :

(i) Magnesium occurs in the combined state in nature and it is the essential constituent of chlorophyll, the green colouring matter of the plants.

(ii) The important minerals of magnesium are.
   - (a) Magnesite, $MgCO_3$
   - (b) Dolomite, $MgCO_3.CaCO_3$
   - (c) Carnallite, $KCl.MgCl_2.6H_2O$
   - (d) Epsom salt, $MgSO_4.7H_2O$
   - (e) Asbestos, $CaMg_3\ (SiO_3)_4$
   - (f) Talc, $Mg_2(Si_2O_5)_2.Mg(OH)_2$

EXTRACTION :

It is extracted by the electrolysis of fused mixture of magnesium chloride (which is obtained from carnallite and magnesite), NaCl and $CaCl_2$ (added to provide conductivity to the electrolyte and to lower the fusion temperature of anhydrous $MgCl_2$) at 700ºC in ***Dow's process***. In Dow's process, $MgCl_2$ is obtained from sea water as $MgCl_2.6H_2O$ which can be changed to anhydrous $MgCl_2$ only by passing dry HCl gas through it because even by strong heating it gets hydrolysed by its own water of crystallisation.

$$MgCl_2.6H_2O + HCl \longrightarrow MgCl_2 + 6H_2O + HCl$$

$$MgCl_2.6H_2O \xrightarrow[\text{Heating}]{\text{Strong}} MgO + 2HCl + 5H_2O$$

Anhydrous $MgCl_2$ is fused with anhydrous NaCl and $CaCl_2$ and electrolysed at 700ºC.

$$MgCl_2 \longrightarrow Mg^{2+} + 2Cl^-$$

At Cathode : $Mg^{2+} + 2e^- \longrightarrow Mg$

At anode: $Cl^- \longrightarrow Cl + e^-;\ Cl + Cl \longrightarrow Cl_2 \uparrow$

USES OF MAGNESIUM :

(i) Mg being a light metal forms alloys with Al and Zn which are used in aircraft construction. e.g., ***elektron*** (95% Mg + 5% Zn) used in construction of aircraft, magnalium (1-15% Mg + 85-99% Al) used in construction of aircraft and light instruments.

(ii) Magnesium powder is used in flash bulbs used in photography.

COMPOUNDS OF MAGNESIUM

MAGNESIUM OXIDE, MAGNESIA, MgO :

With $MgCl_2$, it forms a mixture of composition $MgCl_2.5MgO.xH_2O$ which is known as ***Sorel's cement*** or *magnesia cement*.

MAGNESIUM HYDROXIDE, MILK OF MAGNESIA, $Mg(OH)_2$:

Its aqueous suspension is used in medicine as an antacid.

MAGNESIUM SULPHATE OR EPSOM SALT, $MgSO_4.7H_2O$:

It shows isomorphous nature with $ZnSO_4.7H_2O$, deliquesence and efflorescence. It is used as a purgative in medicine and as a stimulant to increase the secretion of bile.

MAGNESIUM CARBONATE, MAGNESITE, $MgCO_3$:

(i) It dissolves in water in the presence of CO_2.

$$MgCO_3 + H_2O + CO_2 \longrightarrow Mg(HCO_3)_2$$

(ii) Its 12% aqueous solution is known as fluid magnesia and is used as an antacid, laxative and in tooth pastes.

MAGANESIUM CHLORIDE, $MgCl_2.6H_2O$:

It is a deliquescent, white crystalline solid.

$$MgCl_2 + 6H_2O \xrightarrow{\text{Heat}} Mg(OH)Cl + HCl + 5H_2O$$

METALLURGY OF CALCIUM

OCCURRENCE AND IMPORTANT MINERALS :

(i) It is an important constitutent of bones and teeth (as calcium phosphate), sea shells and corals (as calcium carbonate).

(ii) The important minerals are
   - (a) Limestone, marble, chalk or calcite, $CaCO_3$
   - (b) Dolomite, $MgCO_3.CaCO_3$
   - (c) Gypsum, $CaSO_4.2H_2O$
   - (d) Fluorspar, CaF_2
   - (e) Anhydrite, $CaSO_4$
   - (f) Hydroxyapatite, $3Ca_3(PO_4)_2.Ca(OH)_2$
   - (g) Phosphorite, $Ca_3(PO_4)_2$.

EXTRACTION :

It is extracted by the electrolysis of a fused mixture of calcium chloride and calcium fluoride (lowers the fusion temperature of the electrolyte).

USES OF CALCIUM :

(i) It is used to remove air from vaccum tubes, sulphur from petroleum and oxygen from molten steel.

(ii) It is used as a reducing agent in the extraction of such metals from their oxides where carbon is ineffective.

COMPOUNDS OF CALCIUM

CALCIUM OXIDE, QUICK LIME, BURNT LIME, LIME, CaO :

Preparation:

(i) By the thermal decomposition of calcium carbonate.

$$CaCO_3 \xrightarrow{1070-1270K} CaO + CO_2;\ \Delta H = +1080\,kg$$

Properties:

(i) It is a basic oxide.

(ii) Its aqueous suspension is known as ***slaked lime*** $Ca(OH)_2$.

$$\underset{\text{Burnt lime}}{CaO} + H_2O \xrightarrow{\text{hissing sound}} \underset{\text{Slaked lime}}{Ca(OH)_2} + \text{Heat}$$

(iii) On heating with ammonium salts it gives ammonia

$$CaO + 2NH_4Cl \xrightarrow{\Delta} CaCl_2 + 2NH_3 + H_2O$$

(iv) It reacts with carbon to form calcium carbide.

$$CaO + 3C \longrightarrow \underset{\text{Calcium carbide}}{CaC_2} + CO$$

(v) It is used as basic flux, for removing hardness of water for preparing **mortar** (CaO + Sand + Water).

CALCIUM HYDROXIDE, SLAKED LIME, LIME WATER, $Ca(OH)_2$:

Preparation:

(i) By dissolving quick lime in water.

$$CaO + H_2O \longrightarrow Ca(OH)_2 ; \quad \Delta H = -63kJ$$

Properties:

(i) Its suspension in water is known as milk of lime.

(ii) It gives $CaCO_3$ (milky) and then $Ca(HCO_3)_2$ with CO_2.

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{(Milkiness)}}{CaCO_3} + H_2O$$

$$CaCO_3 + H_2O + \underset{\text{(Excess)}}{CO_2} \longrightarrow \underset{\text{(Soluble)}}{Ca(HCO_3)_2}$$

(iii) It reacts with Cl_2 to give bleaching powder $CaOCl_2$.

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$

CALCIUM CHLORIDE, $CaCl_2.6H_2O$:

(i) It is a deliquescent solid which is a by-product of Solvay's process.

(ii) Fused Calcium chloride is a good **dessicant** (drying agent), but it can not be used to dry alcohol or ammonia as it forms addition product with them.

CALCIUM CARBONATE, LIMESTONE, MARBLE, CHALK, SLATE, CALCITE, $CaCO_3$:

Preparation:

(i) By passing CO_2 through lime water.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 \downarrow + H_2O$$

Properties:

(i) It is insoluble in H_2O but dissolves in the presence of CO_2, due to the formation fo calcium bicarbonate.

$$\underset{\text{Insoluble}}{CaCO_3} + H_2O + CO_2 \longrightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$$

GYPSUM, CALCIUM SULPHATE DIHYDRATE, $CaSO_4.2H_2O$:

(i) It is naturally occurring calcium sulphate and also known as **alabaster.**

(ii) On heating at 390K, it gives plaster of paris.

(iii) It is added to cement to slow down its rate of setting.

PLASTER OF PARIS, CALCIUM SULPHATE HEMIHYDATE, $CaSO_4.1/2\ H_2O$:

(i) When it is mixed with water, it forms first a plastic mass which sets into a solid mass with slight expansion due to rehydration and its reconversion into gypsum.

$$\underset{\text{Plaster of paris}}{CaSO_4.\frac{1}{2}H_2O} + 1\frac{1}{2}H_2O \xrightarrow{\text{setting}} \underset{\text{Gypsum (orthorhombic)}}{CaSO_4.2H_2O}$$

$$\downarrow \text{hardening}$$

$$\underset{\text{Gypsum (monoclinic)}}{CaSO_4.2H_2O}$$

(ii) On heating at about 200ºC, it also forms dead burnt plaster of paris (it has no tendency to set).

CALCIUM CARBIDE OR CALCIUM ACETYLIDE, CaC_2:

Preparation:

(i) By heating a mixture of quick lime (CaO) and powdered coke in an electric furnace at 3300K.

$$CaO + 3C \xrightarrow{3300K} CaC_2 + CO$$

Properties:

(i) It reacts with water to form acetylene.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + HC \equiv CH$$

(ii) When heated with nitrogen, it forms calcium cyanamide which on reaction with steam under pressure gives NH_3.

$$CaC_2 + N_2 \xrightarrow{1373K} \underbrace{CaCN_2 + C}_{\text{Nitrolim}}$$

$$CaCN_2 + \underset{\text{(Steam)}}{3H_2O} \xrightarrow[\text{Pressure}]{} CaCO_3 + 2NH_3$$

(iii) ***Nitrolim*** (a mixture of calcium cyanamide and carbon) is used as a fertilizer.

BLEACHING POWDER, $CaOCl_2$ (CALCIUM HYPOCHLORITE, CHLORIDE OF LIME):

Preparation:

By passing a current of chlorine over dry slaked lime.

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$

Manufacture : The manufacture of bleaching powder is carried out in

(i) **Hasenclever plant** or (ii) **Bachmann's plant**

Properties :

(i) It is a mixture (mixed salt) of calcium hypochlorite $(Ca.(OCl)_2.4H_2O)$ and basic calcium chloride $(CaCl_2.Ca(OH)_2.H_2O)$.

(ii) Its aqueous solution gives Ca^{2+}, Cl^- and OCl^- ions.

(iii) With dil. H_2SO_4, it gives nascent oxygen which causes its oxidising and bleaching power.

$$2CaOCl_2 + H_2SO_4 \longrightarrow CaCl_2 + CaSO_4 + 2HClO$$

$$HClO \longrightarrow HCl + O$$

(iv) With excess of dil. H_2SO_4 (or CO_2), it forms Cl_2 known as **available chlorine**.

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$$

$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$$

The average percentage of **available chlorine is 35 - 40%.** Theoretically it should be 49%, which diminishes on keeping the powder due to following change

$$6CaOCl_2 \rightarrow 5CaCl_2 + Ca(ClO_3)_2$$

Available chlorine is estimated by

(a) Arsenite method (Penot's method)

$$Na_3AsO_3 + CaOCl_2 \rightarrow Na_3AsO_4 + CaCl_2$$

(b) Iodometric method (Bunsen and Wagner's method)

$$CaOCl_2 + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + Cl_2 + H_2O$$
$$2KI + Cl_2 \rightarrow 2KCl + I_2$$
$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

(v) It gives O_2 in presence of catalyst $COCl_2$.

$$2CaOCl_2 \xrightarrow{COCl_2} 2CaCl_2 + O_2$$

Uses : It is used for bleaching, as disinfectant and germicide in sterlisation of water, for making wool unshrinkable and in the manufacture of Chloroform.

CEMENT :

Cement is essentially a mixture of complex silicates and aluminates of Ca containing less than 1.0% free lime and some gypsum ($CaSO_4.2H_2O$)

Composition : An approximate composition is as follows :

1.	Lime	CaO	60-69%	62%
2.	Silica	SiO_2	17-25%	22%
3.	Alumina	Al_2O_3	3-8%	7.5%
4.	Magnesia	MgO	1-5%	2.5%
5.	Iron oxide	Fe_2O_3	0.5-5%	2.5%
6.	Sulphur trioxide	SO_3	1-3%	1.5%
7.	Sodium oxide	Na_2O	0.3-1.5%	1.0%
8.	Potassium oxide	K_2O	0.3-1.5%	1.0%

Ratio of Silica and alumina

$$\frac{\%\text{ of }SiO_2}{\%\text{ of }Al_2O_3} = 2.5 - 4$$

Ratio of CaO and $6(SiO_2 + Al_2O_3 + Fe_2O_3)$

$$\frac{\%\text{ of CaO}}{\%\text{ of }SiO_2 + \%\text{ of }Al_2O_3 + \%\text{ of }Fe_2O_3} = 1.9 - 2.1$$

White Cement : It does not contain ferric oxide

Process : Two processes are employed

(i) Wet process (ii) Dry process

Raw material : Lime and Clay

Manufacture :

$$\text{Clay + lime} \xrightarrow[\text{strong}]{\Delta} \text{Cement clinker} \xrightarrow[\substack{2-3\% \\ \text{by weight}}]{\text{Gypsum}} \text{Cement}$$

Gypsum regulates the setting time

Setting of Cement : When mixed with water, the cement forms a gelatinous mass sets to hard mass when three dimensional cross links are formed between ... Si-O-Si---and ---Si-O-Al--- chains.

The reactions involved in the setting of cement are :

(i) **Hydration :** Hydration of $3CaO.Al_2O_3$ and $2CaOSiO_2$ forming colloidal gel.

(ii) **Hydrolysis :** Hydrolysis of $3CaOAl_2O_3$ and $3CaO.SiO_2$ forming precipitates of $Ca(OH)_2$ and $Al(OH)_3$

Fly ash : A waste product of steel industry possess properties similar to cement. It is added to cement to reduce its cost.

Rice Husk : It has high silica content and employed to make cement.

Exercise-1 | NCERT BASED QUESTIONS

Very Short/Short Answer Questions

1. What is the function of adding gypsum to clinker cement ?
2. Why is anhydrous $CaSO_4$ used as drying agent? Why not plaster of paris ?
3. How the caves are formed in limestone regions ?
4. The crystalline salts of alkaline earth metals contain more water of crystallisation than the corresponding alkali metal salts, why?
5. How is slaked lime prepared ?
6. Account for the following :

   Be has less negative value of the reduction potential (E°)
7. What happens when
   (i) Calcium is treated with nitrogen.
   (ii) Calcium is treated with dilute sulphuric acid.
   (iii) Calcium is heated in the atmosphere of SO_2.
   (iv) Calcium is treated with cold water .
8. What happens when
   (i) Plaster of paris is mixed with water.
   (ii) Gypsum is heated at 473 K.
9. Arrange the following in the order of property indicated :
   (i) $CaCl_2$, $MgCl_2$, $BeCl_2$, $SrCl_2$: Ionic character
   (ii) $Sr(OH)_2$, $Ba(OH)_2$, $Be(OH)_2$, $Mg(OH)_2$: Basic character
   (iii) $BeSO_4$, $SrSO_4$, $CaSO_4$, $BaSO_4$: Increasing solubility in water
10. Alkaline earth metal ions have a tendency to form complexes, whereas it is not so in case of alkali metals.
11. Discuss thermal stability and the solubility of the oxosalts of alkaline earth metals.
12. Why is calcium preferred over sodium to remove last traces of moisture from alcohol?

Long Answer Questions

13. Complete the following equations for the reaction between
   (i) $Ca + H_2O$ (ii) $Ca(OH)_2 + Cl_2$
   (iii) $BeO + NaOH$ (iv) $BeCl_2 + LiAlH_4$
   (v) $Ca_3N_2 + H_2O$
14. Give Reasons
   (i) Alkaline earth metal hydroxides are less basic than alkali metal hydroxides.
   (ii) Be resembles Al.
   (iii) The fluorides of alkaline earth & alkali metal are relatively less soluble than chlorides

Multiple Choice Questions

15. The first ionization energies of alkaline earth metals are higher than those of the alkali metals. This is because
   (a) there is an increase in the nuclear charge of the alkaline earth metals
   (b) there is a decrease in the nuclear charge of the alkaline earth metals
   (c) there is no change in the nuclear charge
   (d) None of the above
16. The first ionization energy of magnesium is lower than the first ionization energy of
   (a) lithium (b) sodium
   (c) calcium (d) beryllium
17. Some of the Group 2 metal halides are covalent and soluble in organic solvents. Among the following metal halides, the one which is soluble in ethanol is
   (a) $BeCl_2$ (b) $MgCl_2$
   (c) $CaCl_2$ (d) $SrCl_2$
18. Which of the following has correct increasing basic strength?
   (a) $MgO < BeO < CaO < BaO$
   (b) $BeO < MgO < CaO < BaO$
   (c) $BaO < CaO < MgO < BeO$
   (d) $CaO < BaO < BeO < MgO$
19. Chemical A is used for water softening to remove temporary hardness. A reacts with Na_2CO_3 to generate caustic soda. When CO_2 is bubbled through A, it turns cloudy. What is the chemical formula of A
   (a) $CaCO_3$ (b) CaO
   (c) $Ca(OH)_2$ (d) $Ca(HCO_3)_2$
20. Thermal stability of alkaline earth metal carbonates decreases in order
   (a) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$
   (b) $BaCO_3 > SrCO_3 > MgCO_3 > CaCO_3$
   (c) $CaCO_3 > SrCO_3 > MgCO_3 > BaCO_3$
   (d) None of these
21. Dehydration of hydrates of halides of calcium, barium and strontium i.e., $CaCl_2.6H_2O$, $BaCl_2.2H_2O$, $SrCl_2.2H_2O$, can be achieved by heating. These become wet on keeping in air. Which of the following statements is correct about these halides?
   (a) act as dehydrating agent
   (b) can absorb moisture from air
   (c) tendency to form hydrate decreases from calcium to barium
   (d) All of the above

22. Which of the following statements is true about $Ca(OH)_2$?
(a) It is used in the preparation of bleaching powder
(b) It is a light blue solid
(c) It does not possess disinfectant property.
(d) It is used in the manufacture of cement.

23. Amphoteric hydroxides react with both alkalies and acids. Which of the following Group 2 metal hydroxides is soluble in sodium hydroxide?
(a) $Be(OH)_2$ (b) $Mg(OH)_2$
(c) $Ca(OH)_2$ (d) $Ba(OH)_2$

24. Dead burnt plaster is
(a) $CaSO_4$ (b) $CaSO_4 \cdot \frac{1}{2}H_2O$
(c) $CaSO_4 \cdot H_2O$ (d) $CaSO_4 \cdot 2H_2O$

Exercise-2 | CONCEPTUAL MCQs

1. The one which does not show variable valency is
(a) barium (b) titanium
(c) copper (d) lead

2. Alkaline earth metals form ions of the general formula
(a) M^{2+} (b) M^{+} (c) M (d) M^{2-}

3. The number of covalent bonds formed by beryllium is
(a) 2 (b) 3 (c) 4 (d) 5

4. Alkaline earth metals show typical characteristics of
(a) inner transition elements (b) noble gases
(c) representative elements (d) transition elements.

5. The elements of group-2 are called alkaline earth metals because
(a) they are alkaline in nature
(b) they occur in earth's crust and form alkaline salts
(c) their oxides are alkaline and occur in earth's crust
(d) these are s-block elements.

6. Alkaline earth metals are
(a) reducing agents (b) oxidising agents
(c) amphoteric (d) acidic

7. Of the following, most reactive alkaline earth metal is
(a) beryllium (b) barium
(c) calcium (d) strontium

8. The oxidation state shown by alkaline earth metals is
(a) +2 (b) +1, +2 (c) –2 (d) –1, –2

9. Which of the following ions has the largest ionic radius?
(a) Be^{2+} (b) Mg^{2+}
(c) Ca^{2+} (d) Sr^{2+}

10. Density is lowest for
(a) Mg (b) Ca (c) Sr (d) Ba

11. The first ionization energies of alkaline earth metals are higher than those of the alkali metals. This is because
(a) there is an increase in the nuclear charge of the alkaline earth metals
(b) there is a decrease in the nuclear charge of the alkaline earth metals
(c) there is no change in the nuclear charge
(d) None of these

12. The first ionization potential of Mg is
(a) less than Al
(b) more than Al
(c) equal to Al
(d) can be less or more than Al

13. The first ionization potentials (eV) of Be and B respectively are
(a) 8.29, 9.32 (b) 9.32, 9.32
(c) 8.29, 8.29 (d) 9.32, 8.29

14. Which of the following has maximum ionization energy
(a) $Ba \longrightarrow Ba^{+} + e^{-}$ (b) $Be \longrightarrow Be^{+} + e^{-}$
(c) $Ca \longrightarrow Ca^{2+} + 2e^{-}$ (d) $Mg \longrightarrow Mg^{2+} + 2e^{-}$

15. The alkaline earth metals Ba, Sr, Ca and Mg may be arranged in the order of their decreasing first ionisation potential as
(a) Mg, Ca, Sr, Ba (b) Ca, Sr, Ba, Mg
(c) Sr, Ba, Mg, Ca (d) Ba, Mg, Ca, Sr

16. The first ionization energy of magnesium is lower than the first ionization energy of
(a) lithium (b) sodium
(c) calcium (d) beryllium

17. The most electropositive amongst the alkaline earth metals is
(a) beryllium (b) magnesium
(c) calcium (d) barium

18. The most electronegative alkaline earth metal is
(a) Be (b) Mg
(c) Ca (d) Ra

19. Which of the following metals has the highest melting point ?
(a) Be (b) Mg
(c) Ca (d) Ba

20. Which of the following has exceptionally high melting point
(a) MgO (b) NaOH
(c) NaCl (d) KCl

21. The compounds of alkaline earth metals have the following magnetic nature
(a) diamagnetic (b) paramagnetic
(c) ferromagnetic (d) antiferromagnetic

22. Among the alkaline earth metals, the element forming predominantly covalent compound is
(a) Ba (b) Sr
(c) Ca (d) Be

23. As the nuclear charge increases from neon to calcium, the orbital energies
(a) increase (b) increase very rapidly
(c) increase very slowly (d) decreases

24. The following compounds have been arranged in order of their increasing thermal stabilities. Identify the correct order.
K_2CO_3 (I) $MgCO_3$ (II)
$CaCO_3$ (III) $BeCO_3$ (IV)
(a) I < II < III < IV (b) IV < II < III < I
(c) IV < II < I < III (d) II < IV < III < I

25. One which is not dissolved by dilute hydrochloric acid is
(a) ZnS (b) MnS
(c) $BaCO_3$ (d) $BaSO_4$

26. The hydroxide which is best soluble in water is
(a) $Ba(OH)_2$ (b) $Mg(OH)_2$
(c) $Sr(OH)_2$ (d) $Ca(OH)_2$

27. The order solubility in water of alkaline earth metal sulphates down the group is Be > Mg > Ca > Sr > Ba. This is due to increases in
(a) ionization energy (b) melting point
(c) coordination number (d) All of these

28. Which of the following are arranged in increasing order of solubilities?
(a) $CaCO_3 < KHCO_3 < NaHCO_3$
(b) $NaHCO_3 < KHCO_3 < CaCO_3$
(c) $KHCO_3 < NaHCO_3 < CaCO_3$
(d) $CaCO_3 < NaHCO_3 < KHCO_3$

29. Which of the following is least soluble in water?
(a) $BeSO_4$ (b) $BaSO_4$
(c) $CaSO_4$ (d) $SrSO_4$

30. Which of the following sulphates has highest solubility in water?
(a) $BaSO_4$ (b) $CaSO_4$
(c) $BeSO_4$ (d) $MgSO_4$

31. The ion having highest mobility in aqueous solution is
(a) Be^{2+} (b) Mg^{2+}
(c) Ca^{2+} (d) Ba^{2+}

32. Which one of the following is least soluble in water?
(a) BaF_2 (b) MgF_2
(c) CaF_2 (d) SrF_2

33. The characteristic outer electronic configuration of alkaline earth metals is
(a) ns^1 (b) ns^2
(c) $ns^2\ np^2$ (d) $ns^2\ np^1$

34. Which of the following is strongest base?
(a) $Al(OH)_3$ (b) $Mg(OH)_2$
(c) $Ca(OH)_2$ (d) $Ba(OH)_2$

35. As the alkaline earth metals (except Be) tend to lose their valence electrons readily, they act as
(a) weak oxidising agents (b) weak reducing agents
(c) strong oxidising agents (d) strong reducing agents

36. Which of the alkaline earth metals is the strongest reducing agent?
(a) Ca (b) Sr
(c) Ba (d) Mg

37. The correct order of increasing ionic character is
(a) $BeCl_2 < MgCl_2 < CaCl_2 < BaCl_2$
(b) $BeCl_2 < MgCl_2 < BaCl_2 < CaCl_2$
(c) $BeCl_2 < BaCl_2 < MgCl_2 < CaCl_2$
(d) $BaCl_2 < CaCl_2 < MgCl_2 < BeCl_2$

38. A salt on treatment with dil. HCl gives a pungent smelling gas and a yellow precipitate. The salt gives green flame test and a yellow precipitate with potassium chromate. The salt is
(a) $NiSO_4$ (b) BaS_2O_3
(c) PbS_2O_3 (d) $CuSO_4$

39. A metal is burnt in air and the ash on moistening smells of NH_3. The metal is
(a) Na (b) Fe
(c) Mg (d) Al

40. The carbide of which of the following metals on hydrolysis gives allylene or propyne?
(a) Be (b) Ca
(c) Al (d) Mg

41. Magnesium burns in CO_2 to form
(a) MgO + C (b) MgO + CO
(c) $MgCO_3$ (d) MgO

42. Which of the following will liberate hydrogen by its reaction with hydrochloric acid?
(a) Copper (b) Phosphorus
(c) Mercury (d) Magnesium

43. Alkaline earth metals are not found free in nature because of
(a) their thermal instability
(b) their low melting points
(c) their high boiling points
(d) their greater chemical reactivity

44. Ionic hydride is not formed by
(a) Be (b) Ca
(c) Ba (d) Sr

45. Which of the following alkaline earth metal hydroxides is amphoteric in character
(a) $Be(OH)_2$ (b) $Ca(OH)_2$
(c) $Sr(OH)_2$ (d) $Ba(OH)_2$

46. A chloride dissolves appreciably in cold water. When placed on a Pt wire in Bunsen flame, no distinctive colour is noted. Which cation could be present?
(a) Be^{2+} (b) Ba^{2+}
(c) Pb^{2+} (d) Ca^{2+}

47. Halides of alkaline earth metals form hydrates such as $MgCl_2.6H_2O$, $CaCl_2.6H_2O$, $BaCl_2.2H_2O$ and $SrCl_2.2H_2O$. This shows that halides of group 2 elements
(a) are hygroscopic in nature
(b) act as dehydrating agents
(c) can absorb moisture from air
(d) All of the above

48. Which of the followng has lowest melting point?
(a) SrF_2 (b) BeF_2
(c) MgF_2 (d) CaF_2

49. Amongst LiCl, RbCl, $BeCl_2$ and $MgCl_2$ the compounds with greatest and the least ionic character, respectively, are
(a) LiCl and RbCl (b) RbCl and $BeCl_2$
(c) RbCl and $MgCl_2$ (d) $MgCl_2$ and $BeCl_2$

50. Melting point of calcium halides decreases in the order
(a) $CaF_2 > CaCl_2 > CaBr_2 > CaI_2$
(b) $CaI_2 > CaBr_2 > CaCl_2 > CaF_2$
(c) $CaBr_2 > CaI_2 > CaF_2 > CaCl_2$
(d) $CaCl_2 > CaBr_2 > CaI_2 > CaF_2$

51. Which liberates ammonia when treated with water?

(a) Li_3N (b) Mg_3N_2

(c) $CaCN_2$ (d) All of these

52. In the reaction $\underset{\text{(steam)}}{Mg + H_2O} \rightarrow X + H_2$; X is

(a) MgO (b) $Mg(OH)_2$

(c) MgH_2 (d) None of these

53. The value of x is maximum for

(a) $MgSO_4.x\,H_2O$

(b) $CaSO_4.x\,H_2O$

(c) $BaSO_4.x\,H_2O$

(d) All have the same value of x.

54. Which of the following shows high tendency to form a peroxide?

(a) Lithium (b) Beryllium

(c) Magnesium (d) Radium

55. Which of the following alkaline earth metal oxides shows a coordination number four?

(a) BeO (b) MgO

(c) SrO (d) CaO

56. The basic character of the oxides MgO, SrO, K_2O, NiO, Cs_2O increases in the order

(a) $MgO > SrO > K_2O > NiO > Cs_2O$

(b) $Cs_2O < K_2O < MgO < SrO < NiO$

(c) $NiO < MgO < SrO < K_2O < Cs_2O$

(d) $K_2O < NiO < MgO < SrO < Cs_2O$

57. Which of the following has correct increasing basic strength?

(a) MgO<BeO<CaO<BaO (b) BeO<MgO<CaO<BaO

(c) BaO<CaO<MgO<BeO (d) CaO<BaO<BeO<MgO

58. Among the following oxides, the one which is most basic is

(a) ZnO (b) MgO

(c) Al_2O_3 (d) N_2O_5

59. Which of the following peroxides is thermally most stable?

(a) SrO_2 (b) MgO_2

(c) CaO_2 (d) BaO_2

60. Mark the compound which does not contain calcium carbonate?

(a) Fluorspar (b) Iceland spar

(c) Marble (d) Limestone

61. Thermal stability of alkaline earth metal carbonates decreases in order

(a) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$

(b) $BaCO_3 > SrCO_3 > MgCO_3 > CaCO_3$

(c) $CaCO_3 > SrCO_3 > MgCO_3 > BaCO_3$

(d) None of these

62. Which of the following metal carbonates decomposes on heating ?

(a) $MgCO_3$ (b) Na_2CO_3

(c) K_2CO_3 (d) Rb_2CO_3

63. Which of the following is incorrect?

(a) Mg burns in air releasing dazzling light rich in UV rays.

(b) $CaCl_2.6H_2O$ when mixed with ice gives freezing mixture

(c) Mg cannot form complexes

(d) Be can form complexes due to its very small size

64. Chemical A is used for water softening to remove temporary hardness. A reacts with Na_2CO_3 to generate caustic soda. When CO_2 is bubbled through A, it turns cloudly. What is the chemical formula of A

(a) $CaCO_3$ (b) CaO

(c) $Ca(OH)_2$ (d) $Ca(HCO_3)_2$

65. Blanc fire used in paints is

(a) finely divided $BaSO_4$

(b) paste of $Mg(OH)_2$

(c) suspension of slaked lime

(d) $MgCl_2.5MgO.5H_2O$

66. Mg is an important component of which biomolecule occurring extensively in living world?

(a) Haemoglobin (b) Chlorophyll

(c) Florigen (d) ATP

67. A metal X on heating in nitrogen gas gives Y. Y on treatment with H_2O gives a colourless gas which when passed through $CuSO_4$ solution gives a blue colour. Y is

(a) $Mg(NO_3)_2$ (b) Mg_3N_2

(c) NH_3 (d) MgO

68. Which of the following is the component of most of the kidney stones?

(a) $(COO)_2Ca$ (b) $(COO)_2Ba$

(c) $(COONa)_2$ (d) $(COO)_2Mg$

69. A firework gives out crimson coloured light. It contains a salt of

(a) Ca (b) Na

(c) Sr (d) Ba

70. In India at the occasion of marriages, the fire works used give green flame. Which one of the following radicals may be present?

(a) Na^+ (b) K^+

(c) Ba^{2+} (d) Ca^{2+}

71. Which of the following metal ions plays an important role in muscle contraction?

(a) K^+ (b) Na^+

(c) Mg^{2+} (d) Ca^{2+}

72. White enamel of our teeth is

(a) $Ca_3(PO_4)_2$ (b) CaF_2

(c) $CaCl_2$ (d) $CaBr_2$

73. The electric cookers have a coating that protects them against fire. The coating is made of

(a) heavy lead (b) zinc oxide

(c) magnesium oxide (d) sodium sulphate

74. Which of the following is used as a scavenger in metallurgy ?

(a) Be (b) Mg

(c) Ca (d) Sr

Exercise-3 | PAST COMPETITION MCQs

1. The correct order of increasing thermal stability of K_2CO_3, $MgCO_3$, $CaCO_3$ and $BeCO_3$ is **[CBSE-PMT 2007]**

(a) $BeCO_3 < MgCO_3 < CaCO_3 < K_2CO_3$

(b) $MgCO_3 < BeCO_3 < CaCO_3 < K_2CO_3$

(c) $K_2CO_3 < MgCO_3 < CaCO_3 < BeCO_3$

(d) $BeCO_3 < MgCO_3 < K_2CO_3 < CaCO_3$

2. In which of the following the hydration energy is higher than the lattice energy? **[CBSE-PMT 2007]**

(a) $MgSO_4$ (b) $RaSO_4$

(c) $SrSO_4$ (d) $BaSO_4$

3. Which of the following oxides is **not** expected to react with sodium hydroxide? **[CBSE-PMT 2009]**

(a) CaO (b) SiO_2

(c) BeO (d) B_2O_3

4. Which of the following alkaline earth metal sulphates has hydration enthalpy higher than the lattice enthalpy? **[CBSE-PMT 2010]**

(a) $CaSO_4$ (b) $BeSO_4$

(c) $BaSO_4$ (d) $SrSO_4$

5. Property of the alkaline earth metals that increases with their atomic number is **[CBSE-PMT 2010]**

(a) solubility of their hydroxides in water

(b) solubility of their sulphates in water

(c) ionization energy

(d) electronegativity

6. The compound A on heating gives a colourless gas and a residue that is dissolved in water to obtain B. Excess of CO_2 is bubbled through aqueous solution of B, C is formed which is recovered in the solid form. Solid C on gentle heating gives back A. The compound is **[CBSE-PMT 2010]**

(a) $CaSO_4.2H_2O$ (b) $CaCO_3$

(c) Na_2CO_3 (d) K_2CO_3

7. Which of the following compounds has the lowest melting point ? **[CBSE-PMT 2011]**

(a) $CaCl_2$ (b) $CaBr_2$

(c) CaI_2 (d) CaF_2

8. Which one of the following is present as an active ingredient in bleaching powder for bleaching action ? **[CBSE-PMT 2011]**

(a) $CaOCl_2$ (b) $Ca(OCl)_2$

(c) CaO_2Cl (d) $CaCl_2$

9. Match List – I with List –II for the compositions of substances and select the correct answer using the code given below the lists : **[CBSE-PMT 2011M]**

List - I **Substances**	**List - II** **Composition**
(A) Plaster of paris	(i) $CaSO_4.2H_2O$
(B) Epsomite	(ii) $CaSO_4.\frac{1}{2}H_2O$
(C) Kieserite	(iii) $MaSO_4.7H_2O$
(D) Gypsum	(iv) $MgSO_4.H_2O$
	(v) $CaSO_4$

Code :

	(A)	(B)	(C)	(D)
(a)	(iii)	(iv)	(i)	(ii)
(b)	(ii)	(iii)	(iv)	(i)
(c)	(i)	(ii)	(iii)	(v)
(d)	(iv)	(iii)	(ii)	(i)

10. Equimolar solutions of the following substances were prepared separately. Which one of these will record the highest pH value ? **[CBSE-PMT 2012S]**

(a) $BaCl_2$ (b) $AlCl_3$

(c) LiCl (d) $BeCl_2$

11. A metal M readily forms its sulphate MSO_4 which is water-soluble. It forms its oxide MO which becomes inert on heating. It forms an insoluble hyroxide $M(OH)_2$ which is soluble in NaOH solution. Then M is **[AIEEE 2002]**

(a) Mg (b) Ba

(c) Ca (d) Be.

12. The solubilities of carbonates decrease down the magnesium group due to a decrease in **[AIEEE 2003]**

(a) hydration energies of cations

(b) inter-ionic attraction

(c) entropy of solution formation

(d) lattice energies of solids

13. In curing cement plasters water is sprinkled from time to time. This helps in **[AIEEE 2003]**

(a) developing interlocking needle-like crystals of hydrated silicates

(b) hydrating sand and gravel mixed with cement

(c) converting sand into silicic acid

(d) keeping it cool

14. Which of the following on thermal decomposition yields a basic as well as acidic oxide ? **[AIEEE 2012]**

(a) $NaNO_3$ (b) $KClO_3$

(c) $CaCO_3$ (d) NH_4NO_3

Exercise-4 | Applied MCQs

1. Plaster of Paris hardens by
(a) giving off CO_2 (b) changing into $CaCO_3$
(c) uniting with water (d) giving out water

2. Hesenclever's process is a method for the manufacture of
(a) NaOH (b) HNO_3
(c) H_2SO_4 (d) Bleaching powder

3. Oxygen is obtained from bleaching powder by
(a) the action of dilute acid (d) the action of alkali
(c) heating it with lime (d) heating it with cobalt salt

4. Portland cement does not contain
(a) $CaSiO_4$ (b) Ca_2SiO_5
(c) $Ca_2Al_2O_6$ (d) $Ca_3(PO_4)_2$

5. Alkaline earth metal compounds are less soluble in water than corresponding alkali metal compounds because former have
(a) lower lattice energy (b) higher I.P.
(c) higher covalent character (d) lower covalent character.

6. Magnesium wire burns in the atmosphere of CO_2 because
(a) Magnesium acts as an oxidising agent
(b) Magnesium has 2 electrons in the outermost orbit.
(c) Magnesium acts as a reducing agent and removes oxygen from CO_2
(d) None of these

7. When hydrated $MgCl_2 . 6H_2O$ is strongly heated
(a) MgO is formed (b) $Mg(OH)_2$ is formed
(c) Mg(OH)Cl is formed (d) Anhydrous $MgCl_2$ is formed

8. Which component of cement sets at the slowest rate
(a) Dicalcium silicate
(b) Tricalcium silicate
(c) Tricalcium aluminate
(d) Tetracalcium aluminoferrite

9. The cation which forms a yellow precipitate with potassium chromate in acetic acid is
(a) NH_4^+ (b) Ba^{2+} (c) Ca^{2+} (d) Na^+

10. The ionic carbide is
(a) CaC_2 (b) CaO
(c) $Ca(OH)_2$ (d) $Ca(HCO_3)_2$

11. Which category of salts of alkaline earth metals is not found in solid sate, but found in solution state?
(a) Carbonates (b) Bicarbonates
(c) Hydroxides (d) Sulphates

12. BeF_2 is soluble in water whereas fluorides of other alkaline earth metals are insoluble because of
(a) ionic nature of BeF_2
(b) covalent nature of BeF_2
(c) greater hydration energy of Be^{2+} ion as compared to its lattice energy
(d) None of these

13. Electrolysis of fused KCl. $MgCl_2 . 6H_2O$ gives
(a) potassium only
(b) magnesium only
(c) magnesium and chlorine
(d) potassium, magnesium and chlorine

14. Mixture of $MgCl_2$ and MgO is called
(a) Portland cement (b) Sorel's cement
(c) Double salt (d) None of these

15. The metals A and B form oxide but B also forms nitride when both burn in air. The A and B are
(a) Cs, K (b) Mg, Ca
(c) Li, Na (d) K, Mg

16. Magnesium form Mg^{2+} and Mg^+ because :
(a) ionic radius of Mg(II) is smaller than of Mg(I).
(b) hydration energy of divalent magnesium ion is higher.
(c) magnesium (II) carbonate is insoluble in water.
(d) generally higher oxidation states are preferred by metals.

17. Setting of plaster of paris involves :
(a) combination with atmospheric CO_2
(b) oxidation with atmospheric oxygen
(c) hydration to yield another hydrate
(d) dehydration.

18. One of the important use of quick lime is
(a) in bleaching silk (b) in drying gases & alcohol
(c) in dyeing cotton (d) as a purgative.

19. Disodium hydrogen phosphate in presence of NH_4Cl and NH_4OH gives a white precipitate with a solution of Mg^{2+} ion. The precipitate is :
(a) $MgNH_4PO_4$ (b) $MgHPO_4$
(c) $Mg(H_2PO_4)_2$ (d) $Mg_3(PO_4)_2$

20. The metal X is prepared by the electrolysis of fused chloride. It reacts with hydrogen to form a colourless solid from which hydrogen is released on treatment with water. The metal is :
(a) Ca (b) Al (c) Zn (d) Cu

21. Amongst the following hydroxides, the one which has the lowest value of K_{sp} is :
(a) $Ca(OH)_2$ (b) $Mg(OH)_2$ (c) $Be(OH)_2$ (d) $Ba(OH)_2$

22. Beryllium shows diagonal relationship with aluminium. Which of the following similarity is incorrect ?
(a) Be forms beryllates and Al forms aluminates
(b) $Be(OH)_2$ like $Al(OH)_3$ is basic.
(c) Be like Al is rendered passive by HNO_3.
(d) Be_2C like Al_4C_3 yields methane on hydrolysis.

23. A gas reacts with CaO and not with $NaHCO_3$ is :
(a) Cl_2 (b) CO_2 (c) N_2 (d) O_2

24. Substance which absorbs CO_2 and violently reacts with H_2O with sound is :
(a) H_2SO_4 (b) $CaCO_3$ (c) ZnO (d) CaO.

25. When Zeolite, (hydrated sodium Aluminium silicate), is treated with hard water, the sodium ions are exchanged with:
(a) SO_4^{2-} ions (b) H^+ ions
(c) OH^- ions (d) Ca^{2+} ions

Hints & Solutions

EXERCISE 1

1. Gypsum is added to retard the rate of setting of cement.
2. Anhydrous $CaSO_4$ can absorb water to form $CaSO_4 . 2H_2O$. Plaster of paris is not used as a drying agent because it sets into a hard mass by absorbing water.
3. Caves in limestone regions get formed due to the dissolution of calcium carbonate in water containing carbon dioxide.
4. This is because alkaline earth metals have smaller size and higher nuclear charges as compared to alkali metals.
5. By treating quick lime with water, slaked lime is formed.
7. (i) $3Ca(s) + N_2(g) \longrightarrow Ca_3N_2(s)$

   (ii) $Ca(s) + H_2SO_4(aq) \longrightarrow CaSO_4(aq) + H_2(g)$

   (iii) $2Ca(s) + SO_2(g) \longrightarrow 2CaO\,(s) + S(s)$

   (iv) $Ca(s) + 2H_2O\,(\ell) \longrightarrow Ca(OH)_2(aq) + H_2(g)$
8. (i) Plaster of paris quickly solidifies to gypsum with the evolution of heat and also expands slightly.

   (ii) $CaSO_4 . 2H_2O \xrightarrow{473K} \underset{\text{Dead burnt plaster}}{CaSO_4} + 2H_2O$
9. (i) $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2$

   (ii) $Be(OH)_2 < Mg(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

   (iii) $BaSO_4 < SrSO_4 < CaSO_4 < BeSO_4$.
12. Both Na and K can react with water. But Na also reacts with alcohol whereas calcium does not or react slowly.

15. (a) **16.** (d) **17.** (a) **18.** (b) **19.** (c)

20. (a) **21.** (d) **22.** (a) **23.** (a) **24.** (a)

EXERCISE 2

1. (a) Barium shows fixed valency whereas Ti and Cu (transition metals) and Pb (due to inert pair effect) show variable valency.

2. (a)

3. (a) Since Be has two valence electrons, it forms only two covalent bonds.

4. (c)

5. (c) Their oxides are alkaline and occur in earth's crust.

6. (a) Because of low I.E. and high hydration energies.

7. (b) Ba is most electropositive amongst the listed and hence most reactive.

8. (a) **9. (d)**

10. (b) Ca contains vacant 3d orbitals which leads much increase in atomic volume of the element hence has the lowest density.

11. (a)

12. (b) Mg has more IE_1 than Al since the electron has to be removed from completely filled s-valence shell of Mg.

13. (d) **14. (d)** **15. (a)** **16. (d)**

17. (d) **18. (a)**

19. (a) Being small and hard, Be atoms pack closely in the lattice and hence Be has the highest m.pt.

20. (a) Higher the charge on the ions, greater is the lattice energy and hence higher the m.pt. of the ionic solid.

21. (a) M^{2+} ions are present in alkaline earth metal compounds thus leaving all paired electrons in (n-1) s^2p^6 configuration and are diamagnetic.

22. (d)

23. (d) After neon (At No-18), the next electron enters into 4s orbital which has lower energy than 3d orbitals.

24. (b) **25. (d)** **26. (a)**

27. (c) In crystalline sulphates, the co-ordination number of the ions increases from Be to Ba and so also the lattice energy hence solubility in H_2O decreases.

28. (d) Lesser the lattice energy, more will be the solubility in H_2O.

29. (b) **30. (c)**

31. (d) Ba^{2+} is least hydrated hence its size becomes lesser than any other hydrated alkaline earth metal cation and therefore has the highest ionic mobility.

32. (b) As we move down the group, the lattice energies of fluorides decrease more rapidly than the hydration energy and hence the solubilities of the fluorides increase from top to bottom within a group.

33. (b) **34. (d)**

35. (d) Lower the I.E. or higher the negative electrode potential, stronger is the reducing agent.

36. (c) **37. (a)**

38. (b) Since the salt on treatment with dil. HCl gives a pungent smelling gas (SO_2) and a yellow ppt., it must contain $S_2O_3^{2-}$ (thiosulphate ion) and further since it gives green flame test, it must contain Ba^{2+} ion. Hence salt is BaS_2O_3.

39. (c) Mg burns in air to form Mg_3N_2 which then reacts with H_2O to form NH_3.

40. (d) **41. (a)**

42. (d) Since the electrode potential of Mg is lower than that of hydrogen (E° = 0.0 volt), it will reduce H^+ ions to H_2 gas.

43. (d)

44. (d) BeH_2 is covalent.

45. (a) $Be(OH)_2$ is amphoteric while $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$ are all basic.

46. (a) Due to very high I.E. of Be, its valence electrons require high energy to remove (excite) which is not available in Bunsen flame hence Be^{2+} ions do not impart colour to the flame.

47. (d)

48. (b) BeF_2 being covalent has the lowest melting point (800ºC) while all other fluorides melt around 1300ºC

49. (b)

50. (a) As the size of the anion increases, the covalent character increases and hence the mp. decrease.

51. (d) All nitrides react with H_2O to give NH_3 but $CaCN_2$ also react with H_2O to give NH_3.

$$CaNCN + 3H_2O \longrightarrow CaCO_3 + NH_3$$

52. (a) $Mg(OH)_2$ is not formed because of poor solubility of MgO in H_2O.

53. (a) Because of smaller size, Mg^{2+} ions are extensively hydrated.

54. (d) Larger the size of the atom, larger is the tendency to form peroxides.

65. (a) **56. (c)**

57. (b) The basic character of oxides increases down the group.

58. (b) N_2O_5 is strongly acidic, ZnO and Al_2O_3 are amphoteric, therefore, MgO is most basic.

59. (d) The stability of the peroxide increases as the size of the metal increases.

60. (a) Fluorspar is CaF_2 while other compounds listed are different crystalline forms of $CaCO_3$.

61. (a)

62. (a) $MgCO_3$ decomposes on heating to give MgO and CO_2 while alkali metal carbonates do not.

63. (c)

64. (c) $$\underset{\text{temp. hardness}}{Ca(HCO_3)_2} + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$\underset{A}{Ca(OH)_2} + Na_2CO_3 \longrightarrow \underset{\text{Caustic soda}}{2NaOH} + CaCO_3$$

$$\underset{A}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\text{milkiness}}{CaCO_3 \downarrow} + H_2O$$

65. (a) **66. (b)**

67. (b) $$\underset{X}{3Mg} + N_2 \xrightarrow{\Delta} \underset{Y}{Mg_3N_2};$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + \underset{\text{(colourless)}}{2NH_3 \uparrow}$$

$$CuSO_4 + 4NH_3 \longrightarrow \underset{\text{Blue complex}}{[Cu(NH_3)_4]SO_4}$$

68. (a) **69. (c)** **70. (c)** **71. (d)** **72. (b)**

73. (c) MgO being high melting does not catch fire and hence protects the cooker against fire.

74. (c)

EXERCISE 3

1. (a) As the basicity of metal hydroxides increases down the group from Be to Ba, the thermal stability of their carbonates also increases in the same order. Further group 1 compounds are more thermally stable than group 2 because their hydroxide are much basic than group 2 hydroxides therefore, the order of thermal stability is

$BeCO_3 < MgCO_3 < CaCO_3 < K_2CO_3$.

2. (a) In alkaline earth metals ionic size increases down the group. The lattice energy remains constant because sulphate ion is so large, so that small change in cationic sizes do not make any difference. On moving down the group the degree of hydration of metal ions decreases very much leading to decrease in solubility

$\therefore\ BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

3. (a) NaOH is a strong alkali. It combines with acidic and amphoteric oxides to form salts. Since CaO is a basic oxide hence does not reacts with NaOH.

4. (b) Be^{2+} is very small, hence its hydration enthalpy is greater than its lattice enthalpy

5. (a) Lattice energy decreases more rapidly than hydration energy for alkaline earth metal hydroxides. On moving down a group $\therefore$ solubility of their hydroxides increases.

6. (b) $$\underset{A}{CaCO_{3(s)}} \xrightarrow{\Delta} \underset{\text{colourless}}{CO_{2(g)}} \uparrow + \underset{B}{CaO_{(s)}}$$

$$\underset{B}{CaO_{(s)}} + H_2O \longrightarrow Ca(OH)_{2(aq)}$$

$$Ca(OH)_2 + 2CO_2 \longrightarrow \underset{C}{Ca(HCO_3)_{2(aq)}}$$

$$Ca(HCO_3)_{2(s)} \longrightarrow \underset{A}{CaCO_{3(s)}} + CO_{2(g)} + H_2O_{(g)}$$

$\therefore$ **Correct choice : (b)**

7. (c) Melting points of halides decreases as the size of the halogen increases. The correct order is

$CaF_2 > CaCl_2 > CaBr_2 > CaI_2$

8. (b) Active ingredient in bleaching powder for bleaching action is $Ca(OCl)_2$

9. (b) (A) Plaster of paris $= CaSO_4 \cdot \frac{1}{2} H_2O$

(B) Epsomite $= MgSO_4.7H_2O$

(C) Kieserite $= MgSO_4.H_2O$

(D) Gypsum $= CaSO_4.2H_2O$

10. (a) ($AlCl_3$, LiCl & $BeCl_2$)) all these solutions are acidic due to cationic hydrolysis, whereas $BaCl_2$, is salt of strong base and strong acid, hence its solution will almost neutral i.e., pH ≈ 7.

11. (d) Beryllium shows anomalous properties due to its small size.

12. (a) The solubility is governed by $\Delta H_{\text{solution}}$

i.e. $\Delta H_{\text{solution}} = \Delta H_{\text{lattice}} - \Delta H_{\text{Hydration}}$

Due to increase in size the magnitude of hydration energy decreases and hence the solubility.

13. (a) Setting of cement is exothermic process which develops interlocking crystals of hydrated silicates

14. (c) Calcium carbonate on thermal decomposition gives CaO (Basic oxide) and CO_2 (Acidic oxide)

$$CaCO_3 \xrightarrow{\Delta} \underset{\text{Basic oxide}}{CaO} + \underset{\text{Acidic oxide}}{CO_2\uparrow}$$

EXERCISE 4

1. (c) Plaster of Paris reacts with water to form gypsum which is hard.

$$CaSO_4.1/2\ H_2O + 3/2\ H_2O \rightarrow CaSO_4.2H_2O$$

2. (d) Hasenclever and Batchmann's plants are used for the manufacture of bleaching powder (See theory).

3. (a) $2CaOCl_2 + \text{dil.}H_2SO_4 \rightarrow CaCl_2 + CaSO_4 + 2HClO$

$HClO \rightarrow HCl + O$

4. (d) Portland cement is a complex mixture of silicates and aluminates of Ca.

5. (c) The higher the covalent character, the lower the solubility of compound in water.

6. (c) Mg is more reducing in nature than carbon

$CO_2 + 2Mg \rightarrow 2MgO + C$

7. (a) $MgCl_2.6H_2O \xrightarrow{\Delta} MgCl_2.2H_2O \xrightarrow{\Delta}$

$$Mg(OH)Cl \longrightarrow MgO + HCl$$

8. (a) Dicalcium silicate sets at the lowest rate.

9. (b) Ba^{++} with CrO_4^{--} give yellow $BaCrO_4$. It is insoluble in CH_3COOH.

10. (a) CaC_2 calcium carbide is ionic $\left(Ca^{2+}C_2^{2-}\right)$.

11. (b) The bicarbonates of alkaline earth metals exist in solution only

12. (c) Be^{2+} being small in size is heavily hydrated and heat of hydration exceeds the lattice energy. Hence BeF_2 is soluble in water.

13. (d) K and Mg are formed at cathode

$$K^+ + e^- \rightarrow K, Mg^{2+} + 2e^- \rightarrow Mg\ .$$

Chlorine is formed at anode $2\bar{Cl} - 2e^- \rightarrow Cl_2$.

14. (b) The mixture of $MgCl_2$ and MgO is known as sorel's cement.

15. (d) K and Mg, both form oxides

$$K + O_2 \rightarrow KO_2; 2Mg + O_2 \rightarrow 2MgO$$

Mg form nitride also $3Mg + N_2 \rightarrow Mg_3N_2$

K does not form nitride.

16. (b) Statement (b) is correct.

17. (c) $\underset{\text{Plaster of paris}}{CaSO_4.\frac{1}{2}H_2O} \xrightarrow{\text{setting}} \underset{\text{Gypsum (orthorhombic)}}{CaSO_4.2H_2O}$

$$\xrightarrow{\text{hardening}} \underset{\text{Gypsum (monoclinic)}}{CaSO_4.2H_2O}$$

18. (b) CaO (Quick lime) is hygroscopic in nature.

19. (a) $Mg^{++} + Na_2HPO_4 + NH_4OH$

$$\longrightarrow \underset{\text{White ppt}}{Mg(NH_4)PO_4} + 2Na^+ + H_2O$$

20. (a) $Ca + H_2 \longrightarrow CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + H_2$

21. (c) $Be(OH)_2$ is insoluble in water and thus has lowest value of K_{sp}.

22. (b) The $Be(OH)_2$ and $Al(OH)_3$ are amphoteric in nature.

23. (b) $CaO + CO_2 \longrightarrow CaCO_3$.

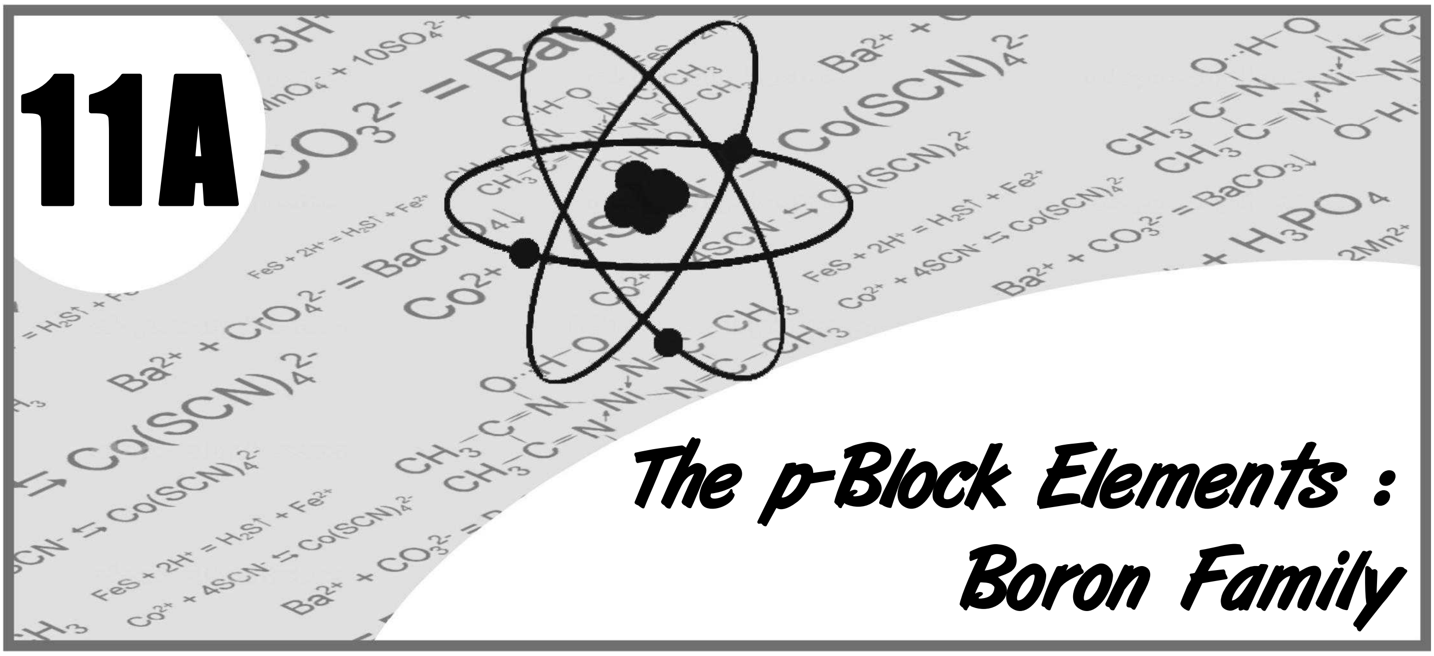
But the CO_2 does not react with $NaHCO_3$.

24. (d) $CaO + CO_2 \longrightarrow CaCO_3$

$CaO + H_2O \longrightarrow Ca(OH)_2$

hissing sound and $\Delta H = -ve$

25. (d) $Na_2Z + Ca^{2+} \longrightarrow CaZ + 2Na^+$



11A

The p-Block Elements : Boron Family

The elements of group 13 are

B - Boron	Al - Aluminium	Ga - Gallium
In - Indium	Tl - Thallium	

Amongst the elements of this group, Al is the third most abundant element found in the earth's crust after oxygen and silicon.

GENERAL CHARACTERISTICS (i.e., PHYSICAL PROPERTIES) OF BORON FAMILY :

(i) ***Electronic configuration :*** The elements of group 13 belong to p-block of the periodic table and these elements contain three electrons in the valence shell, therefore, their valence shell electronic configuration is ns^2np^1.

Element	At. No.	Electronic Confg.	Valence Shell Confg.
B	5	[He] $2s^2$, $2p^1$	$2s^22p^1$
Al	13	[Ne] $3s^2$, $3p^1$	$3s^23p^1$
Ga	31	$[Ar]^3$ $3d^{10}$, $4s^24p^1$	$4s^24p^1$
In	49	[Kr] $4d^{10}$, $5s^25p^1$	$5s^25p^1$
Tl	81	[Xe] $4f^{14}$, $5d^{10}$, $6s^2p^1$	$6s^26p^1$

(ii) ***Atomic radii and ionic radii :***

(a) Atoms and their ions of group 13 elements have smaller size than those of alkaline earth metals of group-2, due to greater nuclear charge of former group than latter group.

(b) Atomic radii increase on going down in the group with an abnormaly at gallium and the unexpected decrease in the atomic size of Ga is due to the presence of electrons in d- orbitals which do not screen the nucleus effectively.

(c) The ionic radii regularly increases from B^{3+} to Tl^{3+}

(iii) ***Density :*** It increases regularly on moving down the group from B to Tl

(iv) ***Melting and boiling points :***

(a) M.P. and b. p. of group 13 elements are much higher than those of group 2 elements

Element	B	Al	Ga	In	Tl
M.p. (K)	2453	933	303	430	576
B.p. (K)	3923	2740	2676	2353	1730

(b) The m. p. decreases from B to Ga and then increases, due to structural changes in the elements

(c) Boron has a very high m. p. because of its three dimensional (B_{12}- **icosahedral**) structure in which B atoms are held together by strong covalent bonds.

(d) Low m. p. of Ga is due to the fact that it consists of only Ga_2 molecules, and Ga remains liquid upto 2273K therefore it is used in high temperature thermometry.

(v) ***Ionisation energy :***

(a) The first I.E. values of group 13 elements are lower than the corresponding values of the alkaline earth metals, due to the fact that removal of electron is easy in former case (p-electron) than latter (s-electron)

This results in the increase of nuclear charge. Consequently the valence electrons are more tightly held leading to high I.E. Similarly we can explain the irregularity in case of Tl on the basis of ineffective shielding of intervening electrons

(b) On moving down the group IE, decreases from B to Al but the next element Ga has slightly higher IE, than Al, it again decreases in In and increases in the last element Tl as follows :

Element	B	Al	Ga	In	Tl
IE, (kJ mol^{-1})	800	577	578	558	590

(c) The irregularity observed in case of Gallium is due to the ineffective shielding of nuclear charge because of intervening d electrons, which cause the increase in nuclear charge leading to high I.E.

(vi) Inert pair effect :

(a) It is the reluctance of the s-electrons of the valence shell to take part in bonding and occurs due to ineffective shielding of the ns^2 electrons by the intervening d and f electrons.

(b) It increases down a group and thus the lower elements of group show lower oxidation states.

(vii) Oxidation states :

(a) B and Al show an oxidation state of +3 only while Ga, In and Tl show oxidation states of both +1 and +3.

(b) As we move down in the group 13, due to inert pair effect, the tendency to achieve +3 oxidation state goes on decreasing and the tendency to acquire +1 oxidation state goes on increasing.

(c) Stability of +1 oxidation state follows the order Ga < In < Tl

(d) Tl^+ compounds are more stable than Tl^{3+} compounds.

(viii) Electropositive (metallic) character :

(a) These elements are less electropositive than the elements of the group 1 and 2 due to their smaller size and higher ionisation energies.

(b) On moving down the group, the electropositive character first increases from B to Al and then decreases from Ga to Tl, due to the presence of d and f orbitals in latter elements.

(ix) Reducing character : It decreases down the group from Al to Tl because of the increase in electrode potential values for M^{3+}/M. Therefore it follows the order.

$$Al > Ga > In > Tl$$

Element B	**Al**	**Ga**	**In**	**Tl**
E^o (V) at 298 K for M^{3+}/M	–1.66	–0.56	–0.34	+1.26

(x) Complex formation : Due to their smaller size and greater charge, these elements have greater tendency to form complexes than the s-block elements.

(xi) Nature of compounds :

(a) The tendency of formation of ionic compounds increases from B to Tl.

(b) Boron forms only covalent compounds where as Al can form both covalent (e.g., anhydrous $AlCl_3$) and ionic compounds (e.g., hydrated $AlCl_3$) because when anhydrous $AlCl_3$ is hydrated, the hydration energy released is sufficient to overcome the ionisation energy of Al.

(c) Gallium forms mainly ionic compounds although anhydrous $GaCl_3$ is covalent .

CHEMICAL PROPERTIES :

Crystalline B is unreactive whereas amorphous B is reactive. It reacts with air at 700ºC as follows :

(a) $4B + 3O_2 \rightarrow 2B_2O_3$;
$2B + N_2 \rightarrow 2BN$

(b) Al is stable in air due to the formation of protective oxide film. Some properties are given below

(i) Action of Air :

(a) $4Al + 3O_2 \rightarrow 2\,Al_2O_3$

(b) Thallium is more reactive than Ga and In, due to the formation of unipositive ion Tl^+.

$$4Tl + O_2 \rightarrow 2\,Tl_2O$$

(ii) Reaction with nitrogen : The elements of group 13 form their corresponding nitrides with the reaction of nitrogen. These nitrides undergo hydrolysis with steam and evolve NH_3

$$2B + N_2 \xrightarrow{\Delta} \underset{\text{Boron nitride}}{2BN}$$

$$2Al + N_2 \xrightarrow{\Delta} \underset{\text{Aluminium nitride}}{2AlN}$$

$$BN + 3H_2O \rightarrow \underset{\text{orthoboric acid}}{H_3BO_3} + NH_3$$

(iii) Action of water :

(a) Both B and Al do not react with water but amalgamated aluminium does react with H_2O evolving H_2.
$2Al(Hg) + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 + Hg$
Aluminium amalgam

(b) Ga and In do not react with pure cold or hot water but Tl forms an oxide on the surface.

(iv) Reaction with alkalies :

(a) Boron dissolves in alkalies on fusion and gives borates.

$$2B + 6NaOH \xrightarrow{\text{fuse}} 2Na_3BO_3 + 3H_2$$

(b) Al and Ga dissolve in concentrated alkalies on heating and form meta-aluminate and gallate respectively.

$$Al + 2NaOH + 2H_2O \xrightarrow{\Delta} \underset{\text{Sod. metaaluminate}}{2NaAlO_2} + 3H_2$$

$$Ga + 2NaOH + 2H_2O \xrightarrow{\Delta} \underset{\text{Sod. gallate}}{2NaGaO_2} + 3H_2$$

(v) Reaction with carbon :

(a) B and Al form carbides with carbon on heating.

$$4B + C \xrightarrow{\Delta} \underset{\text{Boron carbide}}{B_4C} \quad ;$$

$$4Al + 3C \longrightarrow \underset{\text{Aluminium carbide}}{Al_4C_3}$$

(b) Aluminium carbide is ionic and forms methane with water, while boron carbide is covalent having molecular formula $B_{12}C_3$ and it is very hard, hence used as an abrasive.

(vi) Hyrides :

(a) Elements of group 13 do not combine directly with H_2 to form hydrides, therefore, their hydrides have been prepared by indirect methods for example.

$$BF_3 + 3LiBH_4 \xrightarrow{\text{dry ether}} \underset{\text{diborane}}{2B_2H_6} + 3LiF$$

(b) Boron forms a number of hydrides which are called boranes with general formula B_nH_{n+4}(e.g., B_2H_6) and B_nH_{n+6} (e.g., B_4H_{10})

(c) Boranes catch fire in the presence of oxygen with the evolution of heat energy

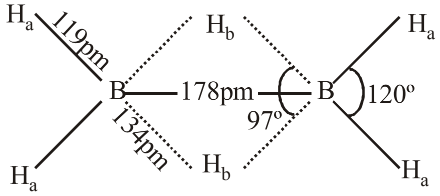
$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O\ ;\ \Delta H = -2008$ kg/mol

(d) Boranes are hydrolysed by water as follows :

$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$

(e) Boranes are quite stable but the stability of hydrides of Al, Ga, In, and Tl decreases on moving down the group because the strength of the M–H bond decreases with increasing size of the element.

(f) ***Structure of diborane*** *:* The simplest boron hydride, i.e. BH_3 does not exist as such but exists as a dimer, B_2H_6, having following structure



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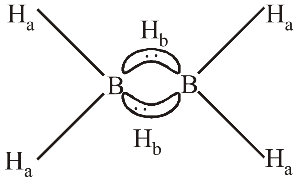


In above structure B atoms are in sp^3 hybrid state. There are six B-H bonds out of which four B-H_a bonds are normal convalent bonds (two centre electron - pair bonds i.e, 2c–2e) present in the same plane while rest two B-H_b bonds behave as bridges containing three centre two electron pairs bonds i.e., 3c–2e (known as banana bonds) and present above and below the plane of the molecules which do not have sufficient number of electrons to form normal covalent bonds are called electron - deficient molecules. Ex. B_2H_6.

(g) Aluminium forms a polymeric hydride of general formula $(AlH_3)_x$ which decomposes into its elements on heating.

(h) B, Al and Ga form complex anionic hydrides, like lithium borohydride, $Li[BH_4]$, lithium aluminium hydride , $Li[AlH_4]$ etc. due to the presence of a vacant p-orbital in their outermost shells which accepts electron pair from H^- ion.

$XH_3 + H^- \rightarrow [XH_4]^-$ where X= B, Al and Ga.

(vii) Oxides :

(a) Except Tl all the elements of group 13 form oxides (general formula, M_2O_3) on heating with oxygen

$$4M + 3O_2 \xrightarrow{\Delta} 2M_2O_3\ (M = B \text{ to In})$$

(b) Tl forms thallium (I) oxide, Tl_2O which is more stable than thallium (III) oxide, Tl_2O_3 because of inert pair effect.

(c) B_2O_3 and Al_2O_3 can also be prepared by following method :

$$\underset{\text{orthoboric acid}}{2H_3BO_3} \xrightarrow[-2H_2O]{373K} \underset{\text{Metaboric acid}}{2HBO_2}$$

$$\xrightarrow{\text{red heat}} \underset{\substack{\text{Boric acid}\\ \text{or boron sesquioxide or}\\ \text{Boric anhydride}}}{B_2O_3} + H_2O$$

$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

$4Al(NO_3)_3 \rightarrow 2Al_2O_3 + 12NO_2 + 3O_2$

(d) The hardest alumina, α–Al_2O_3, which is stable at high temperature, resistant to hydration and attacked by acids, is called corundum and is used as an abrasive where as γ –Al_2O_3 is known as activated alumina and used in column chromatography.

(viii) Hydroxides :

Amalgamated aluminium reacts with H_2O and forms its hydroxide.

$$\underset{\text{Aluminium amalgam}}{2Al(Hg)} + 6H_2O \rightarrow Al(OH)_3 + 3H_2 + Hg$$

However, $B(OH)_3$ can also be prepared by the reaction of B_2O_3 and H_2O

$B_2O_3 + 3H_2O \rightarrow 2B(OH)_3 + 2H_3BO_3$

(ix) Nature of oxides and hydroxides :

(a) $B(OH)_3$ or H_3BO_3 is soluble in water, whereas all other hydroxides are practically insoluble in water.

(b) On moving down the group, there is a change from acidic to amphoteric and then to basic character of oxides and hydroxides of group 13 elelments.

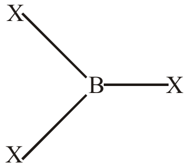
(x) Preparation of halides :

(a) All the elements of boron family (except thallium which forms thallous monohalides) form trihalides of type MX_3 where X= F, Cl, Br and I.

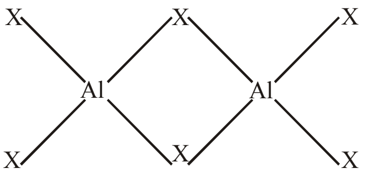
$B_2O_3 + 3C + 3Cl_2 \rightarrow 2BCl_3 + 3CO$

$Al_2O_3 + 3C + 3Cl_2 \rightarrow 2AlCl_3 + 3CO$

(b) All the boron trihalides, BX_3 and aluminium trihalides AlX_3 (except AlF_3 which is ionic) are covalent compounds whereas former exist as only monomers and latter as dimers, because boron atom is too small to co-ordinate with four large halide ions and in case of much smaller F^- ion , the energy released during the formation of the bridge structure is not sufficient for the cleavage of the typical pπ-pπ bond in BF_3.



BX_3



Al_2X_6

(c) BF_3 is a colourless gas, BCl_3 and BBr_3 are colourless fuming liquids whereas BI_3 is a white fusible solid at room temperature.

(d) The covalent character of trihalides decreases on moving from Ga to Tl.

(e) Hybridisation of Boron in BCl_3 is sp^2

(xi) Nature of Trihalies :

(a) Trihalides of group 13 elements behave as lewis acids due to having a strong tendency to accept a pair of electrons.

(b) The relative strength of lewis acids of boron trihalides increases in the order :

$$BF_3 < BCl_3 < BBr_3 < BI_3.$$

(c) The halides of group 13 elements behave as lewis acids and the acidity character decreases as follows:

$$BX_3 > AlX_3 > GaX_3 > InX_3 \text{ (where X=Cl, Br or I)}$$

(d) BF_3 and anhydrous $AlCl_3$ are used as a catalyst in Friedel Crafts reactions.

(e) $TlCl_3$ decomposes to TlCl and Cl_2 above 40ºC and hence acts as an oxidising agent, whereas $TlBr_3$ converts into $Tl[TlBr_4]$ at room temperture.

$$TlCl_3 \xrightarrow[>40^\circ C]{\Delta} TlCl + Cl_2; \quad 2TlBr_3 \rightarrow Tl[TlBr_4] + Br_2$$

While TlI_3 is an ionic compound containing Tl(I) and I_3^- ions.

ANOMALOUS BEHAVIOUR OF BORON :

Boron shows anomalous behaviour as compared to other member of the group, due to the following reasons.

(i) It has smallest size in the group.

(ii) It has high ionisation energy.

(iii) It has highest electronegativity in the group.

(iv) It does not have any vacant d-orbital in valance shell

A few points of difference are :

(i) It is a non-metal while other members of the group are metallic in character.

(ii) It shows allotropy as crystalline and amorphous while other members do not.

(iii) It has the highest m. p. and b.p. amongst the elements of group 13.

(iv) It forms only covalent compounds while other members form both ionic and covalent compounds.

(v) It forms a number of hydrides which are quite stable while those of other members are less stable.

(vi) The halides of boron exist as monomers while $AlCl_3$ exists as a dimer.

(vii) The oxides and hydroxides of boron are weak acidic while those of aluminium are amphoteric and those of other elements are basic.

(viii) It does not react with steam but other elements decompose steam.

(ix) It can be oxidised by concentrated HNO_3 while aluminium is passive due to the formation of oxide layer on the surface.

$$2B + 6HNO_3 \rightarrow \underset{\text{Boric acid}}{2H_3BO_3} + 6NO_2$$

DIAGONAL RELATIONSHIP BETWEEN BORON AND SILICON :

Boron shows resemblance with its diagonal element silicon of group 14. Some of the important points are given below :

(i) Both B and Si are non- metals.

(ii) Both are semi- conductor.

(iii) Both do not form ions, i.e., B^{3+} and Si^{4+}.

(iv) Both B and Si form covalent hydrides : boranes i.e., B_2H_6, B_4H_6 etc. and silanes, i.e., SiH_4, Si_2H_6 etc. respectively, which catch fire when exposed to air.

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$$

$$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$$

(v) Both form covalent, and volatile halides which fume in moist air due to release of HCl fumes.

$$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl\uparrow$$

$$SiCl_4 + 4H_2O \rightarrow H_4SiO_4 + 4HCl\uparrow$$

(vi) Both form solid oxides which are acidic and dissolve in alkalies forming borates and silicates respectively.

$$B_2O_3 + 2NaOH \rightarrow 2NaBO_2 + H_2O$$

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

(vii) Both react with electropositive metals and form binary compounds, which yield mixture of boranes and silanes on hydrolysis. Both B and Si form hydroxides boric acid $B(OH)_3$ and silicic acid $Si(OH)_4$ respectively which are weak acids.

$$3Mg + 2B \xrightarrow{\Delta} Mg_3B_2$$

$$Mg_3B_2 \xrightarrow{H_2O/H^+} \text{Mixture of boranes}$$

$$2Mg + Si \xrightarrow{\Delta} Mg_2Si$$

$$Mg_2Si \xrightarrow{H_2O/H^+} \text{mixture of silanes}$$

METALLURGY OF BORON

OCCURRENCE AND IMPORTANT MINERALS OF BORON :

It does not occur in the free state in nature. It forms electron deficient compounds.

Its important minerals are

(a) Borax (or Tincal), $Na_2B_4O_7.10H_2O$ or $Na_2[B_4O_5(OH)_4]8H_2O$

(b) Kernite, $Na_2B_4O_7.2H_2O$ or $Na_2[B_4O_5(OH)_4]$

(c) Orthoboric-acid H_3BO_3

(d) Colemanite, $Ca_2B_6O_{11}.5H_2O$ or $Ca_2[B_3O_4(OH)_3]_2 2H_2O$

(e) Boracite, $2Mg_3B_8O_{15}.\ MgCl_2$

ISOLATION :

Elemental boron in the form of dark brown powder is obtained by following methods :

(i) By reduction of boric oxide with highly electropositve metals like K, Mg, Al, Na etc. in the absence of air

$$B_2O_3 + 6K \xrightarrow{\text{Heat}} 2B + 3K_2O$$

(ii) By the reaction of boron halides with hydrogen at high temperature.

$$2BCl_3 + 3H_2 \xrightarrow{1270K} 2B + 6HCl$$

(iii) By thermal decomposition of boron triiodide over red hot tungsten filament.

$$2BI_3 \xrightarrow{\text{W heat}} 2B + 3I_2$$

(iv) By thermal decomposition of boron hydrides

$$B_2H_6 \xrightarrow{\Delta} 2B + 3H_2$$

USES OF BORON :

(i) As a semiconductor

(ii) Boron steel or boron carbide rods are used to control the nuclear reactions.

$$_5B^{10} + _0n^1 \rightarrow _5B^{11}$$

COMPOUNDS OF BORON

BORON HYDRIDES OR BORANES :

Boron forms hydrides of the type B_nH_{n+4} and B_nH_{n+6} which are called Boranes.

Preparation :

(i) $8BF_3 + 6LiH \rightarrow B_2H_6 + 6LiBF_4$

(ii) $4BCl_3 + LiAlH_4 \rightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$

Properties :

(i) All boranes are called as electron – deficient compounds because boron in boranes never completes its octet.

(ii) On reaction with water boric acid is formed.

BORAX OR SODIUM TETRABORATE DECAHYDRATE, $Na_2B_4O_7.10H_2O$ OR $Na_2[B_4O_5(OH)_4]8H_2O$:

Preparation :

(i) It occurs naturally as tincal in dried up lakes of Sri Lanka , USA and India.

(ii) By the boiling of mineral colemanite with a solution of Na_2CO_3.

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}} + 2Na_2CO_3 \rightarrow 2CaCO_3 + 2NaBO_2 + \underset{\text{Borax}}{Na_2B_4O_7}$$

Above $NaBO_2$ can be reconverted by passing CO_2 through it.

$$4NaBO_2 + CO_2 \rightarrow Na_2CO_3 + Na_2B_4O_7$$

Properties :

(i) Its aqueous solution is basic in nature due to hydrolysis.

$$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$$

(ii) On heating with ethyl alcohol and conc. H_2SO_4, it gives volatile vapours of triethylborate which burn with a green edged flame.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$$

$$H_3BO_3 + 3C_2H_5OH \rightarrow \underset{\text{Triethylborate}}{B(OC_3H_5)_3} + 3H_2O$$

(iii) ***Action of heat*** *:* $Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\text{Heat, swells}}$

$$\underset{\text{Anhydrous}}{Na_2B_4O_7} \xrightarrow{740^\circ C} \underset{\text{Sodium Metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$$

Glassy mass (Borax bead)

Borax bead is used for the detection of coloured basic radicals under the name ***borax bead test in*** which on heating borax bead combines readily with a number of coloured transition metal oxides such as Co, Ni, Cr, Cu, Mn etc. to form the corresponding metaborates which possess characteristic colours.

$$CoSO_4 \xrightarrow{\Delta} CoO + SO_3;$$

$$CoO + B_2O_3 \rightarrow \underset{\text{cobalt metaborate (blue)}}{Co(BO_2)_2}$$

Basic radical of a salt	Cu	Fe	Co	Cr	Ni
Colours of metaborates	Blue	Green	Blue	Green	Brown

Uses : It is used in making optical and hard glasses and in the borax bead test.

BORIC ACID OR ORTHOBORIC ACID, H_3BO_3 OR $B(OH)_3$:

Preparation

(i) By treating borax with dil HCl or dil H_2SO_4

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3$$

(ii) By passing SO_2 through a mixture of powdered mineral colemanite in boiling water.

$$Ca_2B_6O_{11} + 4SO_2 + 11H_2O \rightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$$

Properties :

(i) It is a very weak monobasic acid. It does not act as a proton donor but accepts a hydroxyl ion i.e., it behaves as a lewis acid.

$$H_3BO_3 + H_2O \rightarrow [B(OH)_4]^- + H^+$$

(ii) With C_2H_5OH and conc. H_2SO_4, it gives triethylborate.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} B(OC_2H_5)_3 + 3H_2O$$

(iii) With NaOH, it gives sodium metaborate

$$H_3BO_3 + NaOH \rightarrow NaBO_2 + 2H_2O$$

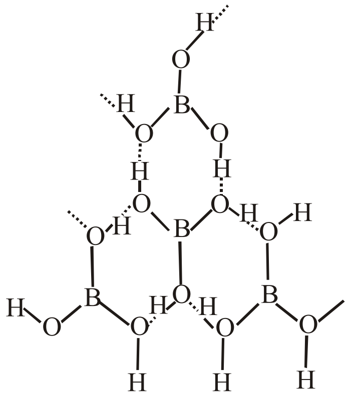
(iv) ***Heating effect*** *:*

$$\underset{\text{Orthoboric acid}}{H_3BO_3} \xrightarrow{273K} \underset{\text{Metaboric acid}}{HBO_2} \xrightarrow{433K} \underset{\text{Tetraboric acid}}{H_2B_4O_7} \xrightarrow[\text{hot}]{\text{red}} \underset{\text{Boron trioxide}}{B_2O_3}$$

(Boric anhydride)

Uses : As an antiseptic and eye lotion under the name *Boric lotion,* and as a food preservative.

Structure : It has a layer structure in which planar BO_3^{3-} units are linked by H- bonding, as shown in fig.



BORON HALIDES , BX_3, (WHERE, X= F, Cl, Br OR I):

Preparation : By the reaction of boron and halogens at high temperature.

$$2B + 3X_2 \xrightarrow{\text{heat}} 2BX_3$$

Properties :

(i) BF_3 and BCl_3 are gases, BBr_3 is a volatile liquid and BI_3 is a solid at room temperature.

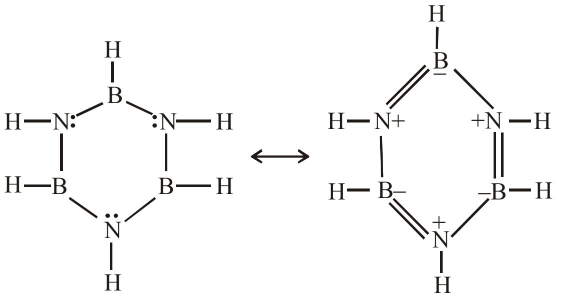
(ii) These are covalent in nature and act as lewis acids. The decreasing order of acid strength is.
$BI_3 > BBr_3 > BCl_3 > BF_3$

BORAZINE OR BORAZOLE OR TRIBORINE TRIAMINE, $B_3N_3H_6$:

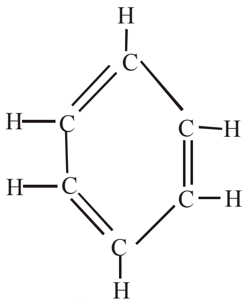
It is a colourless liquid having a six membered ring of alternating B and N atoms. It is also called inorganic benzene. It is prepared by B_2H_6 as follows:

$$3B_2H_6 + 6NH_3 \xrightarrow{180°C} 2B_3N_3H_6 + 12H_2$$

The π electrons in borazine are only partially delocalised. It is much more reactive than benzene, because there is a retention of partial negative charge by nitrogen atoms in latter case. It is **isosteric** (presence of same number of atoms and electrons) with benzene.



Borazine



Benzene

METALLURGY OF ALUMINIUM

OCCURRENCE AND IMPORTANT MINERALS :

It is the most abundant metal found in the earth's crust. It does not occur in the free state in nature.

Its important minerals are :

(a) Bauxite, $Al_2O_3 . 2H_2O$

(b) Diaspore, $Al_2O_3 . H_2O$

(c) Corundum, Al_2O_3

(d) Cryolite, $Na_3 AlF_6$

(e) Alunite or alum stone, $K_2SO_4 . Al_2(SO_4)_3 . 3Al(OH)_3$

(f) Feldspar, $K_2O . Al_2O_3\ 6SiO_2$

(g) Mica, $KAl_3Si_3O_{10}(OH)_2$

(h) Kaolinite, $Al_2O_3 . 2SiO_2 . 2H_2O$

EXTRACTION :

Aluminium metal is extracted from bauxite. It involves following steps.

(i) Purification of bauxite : Bauxite usually contains silica as impurity. These impurities must be removed before electrolysis, since aluminium, once prepared, cannot be freed of other metals by refining it. The bauxite is first purified by any of the following processes depending upon the nature of impurities present in it.

(a) **Bayer's process :**

$$\text{Finely powdered bauxite} \xrightarrow[FeO \to Fe_2O_3]{\text{Roasted}} \text{Roasted ore}$$

$$\xrightarrow[\substack{\text{High pressure(150°C, 80atm)} \\ \text{filtered, } Fe_2O_3 \text{ as residue}}]{\text{Caustic soda solution}} Al(OH)_3 \xrightarrow{\text{heat}} \underset{\text{pure}}{Al_2O_3}$$

The reactions involved are given below.

$$\underset{\text{Bauxite}}{Al_2O_3.2H_2O} + 2NaOH \rightarrow \underset{\substack{\text{Sod. meta} \\ \text{aluminate}}}{2NaAlO_2} + 3H_2O$$

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 \downarrow + NaOH$$

$$2Al(OH)_3 \xrightarrow{1473K} \underset{\text{Alumina}}{Al_2O_3} + 3H_2O$$

(b) Hall's process :

$$\text{Bauxite (Fine powder)} \xrightarrow[\substack{\text{fused, extracted with water} \\ \text{residue } SiO_2, Fe_2O_3}]{+Na_2CO_3} \text{solution}$$

$$\xrightarrow[\substack{\text{50–60°C and filtraed} \\ \text{filtrate}(Na_2CO_3)}]{CO_2} \text{ppt. } Al(OH)_3 \xrightarrow{\text{Heat}} \text{Pure} Al_2O_3$$

The reactions involved are given below.

$$Al_2O_3 . 2H_2O + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2 + 2H_2O$$

$$2NaAlO_2 + 3H_2O + CO_2 \xrightarrow{323–333K} 2Al(OH)_3 \downarrow + Na_2CO_3$$

(c) **Serpek's process :** This process is employed when silica content of ore is high.

$$\text{Finely powdered bauxite} \xrightarrow[\text{Heated to 1800°C}]{+\text{coke} + N_2}$$

silica reduced to Si which volatalises

+ Alumina form aluminium nitride AlN

$\downarrow$ hydrolysis

$$\text{Pure } Al_2O_3 \xleftarrow{\text{Heated}} \underset{\text{(ppt)}}{Al(OH)_3}$$

$\downarrow$

Filtrate

(sod. aluminate + sod. silicate)

The involving reactions are given below.

$$Al_2O_3.\,2H_2O + N_2 + 3C \xrightarrow{2000K} 2AlN + 3CO\uparrow + 2H_2O$$

$$SiO_2 + 2C \longrightarrow Si\uparrow + 2CO\uparrow$$

$$AlN + 3H_2O \longrightarrow Al(OH)_3\downarrow + NH_3$$

(ii) ***Electrolysis of fused alumina (Hall and Heroult's process) :*** Since pure alumina is a bad conductor of electricity, therefore it is dissolved in molten cryolite. Na_3AlF_6 and fluorspar, CaF_2 to decrease its fusion temperature. The molten electrolyte is covered with a layer of powdered coke to prevent oxidation and loss of heat due to radiation.

The reactions are :

$$Na_3AlF_6 \rightleftharpoons 3NaF + AlF_3$$

$$AlF_3 \rightleftharpoons Al^{3+} + 3F^-$$

At cathode : $Al^{3+} + 3e^- \rightarrow Al$

At anode : $F^- \rightarrow e^- + F$

$$2Al_2O_3 + 12F \rightarrow 4AlF_3 + 3O_2$$

$$2C + O_2 \rightarrow 2CO\ ;$$

$$2CO + O_2 \longrightarrow 2CO_2$$

(iii) ***Refining of aluminium :*** It is refined by Hoope's electrolytic process, which is carried out in a graphite lined bath which acts as the anode and carbon cathodes are used. The refining cell consists of three fused layer's of different densities.

(a) The bottom layer is of molten impure aluminium (anode)

(b) The middle layer is of fused cryolite and barium fluoride

(c) The upper layer is of pure aluminium (cathode)

There is a new method of extraction of Aluminium in which the purification of the oxide is not of much importance. In this method, $AlCl_3$ vapour is passed through the fused oxide at 1000ºC

$$2Al_2O_3 + 2AlCl_3 \rightarrow \underset{\text{Aluminium monochloride}}{6AlCl} + 3O_2$$

The above aluminium monochloride vapour is unstable when cooled and disproportionates below at 800ºC.

$$3AlCl \rightarrow AlCl_3 + 2Al$$

USES :

(i) A mixture of aluminium powder and aluminium nitrate is known as ***Ammonal*** and is used in bombs.

(ii) A mixture of Al powder in linseed oil is used as silver paint.

(iii) The reduction of metal oxides by aluminium is called aluminothermy or thermite process or ***Goldschmidt aluminothermite process***.

COMPOUNDS OF ALUMINIUM

ANHYDROUS ALUMINIUM CHLORIDE, $AlCl_3$ (OR Al_2Cl_6) :

Preparation : It can not be prepared by heating $AlCl_3.\,6H_2O$ because of its hydrolysing tendency by its own water as below.

$$2AlCl_3.\,6H_2O \xrightarrow{\Delta} 2Al(OH)_3 + 6HCl$$

$$2Al(OH)_3 \xrightarrow{\text{heat}} Al_2O_3 + 3H_2O$$

However, it can be prepared by following methods:

(i) By passing dry chlorine or HCl gas over heated Al.

$$2Al + 3Cl_2 \xrightarrow{\text{heat}} 2AlCl_3$$

$$2Al + 6HCl \xrightarrow{\text{heat}} 2AlCl_3 + 3H_2$$

(ii) By heating a mixture of alumina and carbon in a current of dry chlorine.

$$Al_2O_3 + 3C + 3Cl_2 \xrightarrow{\text{heat}} 2AlCl_3 + 3CO$$

Properties :

(i) It fumes in moist air due to hydrolysis

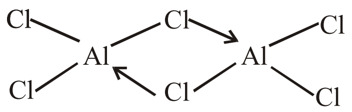
$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$$

The resulting solution is acidic due to the formation of HCl.

(ii) It behaves as lewis acid.

(iii) It is a covalent solid and dissolves in organic solvents like C_6H_6 etc.

Structure : It exists as dimer Al_2Cl_6 in which each Al atom is terahedrally surrounded by four Cl atoms as below.



USES :

(i) As a catalyst in Friedel - Craft reactions

(ii) As a mordant in dyeing

ALUMINIUM OXIDE OR ALUMINA Al_2O_3 :

It is the most stable compound of aluminium and occurs in nature as colourless corundum and several coloured oxides, (when present in combination with different metal oxides) like ruby (red), topaz (yellow), sapphire (blue), amethyst (voilet) and emerald (green), which are used as precious stones (gems).

THERMITE :

A mixture of aluminium powder and ferric oxide in the ratio 1: 3.

ALUMINIUM SULPHATE, $Al_2(SO_4)_3$:

It is used for obtaining H_2S in pure form and for making fire proof clothes.

ALLOYS OF ALUMINIUM :

	Alloy	Composition	Properties	Uses
(i)	Duralumin	$\underset{(95\%)}{Al} + \underset{(4\%)}{Cu} + \underset{(0.5\%)}{Mg} + \underset{(0.5\%)}{Mn}$	Light, tough, ductile	Aeroplanes and automobile parts
(ii)	Aluminium Bronze	$\underset{(90\%)}{Al} + \underset{(10\%)}{Cu}$	Light, strong, golden lustre	Coins, jewellery
(iii)	Alcald	Duralumin coated with pure aluminium	corrosion resistant, strong	aircraft industry
(iv)	Magnalium	$\underset{(83\%)}{Al} + \underset{(15\%)}{Mg} + \underset{(2\%)}{Ca}$	Light, tough and strong	Balance beams and machinery
(v)	Alnico	$\underset{(20\%)}{Al} + \underset{(50\%)}{Fe} + \underset{(20\%)}{Ni} + \underset{(10\%)}{Co}$	Highly Magnetic	Permanent magnets

ALUMS :

The term alum is given to double sulphates of the type X_2SO_4, $Y_2(SO_4)_3$. $24H_2O$ where X represents a monovalent cation such as Na^+, K^+ and NH_4^+ Rb^+, Cs^+, Ag^+ while Y is a trivalent cation such a Al^{3+}, Cr^{3+} and Fe^{3+}, Co^{3+}, Ga^{3+}, V^{3+}, Ti^{3+}. (Li^+ is too small to be accomodated in the lattice)

General formula :

$$M'_2SO_4M'''_2(SO_4)_3 24H_2O \text{ or } M'M'''(SO_4)_2.12H_2O$$

Some important alums are :

(a)	Potash alum	$K_2SO_4.Al_2(SO_4)_3.\ 24H_2O$
(b)	Sodium alum	$Na_2SO_4.Al_2(SO_4)_3.\ 24H_2O$
(c)	Ammonium alum	$(NH_4)_2SO_4.Al_2(SO_4)_3.\ 24H_2O$
(d)	Ferric alum	$(NH_4)_2SO_4.\ Fe_2(SO_4)_3.\ 24H_2O$
(e)	Chrome alum	$K_2SO_4.\ Cr_2(SO_4)_3.\ 24H_2O$

Out of these, potash alum is the most important which is prepared in the laboratory by mixing hot solutions of equimolar quantities of K_2SO_4 and $Al_2(SO_4)_3$. The resulting solution on concentration and crystallization gives potash alum (emperical formula is $KAl(SO_4)_2.\ 12H_2O$).

Pseudo alums : When monovalent element of ordinary alums is replaced by a bivalent element eg Mn^{2+}, Fe^{2+}, Mg^{2+}, Cu^{2+} or Zn^{2+}, the alums are called pseudo alums.

Examples : $FeSO_4, Al_2(SO_4)_3.24H_2O$

Ferrous aluminium pseudo alum

$MnSO_4.Al_2(SO_4)_3.24H_2O$

Manganese aluminium pseudo alum

Properties :

(i) Potash alum is a white crystalline compound.

(ii) The aqueous solution of all alums is acidic due to hydrolysis of $Al_2(SO_4)_3$, $Cr_2(SO_4)_3$ or $Fe_2(SO_4)_3$ as given below.

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2SO_4$$

(iii) On heating all alums lose water of crystallization and swell up. The anhydrous alum is known as burnt alum.

(iv) Ionisation of aqueous solution of a double salt is as

$$K_2SO_4.\ Al_2(SO_4)_2.\ 24H_2O \rightarrow$$

$$2K^+ + 2Al^{3+} + 3SO_4^{2-} + 24H_2O$$

Uses :

(i) In purification of water

(ii) For sizing of paper

(iii) As a syptic to stop bleeding

(iv) As a mordant in dyeing and tanning of leather

Exercise-1 | NCERT BASED QUESTIONS

Very Short/ Short Answer Questions

1. Why boron forms electron deficient compounds?

2. Why boron halides do not exist as dimer while $AlCl_3$ exists as Al_2Cl_6?

3. The +1 oxidation state is more stable than the + 3 oxidation state for thallium.

4. Why is boron used in nuclear reactors?

5. Between AlF_3 and $AlCl_3$ which one will have a higher melting point.

6. BCl_3 exists but BH_3 does not. Explain.

7. Explain why boron halides don't conduct electricity in the liquid state?

8. What is the use of boron nitride?

9. (a) Why BF_3 forms adduct with ammonia? Explain with reaction.

(b) How does electron deficient compound BF_3 achieve electronic saturation, i. e., fully occupied outer electron shells?

10. What happens when borax solution is acidified? Write a balanced equations to support your answer.

11. (a) Which one is more soluble in diethyl ether, anhydrous $AlCl_3$ or hydrated $AlCl_3$?

(b) Why BBr_3 is a stronger Lewis acid than BF_3?

12. Account for the following :

(a) Aluminium sulphide gives a foul odour when it becomes damp.

(b) Although aluminium is above hydrogen in the electrochemical series, still it is stable in moist air.

Long Answer Questions

13. (i) Compound X on reduction with $LiAlH_4$ gives a hydride Y. The compound Y reacts with air explosively resulting in boron trioxide. Identify X and Y. Give balanced equations involved in the formation of Y and its reaction with air.

(ii) Assign reasons for each of the

(a) Gallium (+1) undergoes dispro-portionation reactions.

(b) Unlike In^+, Tl^+ is more stable with respect to disproportionation.

(c) InCl undergoes disproportionation but TlCl does not.

14. (a) Why borazine is called inorganic benzene?

(b) Why Ga has smaller atomic radii than aluminium?

(c) Why aluminium is used as a structural material ?

Multiple Choice Questions

15. The element which exists in liquid state for a wide range of temperature and can be used for measuring high temperature is

(a) B (b) Al

(c) Ga (d) In

16. The exhibition of highest co-ordination number depends on the availability of vacant orbitals in the central atom. Which of the following elements is not likely to act as central atom in MF_6^{3-} ?

(a) B (b) Al

(c) Ga (d) In

17. Identify the statement that is not correct as far as structure of diborane is concerned

(a) There are two bridging hydrogen atoms and four terminal hydrogen atoms in diborane

(b) Each boron atom forms four bonds in diborane

(c) The hydrogen atoms are not in the same plane in diborane

(d) All, B – H bonds in diborane are similar

18. Aluminium vessels should not be washed with materials containing washing soda because

(a) washing soda is expensive

(b) washing soda is easily decomposed

(c) washing soda reacts with aluminium to form soluble aluminate

(d) washing soda reacts with aluminium to form insoluble aluminium oxide

19. Which is false in case of boric acid H_3BO_3?

(a) It acts as a tribasic acid.

(b) It has a planar structure.

(c) It acts as a monobasic acid.

(d) It is soluble in hot water.

20. Aluminium chloride is a/an

(a) Bronsted - Lowery acid

(b) Arhenius acid

(c) Lewis acid

(d) Lewis base

21. A compound X, of boron reacts with NH_3 on heating to give another compound Y which is called inorganic benzene. The compound X can be prepared by treating BF_3 with Lithium aluminium hydride. The compounds X and Y are represented by the formulas.

(a) $B_2H_6, B_3N_3H_6$ (b) $B_2O_3, B_3N_3H_6$

(c) $BF_3, B_3N_3H_6$ (d) $B_3N_3H_6, B_2H_6$

22. $AlCl_3$ on hydrolysis gives
(a) $Al_2O_3.H_2O$ (b) $Al(OH)_3$
(c) Al_2O_3 (d) $AlCl_3.6H_2O$

23. Which is not correct?
(a) Al acts as a reducing agent
(b) Al does not react with steam even at higher temperature
(c) Al forms a number of alloys with other metals
(d) Al is ionic in all its compounds

24. Ionisation enthalpy ($\Delta_i H_1$ kJ mol^{-1}) for the elements of Group 13 follows the order.
(a) $B > Al > Ga > In > Tl$
(b) $B < Al < Ga < In < Tl$
(c) $B < Al > Ga < In > Tl$
(d) $B > Al < Ga > In < Tl$

Exercise-2 | CONCEPTUAL MCQs

1. The state of hybridization of B in BCl_3 is
(a) sp^3 (b) sp^2
(c) sp (d) sp^3d^2

2. The type of hybridization of boron in diborane is
(a) sp (b) sp^2
(c) sp^3 (d) sp^3d^2

3. Specify the coordination geometry around and hybridization of N and B atoms in a 1: 1 complex of BF_3 and NH_3
(a) N : tetrahedral, sp^3; B : tetrahedral, sp^3
(b) N : pyramidal, sp^3; B : pyramidal, sp^3
(c) N : pyramidal, sp^3; B : planar, sp^3
(d) N : pyramidal, sp^3; B : tetrahedral, sp^3

4. Which one of the following elements has the highest melting point ?
(a) Boron (b) Aluminium
(c) Gallium (d) Thallium

5. The element which shows least metallic character is
(a) Indium (b) Boron
(c) Aluminium (d) Gallium

6. Which of the following does not form M^{3+} ion?
(a) Boron (b) Aluminium
(c) Indium (d) Gallium

7. Which of the following does not react with aqueous NaOH ?
(a) B (b) Al
(c) Ga (d) Tl

8. B_2O_3 is
(a) acidic (b) basic
(c) amphoteric (d) None of these

9. Boric acid is polymeric due to
(a) its acidic nature
(b) the presence of hydrogen bonds
(c) its monobasic nature
(d) its geometry

10. $B(OH)_3$ is
(a) monobasic acid (b) dibasic acid
(c) tribasic acid (d) triacidic base

11. Which of the following hydroxide is acidic ?
(a) $Al(OH)_3$ (b) $Ca(OH)_3$
(c) $Tl(OH)_3$ (d) $B(OH)_3$

12. BF_3 acts as an acid according to the concept of
(a) Lewis (b) Bronsted
(c) Arrhenius (d) None of these

13. Which of the following is electron deficient ?
(a) NH_3 (b) BCl_3
(c) PCl_3 (d) None of these

14. NH_3 and BF_3 form an adduct readily because they form
(a) a coordinate bond
(b) a hydrogen bond
(c) an ionic bond
(d) a covalent bond

15. BF_3 is used as a catalyst in several industrial processes due to its
(a) strong reducing nature
(b) weak reducing action
(c) strong Lewis acid nature
(d) weak Lewis acid character

16. Among the halides of the elements of group 13 the one which is most acidic is
(a) BF_3 (b) $AlCl_3$
(c) BCl_3 (d) BBr_3

17. In diborane
(a) 4–bridged hydrogens and two terminal hydrogens are present
(b) 2– bridged hydrogens and four terminal hydrogens are present
(c) 3–bridged and three terminal hydrogens are present
(d) None of these

18. Identify the statement that is not correct as far as structure of diborane is concerned
(a) There are two bridging hydrogen atoms and four terminal hydrogen atoms in diborane
(b) Each boron atom forms four bonds in diborane
(c) The hydrogen atoms are not in the same plane in diborane
(d) All, B – H bonds in diborane are similar

19. BCl_3 does not exist as dimer but BH_3 exists as dimer (B_2H_6) because
(a) chlorine is more electronegative than hydrogen
(b) there is pπ-pπ back bonding in BCl_3 but BH_3 does not contain such multiple bonding
(c) large sized chlorine atoms do not fit in between the small boron atoms where as small sized hydrogen atoms get fitted in between boron atoms
(d) None of these

20. Diborane upon hydrolysis gives
(a) boric anhydride (b) metaboric acid
(c) orthoboric acid (d) boron oxide

21. In reaction
$BF_3 + 3LiBH_4 \rightarrow 3LiF + X$; X is
(a) B_4H_{10} (b) B_2H_6
(c) BH_3 (d) B_3H_8

22. Which of the following mineral does not contain Al ?
(a) Cryolite (b) Mica
(c) Feldspar (d) Fluorspar

23. In the thermite welding process we use
(a) Al powder (b) Fe powder
(c) Ca powder (d) (Al + Fe) mixture

24. In aluminates, the coordination number of Al is
(a) 4 (b) 6
(c) 3 (d) 1

25. Aluminium is
(a) a reducing agent
(b) an oxidising agent
(c) amphoteric
(d) highly electronegative element

26. Al is more reactive than Fe but Al is less easilly corroded than Fe because
(a) it is a noble metal
(b) oxygen forms a protective oxide layer
(c) iron undergoes reaction easily with water
(d) Fe form mono and divalent ions.

27. Corundum is
(a) $Al_2(SO_4)_3$ (b) $Al_2O_3.H_2O$
(c) $Al_2O_3.2H_2O$ (d) Al_2O_3

28. Although Al has a high oxidation potential it resists corrosion because of the formation of a tough, protective coat of
(a) $Al(NO_3)_3$ (b) AlN
(c) Al_2O_3 (d) $Al_2(CO_3)_3$

29. $AlCl_3$ on hydrolysis gives
(a) $Al_2O_3.\ H_2O$ (b) $Al(OH)_3$
(c) Al_2O_3 (d) $AlCl_3.6H_2O$

30. Action of caustic soda on aluminium hydroxide gives a compound having formula
(a) $Al_2(OH)_4$ (b) $Na_2Al(OH)_4$
(c) $NaAlO_2$ (d) Na_3AlO_3

31. $Al(OH)_3$ is
(a) acidic (b) basic
(c) amphoteric (d) neither acidic nor basic

32. A lake can be obtained by making a mixture of a coloured dye with
(a) NH_4OH (b) $Ba(OH)_2$
(c) $Al(OH)_3$ (d) NaOH

33. $AlCl_3$ is
(a) anhydrous and covalent
(b) anhydrous and ionic
(c) covalent and basic
(d) coordinate and acidic

34. Anhydrous $AlCl_3$ is prepared from
(a) conc. HCl and Al metal
(b) aluminium and Cl_2
(c) dry HCl gas + heated Al metal
(d) dil. HCl and Al metal

35. Aluminium chloride is a/an
(a) Bronsted - Lowry acid (b) Arrhenius acid
(c) Lewis acid (d) Lewis base

36. Which member of group 13 does not exhibit the group valency in its compounds ?
(a) Boron (b) Aluminium
(c) Gallium (d) Thallium

37. The highly toxic element of group 13 is
(a) Al (b) B
(c) Ga (d) Tl

38. Which of the following oxides is strongly basic ?
(a) B_2O_3 (b) Al_2O_3
(c) Ga_2O_3 (d) Tl_2O_3

39. Which out of the following compounds does not exist?
(a) BF_3 (b) $TlCl_3$
(c) $TlCl_5$ (d) Both (b) and (c)

40. Which of the following does not give a borax bead test ?
(a) Chromium (b) Ferrous salt
(c) Sodium (d) Cobalt

41. Borazole is known as
(a) organic benzene (b) organic xylene
(c) inorganic benzene (d) inorganic xylene

42. The $I.E_1$ among the group 13 member follows as
(a) $B > Al < Ga < Tl$ (b) $B > Al > Ga > Tl$
(c) $B > Ga > Al > Tl$ (d) $B > Ga < Al < Tl$

43. The melting pt. of group 13 follows the order
(a) $B > Al > Ga > In > Tl$ (b) $B > Al < Ga > In > Tl$
(c) $B > Al > Tl > In > Ga$ (d) $B > Al < Ga < In < Tl$

44. The compounds of boron and hydrogen are collectively called
(a) diboranes (b) borazoles
(c) boracits (d) boranes

45. The bonds present in borazole or inorganic benzene are
(a) $9\,\sigma, 6\pi$ (b) $12\,\sigma, 3\pi$
(c) $6\,\sigma, 9\pi$ (d) $15\,\sigma$ only

46. The aluminium salt commonly used to stop bleeding is

(a) aluminium sulphate (b) potash alum

(c) aluminium chloride (d) aluminium fluoride

47. The nature of the solution of Potash alum is

(a) basic (b) acidic

(c) neutral (d) amphoteric

48. Aluminium vessels should not be washed with materials containing washing soda because

(a) washing soda is expensive

(b) washing soda gets easily decomposed

(c) washing soda reacts with aluminium to form soluble aluminate

(d) washing soda reacts with aluminium to form insoluble aluminium oxide

49. Which out of the following is potash alum ?

(a) $K_2SO_4.Al_2(SO_4)_3.24H_2O$ (b) $K_2SO_4. Cr_2(SO_4)_3.24H_2O$

(c) $K_2SO_4.Fe_2(SO_4)_3.24H_2O$ (d) $[NH_4]_2SO_4.FeSO_4.6H_2O$

Exercise-3 | PAST COMPETITION MCQs

1. In borax bead test which compound is formed? **[CBSE-PMT 2002]**

(a) Ortho-borate (b) Meta-borate

(c) Double oxide (d) Tetra-borate

2. Al_2O_3 can be converted to anhydrous $AlCl_3$ by heating

(a) Al_2O_3 with NaCl in solid state **[CBSE-PMT 2006]**

(b) a mixture of Al_2O_3 and carbon in dry Cl_2 gas

(c) Al_2O_3 with Cl_2 gas

(d) Al_2O_3 with HCl gas

3. The tendency of BF_3, BCl_3 and BBr_3 to behave as Lewis acid decreases in the sequence: **[CBSE-PMT 2010]**

(a) $BCl_3 > BF_3 > BBr_3$

(b) $BBr_3 > BCl_3 > BF_3$

(c) $BBr_3 > BF_3 > BCl_3$

(d) $BF_3 > BCl_3 > BBr_3$

4. Aluminium is extracted from alumina (Al_2O_3) by electrolysis of a molten mixture of : **[CBSE-PMT 2012 S]**

(a) $Al_2O_3 + HF + NaAlF_4$

(b) $Al_2O_3 + CaF_2 + NaAlF_4$

(c) $Al_2O_3 + Na_3AlF_6 + CaF_2$

(d) $Al_2O_3 + KF + Na_3AlF_6$

5. Which of the following structure is similar to graphite?

(a) B (b) B_4C **[NEET 2013]**

(c) B_2H_6 (d) BN

6. Alum helps in purifying water by **[AIEEE 2002]**

(a) forming Si complex with clay partiles

(b) sulphate part which combines with the dirt and removes it

(c) coagulaing the mud particles

(d) making mud water soluble.

7. Aluminium is extracted by the electrolysis of **[AIEEE 2002]**

(a) bauxite

(b) alumina

(c) alumina mixed with molten cryolite

(d) molten cryolite.

8. Aluminium chloride exists as dimer, Al_2Cl_6 in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives **[AIEEE 2004]**

(a) $[Al(OH)_6]^{3-} + 3HCl$

(b) $[Al(H_2O)_6]^{3+} + 3Cl^-$

(c) $Al^{3+} + 3Cl^-$

(d) $Al_2O_3 + 6HCl$

9. Heating an aqueous solution of aluminium chloride to dryness will give **[AIEEE 2005]**

(a) $Al(OH)Cl_2$ (b) Al_2O_3

(c) Al_2Cl_6 (d) $AlCl_3$

10. The structure of diborane (B_2H_6) contains **[AIEEE 2005]**

(a) four 2c-2e bonds and four 3c-2e bonds

(b) two 2c-2e bonds and two 3c-3e bonds

(c) two 2c-2e bonds and four 3c-2e bonds

(d) four 2c-2e bonds and two 3c-2e bonds

11. Which one of the following is the correct statement?

(a) Boric acid is a protonic acid **[AIEEE 2008]**

(b) Beryllium exhibits coordination number of six

(c) Chlorides of both beryllium and aluminium have bridged structures in solid phase

(d) $B_2H_6.2NH_3$ is known as 'inorganic benzene'

12. How can the following reaction be made to proceed in forward direction? **[IIT-JEE 2006]**

$B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na[B(OH)_4] + H_2O$

(a) addition of borax (b) addition of *cis*-1,2-diol

(c) addition of Na_2HPO_4 (d) addition of *trans*-1,2-diol

Exercise-4 | Applied MCQs

1. On adding ammonium hydroxide solution to $Al_2(SO_4)_3$ (aq) :
   (a) A precipitate is formed which does not dissolve in excess of ammonium hydroxide
   (b) A precipitate is formed which dissolves in excess of ammonia solution
   (c) No precipitate is formed
   (d) None of these

2. The purification method used for mineral $Al_2O_3.2H_2O$ is
   (a) froth floatation (b) leaching
   (c) liquation (d) magnetic separation

3. The process used for purification of bauxite ore containing high silica content as impurity is
   (a) Baeyer's process (b) Hall's process
   (c) Hoope's process (d) Serpeck's process

4. Hydrogen forms a bridge in the chemical structure of :
   (a) sodium peroxide (b) diborane
   (c) hydrogen peroxide (d) lithium hydride

5. The role of fluorspar (CaF_2) which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6) is
   (a) as a catalyst
   (b) to make the fused mixture very conducting
   (c) to increase the temperature of the melt.
   (d) to decrease the rate of oxidation of carbon at the anode.

6. In Gold Schmidt reaction, certain metallic oxides are reduced to the metallic state by heating with
   (a) metallic magnesium (b) metallic aluminium
   (c) metallic iron (d) sodium metal

7. The dissolution of $Al(OH)_3$ by a solution of NaOH results in the formation of
   (a) $[Al(H_2O)_4(OH)]^{2+}$ (b) $[Al(H_2O)_2(OH)_4]^-$
   (c) $[Al(H_2O)_3(OH)_3]$ (d) $[Al(H_2O)_6(OH)_3]$

8. Which of the following is pseudo alum ?
   (a) $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$
   (b) $K_2SO_4.Al_2(SO_4)_3.24H_2O$
   (c) $MnSO_4.Al_2(SO_4)_3.24H_2O$
   (d) None of these

9. Which of the following statements about anhydrous aluminium chloride is correct ?
   (a) It exist as $AlCl_3$ molecule
   (b) It is a strong lewis base
   (c) It sublimes at 100°C under vaccum
   (d) It is not easily hydrolysed.

10. The two type of bonds present in B_2H_6 are covalent and
    (a) ionic (b) co-ordinate
    (c) hydrogen bridge bond (d) None of these

11. Orthoboric acid when heated to red hot gives
    (a) metaboric acid (b) pyroboric acid
    (c) boron and water (d) boric anhydride

12. Anodised aluminium is
    (a) Al obtained at anode
    (b) Al prepared electrolytically
    (c) Alloy of Al containing 95% of Al
    (d) Al electrolytially coated with aluminium oxide

13. Which statement regarding H_3BO_3 is not correct ?
    (a) It is a strong tribasic acid
    (b) It is prepared by acidifying an aqueous solution of borax
    (c) It has a layer structure in which planar BO_3 units are joined by H- bonds
    (d) It does not act as proton donor but acts on lewis acid by accepting OH^- ions

14. The precious Ruby stone is
    (a) alumina
    (b) aluminium silicate
    (c) sodium aluminium silicate
    (d) sodium silicate

15. The hybridisation of boron atom in orthoboric acid is
    (a) sp (b) sp^2
    (c) sp^3 (d) sp^3d

16. Which of the following statements is not correct ?
    (a) Al acts as a reducing agent
    (b) Al does not react with steam even at higher temperature
    (c) Al forms a number of alloys with other metals
    (d) Al is ionic in all its compounds

17. Which of the following processes does not involve a catalyst?
    (a) Thermite process (b) Ostwald process
    (c) Contact process (d) Haber process

18. The factor responsible for weak acidic nature of B–F bonds in BF_3 is
    (a) large electronegativity of fluorine
    (b) three centred two electron bonds in BF_3
    (c) $p\pi$ - $d\pi$ back bonding
    (d) $p\pi$ - $p\pi$ back bonding

19. An aqueous solution of $FeSO_4$, $Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are :
    (a) a colourless filtrate and a green residue
    (b) a yellow filtrate and a green residue
    (c) a yellow filtrate and a brown residue
    (d) a green filtrate and a brown residue

20. Which of the following has the minimum heat of dissociation:

(a) $(CH_3)_3N: \rightarrow BF_3$

(b) $(CH_3)_3N: \rightarrow B(CH_3)_2F$

(c) $(CH_3)_3N: \rightarrow B(CH_3)_3$

(d) $(CH_3)_3N: \rightarrow B(CH_3)F_2$

21. Purification of alumina is essential because :

(a) impure alumina has a very high melting point.

(b) impure alumina is a very poor conductor of electricity.

(c) impure alumina cannot react with the oxidizing agent.

(d) it is difficult to purify aluminium metal.

22. Which reaction cannot give anhydrous $AlCl_3$:

(a) Passing dry Cl_2 over heated aluminium powder.

(b) Heating a mixture of alumina and coke in a current of dry Cl_2.

(c) Passing dry HCl over heated aluminium powder.

(d) Heating of $AlCl_3.6H_2O$.

23. The process used for purification of bauxite ore containing iron oxide impurity is known as :

(a) Hoope's process (b) Serpeck's process

(c) Baeyer's process (d) Electrolytic process

24. Which statement is not true about potash alum ?

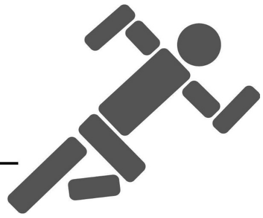
(a) On heating it melts and loses its water of crystallization.

(b) It's aqueous solution is basic in nature.

(c) It is used in dyeing industries.

(d) It's empirical formula is $KAl(SO_4)_2.12H_2O$.

Hints & Solutions



EXERCISE 1

4. Boron can absorb neutrons.

5. AlF_3 is more ionic, therefore, has higher melting point.

7. Boron halides don't conduct electricity in the liquid state because they are covalent compounds.

8. Boron nitride is harder than diamond and is used as an abrasive.

10. Boric acid is formed on acidification of Borax ($Na_2B_4O_7$).

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$$
$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow 4H_3BO_3 + Na_2SO_4$$

15. (c) **16.** (a) **17.** (d) **18.** (c) **19.** (a)

20. (c) **21.** (a) **22.** (b) **23.** (d) **24.** (d)

EXERCISE 2

1. (b) **2. (c)** **3. (a)**

4. (a) Boron has a giant molecule structure like that of diamond therefore it has highest melting point

5. (b)

6. (a) Due to its small size and high ionization energy boron does not form B^{3+} ion.

7. (a) **8. (a)**

9. (b) In Boric acid each B atom is sp^2 hybridized and contains BO_3^{3-} units which are held together by hydrogen bonds.

10. (a)

11. (d) $B(OH)_3$ is acid because it can take OH^- ions.

$$H_3BO_3 \text{ or } B(OH)_3 + OH^- \rightarrow B(OH)_4^-$$

12. (a) Since BF_3 is an electron deficient molecule (according to lewis concept).

13. (b) **14. (a)** **15. (d)** **16. (d)** **17. (b)**

18. (d) **19. (c)** **20. (c)** **21. (b)**

22. (d) Fluorspar (CaF_2) does not contain Al whereas cryolite (Na_3AlF_6) mica $[KAl_3.Si_3O_{10}(OH)_2]$ and feldspar ($KAlSi_3O_8$) contain Al.

23. (a)

24. (b) In aqueous solution the probable aluminate species is $[Al(H_2O)_2(OH)_4]$ hence Al containing co-ordination number 6

25. (a) Because it can lose electrons.

26. (b) The protective oxide layer prevents Al from further corrosion.

27. (d) **28. (c)** **29. (b)**

30. (c) $Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$

31. (c) **32. (c)** **33. (a)**

34. (c) $2Al + 3Cl_2 \xrightarrow{\Delta} 2AlCl_3$ (anhydrous)

35. (c) **36 (c)** **37. (d)**

38. (d) The correct sequence of increasing basic strength is

$$B_2O_3 < Al_2O_3 < Ga_2O_3 < In_2O_3 < Tl_2O_3$$

39. (c) Because Tl $^{+5}$ does not exist

40. (c) Colourless salt or ion (ex. Na) will not give a borax bead test.

41. (c)

42. (c) The IE_1 of Ga is more than that of Al because of the small atomic size and greater effective nuclear charge of Ga.

43. (c) Due to structural changes, melting point, increases from Ga to Tl and Ga has the lowest melting point.

44. (d) **45. (b)** **46. (b)** **47. (b)** **48. (c)**

49. (a)

EXERCISE 3

1. (b) $Na_2B_4O_7 . 10\,H_2O \xrightarrow[-10H_2O]{\Delta}$

$$\underset{\text{anhydrous}}{Na_2B_4O_7} \xrightarrow{\Delta} \underset{\text{sod. metaborate}}{2\,NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$$

$$CuO + B_2O_3 \longrightarrow \underset{\text{cupric meta borate (Blue beed)}}{Cu(BO_2)_2}$$

2. (b) Al_2O_3 can be converted to anhydrous $AlCl_3$ by heating a mixture of Al_2O_3 and carbon in dry Cl_2

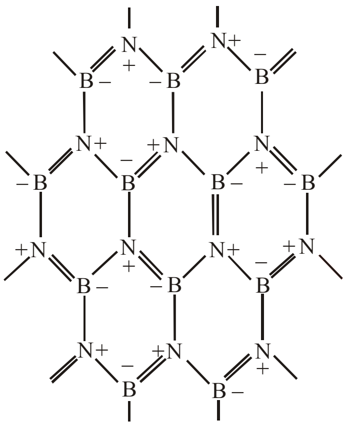
$$Al_2O_3 + 3C + 3Cl_2 \xrightarrow{1000°C} \underset{\text{vapours}}{2AlCl_3} + 3CO \xrightarrow{\text{cooled}} \text{Solid anhydrous aluminium chloride}$$

3. (b) *p-p* overlap between B and F is maximum due to identical size and energy of *p*-orbitals, so electron deficiency in boron of BF_3 is neutralized partially to the maximum extent by back donation. Hence BF_3 is least acidic.

As the size of halogen atom increases from F to I, the extent of overlap between 2*p*-orbital of B and a bigger *p*-orbital of halogen decreases. Therefore the electron deficiency of B increases.

4. (c) Fused alumina (Al_2O_3) is a bad conductor of electricity. Therefore, cryolite (Na_3AlF_6) and fluorspar (CaF_2) are added to purified alumina which not only make alumina a good conductor of electricity but also reduce the melting point of the mixture to around 1140 K.

5. (d) Boron nitride (BN) is known as inorganic graphite. The most stable form is hexagonal one. It has layered structure similar to graphite.



6. (c) Alum furnishes Al^{3+} ions which bring about coagulation of negatively charged clay particles, bacteria etc.

7. (c) Alumina is mixed with cryolite which acts as an electrolyte.

8. (b) $AlCl_6 + 12H_2O \rightleftharpoons 2[Al(H_2O)_6]^{3+} + 6\overline{Cl}$

9. (b) The solution of aluminium chloride in water is acidic due to hydrolysis.

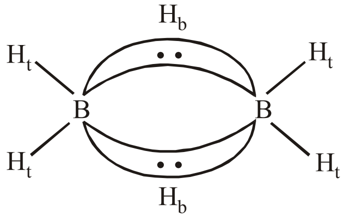
$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl.$$

On heating it till dryness $Al(OH)_3$ is converted into Al_2O_3

$$Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

10. (d) In diborane (B_2H_6) structure there are four 2c-2e bonds and two 3c–2e bonds (see structure of diborane).

Structure of B_2H_6:

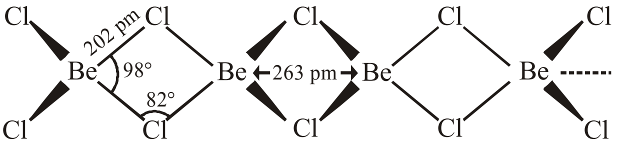


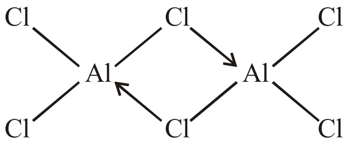
11. (c) The correct formula of inorganic benzene is $B_3N_3H_6$ so (d) is incorrect statement

Boric acid (H_3BO_3 or $\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{B}}-OH$) is a lewis acid so (a) is incorrect statement.

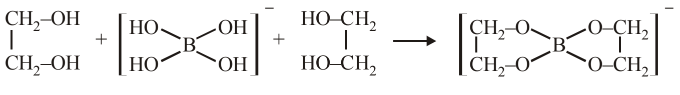
The coordination number exhibited by beryllium is 4 and not 6 so statement (b) is incorrect.

Both $BeCl_2$ and $AlCl_3$ exhibit bridged structures in solid state so (c) is correct statement.





12. (b) *cis*-1,2-diol forms chelated complex ion with the product, $[B(OH)_4]^-$ causing the reaction to proceed in forward direction.



Stable chelated complex ion

EXERCISE 4

1. **(a)** $Al_2(SO_4)_3 + 6NH_4OH \rightarrow 2Al(OH)_3 + 3(NH_4)_2SO_4$

   $Al(OH)_3 + NaOH \rightarrow Na^+[Al(OH)_4]^-$ Soluble complex

   it is insoluble in NH_4OH

2. **(b)** Purification of $Al_2O_3.2H_2O$ is done by leaching. It dissolves the ore leaving behind impurities

3. **(d)** Serpeck's process is employed when silica content of ore is high

4. **(b)** See text for the structure of diborane.

5. **(b)** CaF_2 when added to fused cryolite, lowers the m.0p0. and increases the conductivity.

6. **(b)** Aluminium is reducing in nature. The reduction of Fe_2O_3 by Al is known as Gold Schmidt alumino thermic process

   $2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe \quad \Delta H = -ve$ (exothermic)

7. **(b)** $Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$

   $$\xrightarrow{2H_2O} [Al(OH)_4(H_2O)_2]^-$$

8. **(c)** General formula for alum is

   $M'_2SO_4.M''_2(SO_4)_3.24H_2O$. When M' is replaced by divalent ion the alum is known as pseudo alum.

9. **(c)** $AlCl_3$ is Lewis acid, exists as dimer (Al_2Cl_6) and easily hydrolysed

10. **(c)** B_2H_6 contains hydrogen bridge bonds. These are one electron bonds also known as banana bonds.

11. **(b)** $H_3BO_3 \xrightarrow{100°C} HBO_2 \xrightarrow{160°C}$

    $$H_2B_4O_7 + H_2O \longrightarrow 2B_2O_3 + H_2O$$

12. **(b)** Al electrolytically coated with aluminium oxide is known as anodised aluminium.

13. **(a)** H_3BO_3 is weak monobasic acid

    $$H_3BO_3 + H_2O \rightleftharpoons H_3\overset{+}{O} + H_2\overset{-}{BO_2}$$

14. **(a)** Alumina Al_2O_3 is known as Ruby stone

15. **(b)** The hybridizations of B in H_3BO_3 is sp^2

16. **(d)** Al in its compounds forms covalent bonds.

17. **(a)** In thermite process no catalyst is required

18. **(d)** It is $p\pi - p\pi$ back bonding involving B and F. The smaller atoms show more back bonding.

19. **(c)** The filtrate is yellow due to CrO_4^{2-} ion and residue is brown due to $Fe(OH)_3$.

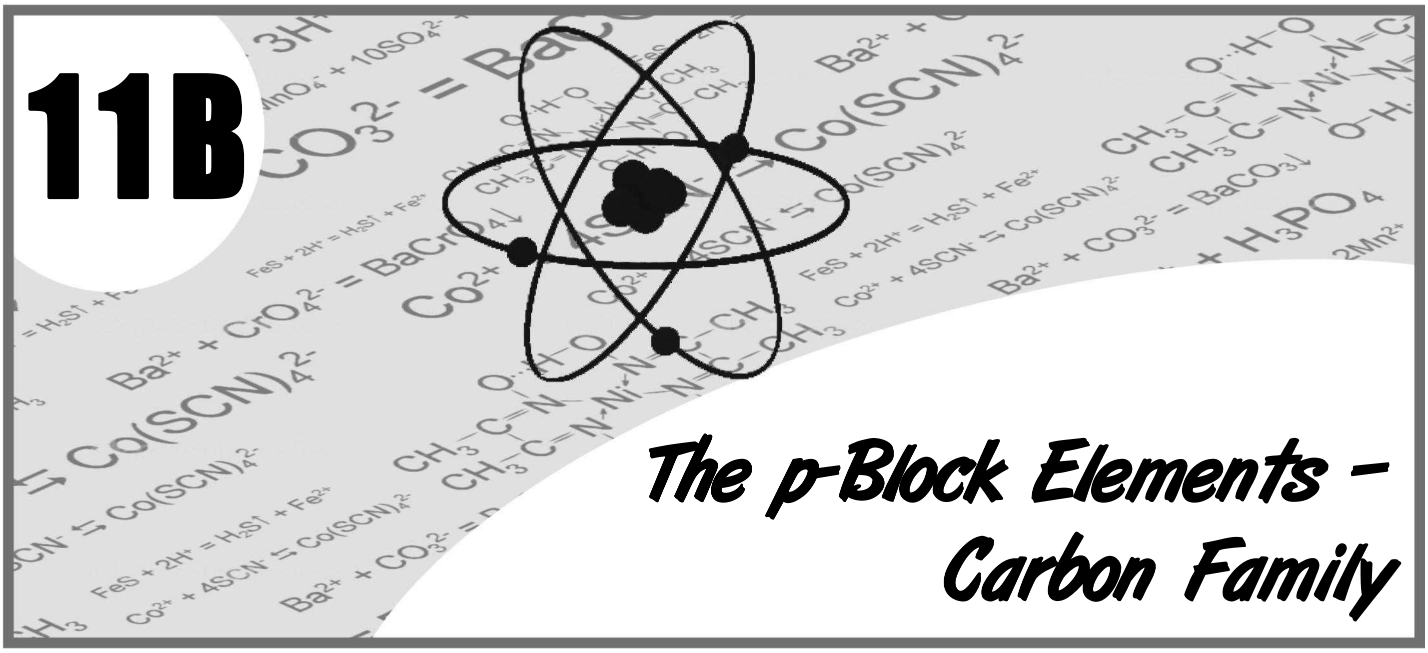
20. **(c)** Due to + I effect of methyl groups the Lewis character of $B(CH_3)_3$ decreases and coordination becomes weaker.

21. **(d)** Statement (d) is correct.

22. **(d)** $2\,AlCl_3.6H_2O \longrightarrow Al_2O_3 + 6HCl + 9H_2O$

23. **(c)** Bauxite ore containing Fe_2O_3 is purified by Baeyer's process.

24. **(b)** Alum form acidic solution due to hydrolysis of Al^{3+}.



11B

The p-Block Elements - Carbon Family

GENERAL CHARACTERISTICS

1. **Electronic configuration :**

Element	*Atomic No.*	*Electronic configuration*	*Valence shell configuration*
Carbon	6	[He] $2s^2 2p^2$	$2s^2 2p^2$
Silicon	14	[Ne] $3s^2 3p^2$	$3s^2 3p^2$
Germanium	32	[Ar] $3d^{10} 4s^2 4p^2$	$4s^2 4p^2$
Tin	50	[Kr] $4d^{10} 5s^2 5p^2$	$5s^2 5p^2$
Lead	82	[Xe] $4f^{14} 5d^{10} 6s^2 6p^2$	$6s^2 6p^2$

2. **Metallic character -** C and Si are non metals, Ge is a metalloid and Sn and Pb are metals.
3. **Appearance -** C is black , Si is light-brown , Ge greyish white, Sn and Pb are silvery white.
4. **Density -** Density increases with the increase in atomic number due to increase in mass per unit volume.
5. **Melting points and Boiling points -** The melting points and boiling points decrease from carbon to lead but carbon and silicon have very high melting and boiling points due to their giant structure.
6. **Oxidation states -** They are as follows

C	Si	Ge	Sn	Pb
(+2) < +4	(+2) < +4	+2 < +4	+2 < +4	+2 > + 4

- The compounds of Ge and Sn in +2 oxidation state are reducing in nature. Since their higher oxidation states +4 are more stable .
- The compounds of Pb in +4 oxidation state are powerful oxidising in nature. Since +2 oxidation state of Pb is more stable .
- The compounds in +2 oxidation state are ionic in nature and in +4 oxidation state are covalent in nature (Fajan's rule)

7. **Negative oxidation states-** Carbon forms C^{4-} and C_2^{2-} in certain compounds e.g.

$$Be_2C\,(Be^{2+} \text{ and } C^{4-}), Al_4C_3\ (Al^{3+}, C^{4-})$$

$$\text{and } CaC_2\ (Ca^{2+} \text{ and } C_2^{2-})$$

8. **Ionisation energy -** It decreases from C to Sn . For Pb it is slightly higher than Sn.
9. **Electronegativity values -** The values decrease from C to Pb but not in a regular manner probably due to filling of d-orbitals in Ge and Sn and f-orbitals in Pb.
10. **Catenation -** It is the tendency of an element to form long chains of identical atoms. The greater the strength of element-element bond, the greater is the strength of catenation.

$C >> Si > Ge \approx Sn > Pb$ (catenation)

Bond →	C– C	Si–Si	Ge– Ge	Sn–Sn
Bond kJ/mole	353.3	225.7	167.2	155.0

11. **Allotropy -** All the elements except Pb show allotrpy.
    Allotropic forms of carbon - Diamond, Graphite and Fullerene
    Amorphous forms of carbon - coal, charcoal etc.
    Silicon (Si) - crystalline and amorphous
    Tin (Sn) - grey tin, white tin and rhombic tin
    Germanium - two crystalline forms
12. **Valency -** All elements exhibit tetravalency. In case of Carbon 406 kJ/ mole of energy is required for promotion of 2s electron to 2p. Formation of two extra bonds provide this energy .
13. **Inert- pair effect -** On descending the group, the stability of +4 oxidation state decreases and that of +2 oxidation state increases.

14. **Atomic and ionic radii -** Both increase from C to Pb
15. **Atomic volume -** Atomic volume shows a regular increase from C to Pb.
16. **Formation of complexes -** C does not give any complex due to non availability of empty d orbitals in valence shell.

    The valence shell of Si and other elements contain d-orbitals and can accomodate more than 8 e^- and can therefore form complexes e.g.

    $$SiF_4 + 2F^- \rightarrow [SiF_6]^{2-}$$

    $$SnCl_4 + 2Cl^- \rightarrow [SnCl_6]^{2-}$$

    The hybridisation in these complexes is sp^3d^2 which is octahedral.
17. **Reactivity :** Increases from C to Pb.
18. **Multiple bonding :** Carbon forms **pπ - pπ** multiple bonds with itself and with S, N and O. Other elements show negligible tendency of this type due to their large size. Others form **dπ - pπ** multiple bonds.

FORMATION OF COMPOUNDS

(i) ***Hydrides :*** All form covalent hydrides .Their number and ease of formation decreases down the group.

- Hydrides of carbon are known as *Alkanes, Alkene* or *Alkynes*.
- Hydrides of Si and Ge are known *Silanes* and *Germanes* but their number is limited.
- The only hydrides of Sn and Pb are SnH_4 (Stannane) and PbH_4 (Plumbane) .
- Their thermal stability decreases down the group.
- Their reducing character increases down the group.

(ii) ***Halides :*** All the elements give tetrahedral and covalent halides of the type MX_4 except $PbBr_4$ and PbI_4, since Pb^{4+} is strong oxidising and Br^- and I^- are strong reducing agent. SnF_4 is ionic.

(a) ***Stability*** - Order of thermal stability with common halogen

$$CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$$

- Order of thermal stability with common metals
  $MF_4 > MCl_4 > MBr_4 > MI_4$

(b) ***Hydrolysis*** - Except CX_4 other tetrahalides are hydrolysed

$$SiX_4 + 2H_2O \rightarrow SiO_2 + 4HX$$

- Ease of hydrolysis
  $SiX_4 > GeX_4 > SnX_4 > PbX_4$
- CX_4 are not hydrolysed due to absence of vacant d-orbitals in valence shell of carbon.

Dihalides -Except carbon other elements form dihalides of the type MX_2 which are more ionic and have higher melting points and boiling points e.g . $SnCl_2$ is a solid whereas $SnCl_4$ is a liquid at room temperature.

- C, Si and Ge form trihalides of the type $MHCl_3$. Pb and Sn do not form trihalides of the type MHX_3

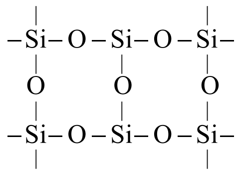
(iii) ***Oxides -*** They form two types of oxides

(a) Mono-oxides of the type MO
CO(neutral) and SiO, GeO, SnO, PbO(all basic)
CO forms a number of coordination compounds with transition metals e.g. $Ni(CO)_4, Fe(CO)_5$ and $Cr(CO)_6$

(b) Dioxides of the type MO_2

$$\underbrace{CO_2, SiO_2}_{\text{Acidic}} \quad \underbrace{GeO_2, SnO_2 \text{ and } PbO_2}_{\text{Amphoteric}}$$

CO_2 is linear, gas at ordinary temperatue. Solid CO_2 is known ***dryice*** or ***drikold.*** SiO_2 is solid with three dimensional network having Si bonded to four oxygen atoms tetrahedrally and covalently.



The bond energy of Si – O bond is 368kJ/mol, therefore SiO_2 is chemically inert and has high melting point. GeO_2, SnO_2 and PbO_2 all are network solids. PbO_2 is a powerful oxidising agent

$$PbO_2 + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O + O_2$$

- Carbon also gives suboxide
  C_3O_2, $O = C = C = C = O$
- Lead also gives mixed oxide
  Pb_3O_4, $2PbO.PbO_2$

(iv) ***Acids -*** All elements give acids of the type H_2MO_3 e.g. H_2CO_3 (carbonic acid), H_2SiO_3 (silicic acid), H_2SnO_3 (meta stannic acid), H_2PbO_3 (meta plumbic acid). Carbonic acid forms two series of salts, bicarbonates (HCO_3^-) and carbonates (CO_3^{--}).

SILICATES

Silicates are metal derivatives of silicic acid H_2SiO_3 and can be obtained by fusing metal oxides or metal carbonates with sand e.g.

$$Na_2CO_3 + SiO_2 \xrightarrow[1780K]{Fuse} (Na_2SiO_3)_n$$

Type of silicates - Silicates contain SiO_4^{4-} tetrahedra formed by sp^3 hybridisation, depending upon the number of O-atoms shared between tetrahedra and fashion, Silicates have been classified into following groups

(i) ***Orthosilicates*** -They contain discrete SiO_4^{4-} tetrahedra, Examples are phenacite Be_2SiO_4, willimite Zn_2SiO_4, zircon $ZrSiO_4$, forsterite Mg_2SiO_4.

(ii) ***Pyrosilicates*** - Here two tetrahedra units are joined by one oxygen atom forming a large discrete $Si_2O_7^{6-}$. Examples are thorteveitite $Se_2(Si_2O_7)$, hemimorphite $Zn_3(Si_2O_7).Zn(OH)_2.H_2O$

(iii) ***Chain silicates*** - Here two oxygen atoms per SiO_4 tetrahedra are shared giving polymeric anion chains. Discrete unit is $(SiO_3^{2-})_n$. Examples: synthetic sodium silicate Na_2SiO_3, lithium silicate Li_2SiO_3, natural spodumene $LiAl(SiO_3)_2$, jodeite $NaAl(SiO_3)_2$, enstalite $MgSiO_3$ and diposide $CaMg(SiO_3)_2$.

(iv) ***Double chains*** -Here two simple chains are held together by shared oxygen atoms. The discrete unit is $(Si_4O_{11}^{6-})_n$. Example mineral tremolde $Ca_2Mg_5Si_{14}O_{11}(OH)_2$

Double chains silicates is also called amphibole

(v) ***Cylic silicates*** - Here two oxygen atoms per SiO_4^{4-} tetrahedra are shared giving discrete unit $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$. Example Beryl $Be_3Al_2Si_6O_{18}$.

(vi) ***Sheet-silicates*** -Here three oxygen atoms per tetrahedra are shared giving two dimensional sheet having discrete unit $(Si_2O_5^{2-})_n$. Example

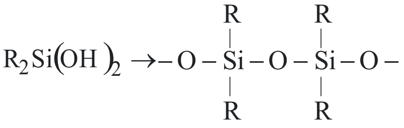
Talc $Mg(Si_2O_5)_2Mg(OH)_2$, Kaolin $Al_2(OH)_4(Si_2O_5)$.

(vii) ***Frame work silicates*** - Here all four oxygen atoms of each tetrahedra are shared. Example are quartz, zeolites, tridymite and crystobalite.

SILICONES

The polymeric compounds containing R_2SiO units, linear cyclic or cross linked are known as silicones. They are manufactured from alkyl substituted chlorosilanes

$$2RCl + Si \xrightarrow[570K]{\text{Cu powder}} R_2SiCl_2 \xrightarrow{2H_2O}$$



$$R_2Si(OH)_2 \rightarrow -O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-$$

Silicone

Silicones are chemically inert, water repellent, heat resistant, good electrical insulators .These are used as lubircants, insulators etc.

CARBIDES

Compounds of carbon with less electronegative elements e.g. Be, B, Si etc are called carbides. These are of three types.

(i) ***Ionic or salt like*** - The carbides of elements of group 1, 2, 13, coinage metals, Zn,Cd. Some lanthanides give ionic or salt like carbides. Prepared by heating oxide with carbon or hydrocarbon at high temperature (2350K)

$$2Be + C \rightarrow Be_2C$$

$$CaO + 3C \rightarrow CaC_2 + CO$$

They are further classified as

(a) ***Acetylides*** *contain* $(-C \equiv C-)^{2-}$. These liberate acetylene on hydrolysis

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + CH \equiv CH$$

They have NaCl type crystal lattice.

(b) ***Methanides*** C^{4-} - These react with water to give methane.

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$

(c) ***Allylides*** - These react with water to give allylene.

$$Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + CH_3C \equiv CH$$

(ii) ***Interstitial carbides*** - These carbides are formed by transition elements especially Cr, Mn and Fe group metals. These are very hard.

(iii) ***Covalent carbides*** - Carbides of B and Si, B_4C and SiC are covalent .SiC is known as *CARBORUNDUM*, used as abrasive and refractory material. B_4C harder than SiC and used as an abrasive.

CARBON

It is widely distributed in the free state (diamond, graphite, coal etc.) and in the combined state (oxides, carbonates hydrocarbons etc.)

Allotropic forms of carbon -The crystalline forms include

(i) **Diamond -**It is beautiful crystalline form, hardest, and has three dimensional polymeric structure, hybridisation of C is sp^3. It is covalent solid, melting point 3650°C, density $3.51 g/cc$ and bad conductor of heat and electricity

When heated at 1800°C - 2000°C, it is converted to graphite.

(ii) **Graphite -**Preparation

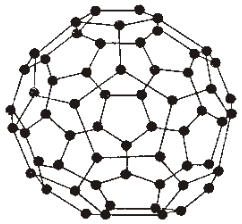
$$3C + SiO_2 \rightarrow SiC + 2CO_2 \rightarrow C + Si\uparrow \text{ (graphite)}$$

It is dark grey, having hexagonal plates, hybrisation of C is sp^2, good conductor of heat and electricity due to free movement of electrons. It was also known as black lead or plumbago. It is very good lubricant.

Aqua dag - suspensions of graphite in water

Oil dag - suspension of graphite in oil lubricants.

(iii) **Fullerene :** Fullerenes are large cage like spheroidal molecules with general formula C_{2n} (where n ≥ 30). Two important member are C_{60} and C_{70}. C_{60} fullerene looks like a soccer ball (so called bucky ball).



Amorphous forms of carbon are

(i) Coal
(ii) Coke
(iii) Charcoal or wood charcoal
(iv) Bone-black or animal charcoal
(v) Lamp-black
(vi) Carbon-black
(vii) Gas carbon
(viii) Petroleum coke

Varieties of coal -

(i) Peat 60 % carbon
(ii) Lignite 70% C
(iii) Bituminous 78%C
(iv) Semi bituminous 83% C
(v) Anthracite 90%C

Anthracite is purest - amorphous form, burns without smokey flame.

Coke- Coal $\xrightarrow{\text{distructive distillation}}$ Coke.

It contains $C = 80 - 90\%$

Uses - Reducing agent in Iron and steel industry for making water gas and graphite.

Wood charcoal -It is obtained by strongly heating wood without access to air. When heated with steam it becomes more activited.

Uses -To remove colouring matters and odoriferous gases.

Bone-black or animal charcoal - It is obtained by destructive distillation of bones in iron retort. By products are bone oil or pyridine.

Uses - As adsorbant. On burning it gives bone ash which is calcium phosphate and used in the manufacture of phosphorous and phosphonic acid.

Lamp black - It is obtained by burning vegetable oils in limited supply of air.

Uses - In the manufacture of printing ink , black paint, varnish and carbon paper.

Carbon black - It is obtained by burning natural gas in limited supply of air.

Uses - Added to rubber mixture for making automobile tyres.

Gas carbon and petrolium coke - When coal is subjected to destructive distillation carbon deposited on walls is scraped and called gas carbon. Similarly petroleum coke is deposited while distilling crude petroleum.

Uses - Both are good conductors of electricity when pressed into sticks they make good electrodes, known as gas electrodes.

Sugar charcoal - It is obtained by heating sugar in absence of air. It is purest form of carbon.

CARBONDIOXIDE CO_2

Preparation -

(i) **Lab method**

$$CaCO_3 + 2\text{ dil. }HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

(ii) **Manufacture**

(a) $CaCO_3 \rightarrow CaO + CO_2$

(b) Fermentation $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + CO_2$

(c) From fuel gases

$$K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3$$

Physical Properties -Colourless, 1.5 times heavier than air, can be poured downwards like H_2O .Animals die in its presence due to lack of O_2 , it is also known as **black damp**.

Chemical properties :

(i) Stability - Fairly stable, decomposed at 1775K.

$$2CO_2 \rightarrow 2CO + O_2$$

(ii) Incombustible and non supporter of combustion but active metals e.g. Mg, Na, K continue burning in a jar of the gas.

$$CO_2 + 2Mg \rightarrow 2MgO + C$$

$$CO_2 + 4Na \rightarrow 2Na_2O + C$$

$$Na_2O + CO_2 \rightarrow Na_2CO_3$$

(iii) Acidic nature -

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

(iv) Lime water -

$$Ca(OH)_2 + CO_2 \rightarrow \underset{\text{ppt}}{CaCO_3 \downarrow} + H_2O \xrightarrow{CO_2} \underset{\text{clear solution}}{Ca(HCO_3)_2}$$

(v) Reduction - $CO_2 + C(\text{red hot coke}) \rightarrow 2CO$

(vi) Photosynthesis-

$$6CO_2 + 6H_2O \xrightarrow{\text{Chlorophyll}} C_6H_{12}O_6 + 6O_2$$

$$6xCO_2 + 5xH_2O \rightarrow (C_6H_{10}O_5)_x + 6xO_2$$

Uses - In household as fire extinguisher. Dry powder **fire extinguisher** contains ($NaHCO_3$ + sand) which is decomposed by heat.

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

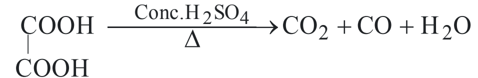
Foamite extinguisher contains baking soda and aluminium sulphate and is used for oil fires.

Structure $\underset{\cdot\cdot}{\ddot{O}} = C = \underset{\cdot\cdot}{\ddot{O}}$. Linear, dipole moment is zero.

Carbon monooxide CO :

Preparation -

(i) Lab method -



$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow[\Delta]{\text{Conc.}H_2SO_4} CO_2 + CO + H_2O$$

oxalic acid

(ii) Manufacture -

(a) Air $\xrightarrow{\text{Red hot coke}} N_2 + CO$ (producer gas)

(b) Steam $\xrightarrow{\text{Red hot coke}} CO + H_2$

(water gas synthesis gas or blue gas)

(iii) Other methods - Heating $K_4[Fe(CN)_6]$ with Conc.H_2SO_4

$$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \rightarrow$$

$$2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

Properties - Neutral, colourless, poisonous, burns with blue flame. Sparingly soluble in water. With haemoglobin it gives **"carboxy haemoglobin"** which destroys its capacity to supply oxygen to the body.

(a) ***Burning*** -Non supporter of combustion. Burns in air with blue flame.

$$2CO + O_2 \rightarrow 2CO_2$$

Reduces ammonical $AgNO_3$

$$2[Ag(NH_3)_2]OH + CO \rightarrow 2Ag + CO_2 + H_2O + 4NH_3$$

Reduces Fehling-solution

$$2CuO + CO \rightarrow Cu_2O + CO_2$$

(b) Reducing nature - Metal oxides are reduced to metals.

$$Fe_2O_3 + 3CO \xrightarrow{117\text{ K}} 2Fe + 3CO_2$$

$$CO + H_2O \xrightarrow[\text{T,P}]{\text{high}} H_2 + CO_2$$

(c) Unsaturated nature -It gives addition products.

$$Cl_2 + CO \xrightarrow[\text{or camphor}]{\text{sunlight}} COCl_2\,(\text{phosgene})$$

$$CO + 2H_2 \longrightarrow CH_3OH$$

$$NaOH + CO \longrightarrow HCOONa$$

$$CO + S \xrightarrow{\Delta} O = C = S\,(\text{carbonyl sulphide})$$

$$CuCl + CO + 2H_2O \rightarrow CuCl.CO.2H_2O$$

(d) Formation of metal carbonyles **-** It acts as lewis base.

$$M + xCO \rightarrow M(CO)_x$$

$$M = Ni, Cr, Mo, Fe\ or\ Co$$

$$\text{structure} : C^- ::: O^+ : \leftrightarrow : C^- \equiv O^+ : \leftrightarrow :C \overset{\leftarrow}{\equiv} O:$$

Uses - In metallurgy of Ni-**Monds process**

$(Ni + 4CO \rightarrow Ni(CO)_4 \xrightarrow{\Delta} Ni + 4CO)$

Manufacture of methanol, phosgene, synthetic petrol, as reducing agent.

Test -

(i) Burns with blue flame.

(ii) Reduces iodine pentaoxide to I_2.

$$I_2O_5 + 5CO \rightarrow I_2 + 5CO_2$$

($CHCl_3$ or CCl_4 layer terms violet)

Carbogen - (mixture of $O_2 + 5 - 10\% CO_2$) is used for artificial respiration for victims of CO poisoning.

FUEL GASES

1. **Water gas (H_2 + CO)**

Preparation : $\underset{\text{Red hot Coke}}{C} + \underset{\text{Steam}}{H_2O} \rightarrow \underset{\text{Water gas}}{CO + H_2}$ - 28kcal

Uses : Burns with blue flame, calorific value 2700 kcal/m^3. Industrial source of hydrogen (**Bosch process**). Manufacture of methyl alcohol (**Patart Processs**) - Synthetic petrol (**Fisher-Tropsch process**). For making carburetted water gas.

2. **Semi water gas :** (mixture of water gas and producer gas)

Preparation : $\text{Steam} + \text{air} \xrightarrow{\text{Red hot coke}} \text{semi water gas}$

Composition : CO = 27.0%, H_2 = 10.9%
CH_4 = 1.28%, CO_2 = 4.50%
N_2 = 56.3%

Properties and uses : Its calorific value 160 - 180 B.T.U. per cubic foot. As fuel in steel industry and for production of power in internal combustion engine.

3. **Producer gas :** Burning coke + limited air → producer gas

Composition : CO = 31.7%, N_2 = 65.7%, CO_2 = 2.5%

Properties and uses : Poisonous, combustible but non supporter of combustion, has low calorific value. Mainly employed as fuel.

4. **Coal gas :**

Preparation : By destructive distillation of coal

Composition : H_2 = 45-55% N_2 = 2-12%
CH_4 = 25-35%, CO_2 = 0-3%
CO = 4-11%, O_2 = 1-1.5%

Ethylene, acetylene, benzene etc = 2.5-5%

Uses : Used as illuminant, as fuel, to provide inert atmosphere in metallurgical processes.

5. **Natural gas :** It is found along with petroleum below the surface of earth.

Composition : CH_4 = 60-80%
Higher hydrocarbons = 2-14%
C_2H_6 = 5-9%, C_3H_8 = 3-18%

Uses : It is used as a fuel. Its partial combustion yields carbon black (reinforcing agent for rubber)

6. **Oil gas :**

Preparation :

$$\text{Kerosene} \xrightarrow[\text{absence of air}]{\text{heated in}} \text{mixture of simple hydrocarbons}$$

Uses : It is used as fuel in laboratories in Bunsen Burners.

7. **Wood gas :**

Preparation : $\text{wood} \xrightarrow[\text{absence of air}]{400°C} CH_4, C_2H_6, H_2, CO, N_2$

Uses : It is used as fuel

8. **Liquified Petroleum gas (LPG)**

Composition : n-Butane + Iso-butane

Uses : It is used as domestic fuel.

9. **Gobar gas :**

Preparation :

$$\text{Cow dung} \xrightarrow[\text{absence of air}]{\text{fermentation}} CH_4(\text{main}),\ CO \text{ and } H_2$$

Uses : As domestic fuel.

British Thermal Unit (B.T.U.) : It represents the amount of heat required to raise the temperature of one pound of water through 1°F. One B.T.U. is equal to 252 calories.

SILICON AND ITS COMPOUNDS

Silicon does not occur free in nature . In abundance it is next to O_2.

OCCURANCE

As oxide SiO_2 (Silica)in sand, quartz, flint. As silicates of Al, Mg , K, Fe etc. Aluminium silcate is **most widely distributed as Felspar** ($KAlSi_2O_3$)**and Mica** [$KH_2Al(SiO_4)_3$], **Feldspar** ($K_2Al_2O_3 6SiO_2$)**, Kaolinite** ($Al_2O_3.2SiO_2.2H_2O$)**.**

PREPARATION OF AMORPHOUS FORM

It is very common and may be obtained by heating powdered quartz or finely divided silica with Mg powder.

$$SiO_2 + 2Mg \rightarrow Si + 2MgO$$

PREPARATION OF CRYSTALLINE FORM

By reduction of $SiCl_4$ with molten Al

$$3SiCl_4 + 4Al \rightarrow 3Si + 4AlCl_3$$

By reduction of highly purified $SiCl_4$ with hydrogen

$$SiCl_4 + 2H_2 \rightarrow Si + 4HCl$$

ZONE-REFINING

Silicon is purified by Zone-refining process because the impurities present in it are more soluble in the liquid phase than in the solid phase.

PROPERTIES

Crystalline form possesses metallic lustre. It is very hard and scratches glass. Crystalline silicon is isomorphous with diamond.

CHEMICAL REACTIONS OF AMORPHOUS SILICON :

Burns in air $Si + O_2 \rightarrow SiO_2$

$$Si + 2F_2 \rightarrow SiF_4$$

$$Si + 2Cl_2 \rightarrow SiCl_4$$

$$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2$$

$$Si + 2H_2O\,(steam) \rightarrow SiO_2 + 2H_2 \uparrow$$

USES

Silicon chips used for computing devices are doped with P,As, Al or Ga to enhance the semiconductor properties.

COMPOUNDS OF SILICON

(i) **SiO_2 (silica) -** It exists in three crystalline forms **Quartz, Trydimite and crystobalite**. Further each form has α and β form. At low temperature the α form is stable and at high temperature the β form is stable .

(ii) ***Sand -*** It is crushed form of quartz produced in nature by weathering of rocks .

(iii) ***Flint -*** It is amorphous silica associated with quartz .

(iv) ***Kiesulguhr -*** Siliceous rock composed of the remains of sea organisms. Used as absorbent for nitroglycerine.

(v) ***Quartz or rock crystal -*** It is purest form of silica It is optically active.

(vi) ***Silicic acid***

(a) *Ortho silicic* acid H_4SiO_4 or $Si(OH)_4$

$$3SiF_4 + 4H_2O \rightarrow 2H_2SiF_6 + H_4SiO_4 \downarrow$$

(b) *Meta silicic* acid H_2SiO_3 or $SiO(OH)_2$

$$Na_2SiO_3 + 2HCl \rightarrow 2NaCl + H_2SiO_3$$

(vii) Silicic acid sol -Colloidal solution of silicic acid.

(viii)Silica gel -Transparent gel of bluish white colour $SiO_2.xH_2O$.

(ix) Water glass or sodium silicate-Sodium silicate containing excess of SiO_2.

$$Na_2SiO_3.SiO_2 \text{ to } NaSiO_3.3SiO_2$$

(x) Silica garden- Aqueous solution of sodium silicate containing crystals of various coloured salts e.g. copper sulphate, cobalt nitrate , manganese chloride, nickel chloride etc.

***(xi) Hydro flurosilicic acid* H_2SiF_6**

$$3SiF_4 + 4H_2O \rightarrow H_4SiO_4 \downarrow + 2H_2SiF_6 \text{ soluble}$$

(xii)Permutit -Artificially perpared sodium aluminium silicate containing varying composition of sodium ,aluminium and silica $Na_2Al_2Si_2O_8.xH_2O$ .Used for softening hard water.

(xiii)Zeolites -They have honey comb like structure and have the general formula $\frac{M_x}{n}(AlO_2)_x.(SiO_2)_y.zH_2O$

$$M = Na^+, K^+ \text{ or } Ca^{++}$$

$$n = \text{Charge on metal}$$

They act as ion exchanger and molecular sieves. They can be artificially perpared by heating **China clay, Silica** and **Na_2CO_3.**

(xiii)Ultramarines - Zeolite type silicates, containing ions like Cl^-, SO_4^{2-}, S^{2-} and not water, are known as ultramarines e.g. $Na_2(Al_6Si_6O_{24})S_2$ Many of them are coloured and used as pigments and calicoprinting.

(xiv)Carborundum - silicon carbide

$$SiO_2 + 2C \rightarrow Si + 2CO$$

$$Si + C \rightarrow SiC$$

It is nearly as hard as diamond .

GLASS

Amorphous, hard, brittle, transparent, transluscent super cooled solution of various silicates and borates of K, Ca and Pb . It has no definite formula but roughly can be represented as

$M'_2O.M''O.xSiO_2$ where $M' = Na, K$ and $M'' = Ba, Zn, Pb$

Raw material used in the manufacture of glass.

(i) SiO_2

(ii) Na_2CO_3, K_2CO_3 or $NaNO_3$ or KNO_3

(iii) Alkaline earth metals e.g. $CaCO_3, BaCO_3$

(iv) oxides of heavy metals

(v) Cullets (pieces of glass)

(vi) Colouring matter

Colouring materials -

Colour	*Substances*	*Colour*	*Substances*
Green	$Cr_2O_3, FeSO_4$	Red	Cu_2O, Selenium oxide
Yellow	Ferric iron, uranate of Na	Lemon yellow	CdS
Purple	MnO_2	Black	NiO
Ruby	$AuCl_3$	Milky white	Na_3AlF_6
Blue	CuO, CoO	Peacock Blue	cupric Salts

Manufacture - Mixture of raw materials $\xrightarrow{1200°C}$ till CO_2 escapes → clear liquid. After some cooling it is used for casting articles

Type of glass -	*Batch*	*Properties*	*Uses*
(i) Soft or soda glass	$Na_2O.CaO.SiO_2$	Soft	Window glass and bottles
(ii) Hard or potash glass	Sand+lime stone $+K_2CO_3$	Hard	Hard glass apparatus
(iii) Flint glass	Sand +Red lead+ K_2CO_3	High refractive index	Optical instrument, prisms
(iv) Pyrex glass	$Na_2O.B_2O_3Al_2O_3SiO_2$	Low coefficient	Glass ware
(v) Jena glass	Zn and Barium Borosilicate	Low coefficient of expansion	Glass wares
(vi) Crookes glass	$K_2O.PbO.CeO_2.SiO_2$	Cuts off U.V. rays	Eye lenses
(vii) Quartz glass or silica glass	Pure SiO_2	Low coefficient of expansion	Scientific wares
(viii) Safety glass or shatter proof glass	Between two glass layers a transparent plastic layer of vinyl acetate resin is placed		Automobile wind shields, goggles etc.
(ix) Reinforced glass	Has network of wires	Does not shatter	
(x) Ground glass	Soft glass with ground surface		

Annealing - The process of slow cooling of glass is known as annealing .The glass becomes soft.

TIN(Sn) :

$[Kr]4d^{10}4s^2 4p^2$

Principal ores of tin - (i) **Cassiterite or Tin stone,** SnO_2 (ii)**Tinpyrites,** $SnS.Cu_2S.FeS$.

Extraction -

(i) ***Concentration*** - By gravity process washing with water and then magnetic separation.

(ii) ***Roasting*** -To remove volatile impurities

$$S + O_2 \rightarrow SO_2$$
$$4As + 3O_2 \rightarrow 2As_2O_3$$

(iii) ***Smelting*** - It is carried out in reverberatory furnace with coal (powdered anthracite)and lime stone.

$$SnO_2 + 2C \rightarrow Sn + 2CO$$
$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2 \ (\text{slag})$$

Sn so obtained contains iron and other metals and called black tin .

(iv) ***Refining*** by (a) **Liquation** (b) **Poling** and (c) **Electrolytic**

Properties - Soft silvery white metal, ductile and malleable. It has maximum number of isotopes and three allotropic forms.

$$\text{Grey} \xrightleftharpoons{18°C} \text{White} \xrightleftharpoons{161°C} \text{Rhombic}$$

Tin cry - It produces a peculiar cracking sound on bending which is known as tin cry.

Tin plague - It is the conversion of white tin to grey tin at low temperature which crumbles into powder.

Tinning - Since tin is not attacked by organic acids the utensils are protected by thin layer of tin .A pinch of NH_4Cl is sprinkled over hot and clean surface, when HCl liberated removes the oxide film.Tin then rubbed over the clean surface with the help of rag dipped in NH_4Cl powder. The utensil is immediately dipped in water to avoid oxide formation .

Tin plating - It involves the depositing of thin protective layer of tin over sheets of iron electrolytically.

Chemical properties - With acids

$$Sn + 2HCl \rightarrow SnCl_2 + H_2 \uparrow$$
$$Sn + dilH_2SO_4 \rightarrow SnSO_4 + H_2$$
$$Sn + 4H_2SO_4(Conc.) \rightarrow Sn(SO_4)_2 + 2SO_2 + 4H_2O$$
$$4Sn + 10HNO_3(dil.) \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$Sn + 4HNO_3(conc.) \rightarrow \underset{\text{Meta stannic acid}}{H_2SnO_3} + 4NO_2 + H_2O$$

With alkali : $Sn + 2NaOH + H_2O \rightarrow Na_2SnO_3 + 2H_2 \uparrow$

With O_2 at 1500°C: $Sn + O_2 \rightarrow SnO_2$

With steam : $Sn + 2H_2O \rightarrow SnO_2 + 2H_2$

COMPOUNDS OF TIN :

(i) ***Stannic Oxide*** *(*SnO_2*)* **-** It occurs naturally as cassiterite.

Preparation - $Sn + O_2 \xrightarrow{\Delta} SnO_2$

$$H_2SnO_3 \xrightarrow{\Delta} SnO_2 + H_2O$$

Properties - White solid, insoluble in water and amphoteric in nature.

$$SnO_2 + 2H_2SO_4 \rightarrow Sn(SO_4)_2 + 2H_2O$$
$$SnO_2 + 2NaOH \rightarrow Na_2SnO_3 + H_2O$$

Uses - As polishing powder, in glass and pottery manufacture.

(ii) ***Stannous oxide (SnO) -***

Preparation - $\underset{\text{Sn(II) oxalate}}{SnC_2O_4} \xrightarrow{\Delta} SnO + CO + CO_2$

Properties : It is black solid and amphoteric in nature.

$$SnO + 2H^+ \rightarrow Sn^{2+} + H_2O$$
$$SnO + 2OH^- \rightarrow SnO_2^{2-} + H_2O$$

(iii) ***Sulphides -*** SnS precipitated by H_2S .It is dark brown solid, soluble in yellow ammonium sulphide forming $(NH_4)_2SnS_3$

(iv) Stannous chlorides ($SnCl_2.2H_2O$ ***) -***

Preparation - $Sn + 2HCl(conc.) \rightarrow SnCl_2 + H_2$

Anhydrous $Sn + 2HCl(dry\ gas) \xrightarrow{\Delta} SnCl_2 + H_2$

Properties -

- White crystalline solid, soluble in water, alcohol and ether.
- Hydrolysed in water

$$SnCl_2 + H_2O \rightarrow Sn(OH)Cl + HCl$$

- Strong reducing agent

$$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4$$
$$2CuCl_2 + SnCl_2 \rightarrow Cu_2Cl_2 + SnCl_4$$
$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

(v) Butter of tin - $SnCl_4.5H_2O$ used as mordant in dyeing.

(vi) Purple of cassius - Colloidal particles of gold absorbed by stannic acid $Sn(OH)_4$ is known as purple of cassius. It is used for colouring glass and pottery.

(vii) Alloys of tin - Some important alloys of tin are

(a)	Solder	Sn 50-70%	Pb 30-50%		
(b)	White metal	Sn 82%	Sb 12%	Cu 6%	
(c)	Brittania metal	Sn 90 %	Sb 7%	Cu 3%	
(d)	Soluminium	Sn 55%	Zn 33%	Al 11%	Cu 1%
(e)	Babbit metal	Sn 90%	Sb 7%	Cu 2%	
(f)	Pewter	Sn 80%	Pb 20%		
(g)	Dental alloy	Alloy of Sn , Ag, and Hg			

LEAD (Pb) : $[Xe]5d^{10}6s^26p^2$

Principal ores - (i) Galena PbS (ii) Anglesite $PbSO_4$(iii) Cerrussite $PbCO_3$.

Extraction from galena - Two important processes are

(a) **Air reduction process**

(b) **Carbon reduction process**

(a) Air reduction process

(i) ***Concentration*** - By froth floatation process

(ii) ***Roasting*** - Roasted in air at **500°C – 600°C.**

$$3PbS + 5O_2 \rightarrow 2PbO + PbSO_4 + 2SO_2$$
$$2PbO + PbS \rightarrow 3Pb + SO_2$$
$$PbSO_4 + PbS \rightarrow 2Pb + 2SO_2$$

(b) Carbon reduction process : Mixed sulphides (PbS & ZnS) are roasted to obtain oxides which are fed into blast furnace with coke and lime.

$$PbO + C \rightarrow Pb + CO$$
$$ZnO + C \rightarrow Zn + CO$$
$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$$

Molten lead tapped off from the bottom.

Purification - Electrolytic method to remove Cu, Ag, Au, Sb etc.

Properties - Bluish, grey lustrous metal which acquires dull appearance when exposed to air due to formation of basic carbonate $(Pb(OH)_2.PbCO)_3$. Poor conductor of electricity.

Chemical properties -

(i) $Pb + S \rightarrow PbS$

(ii) $Pb + 2Cl_2 \rightarrow PbCl_4$

(iii) $2Pb + O_2 \rightarrow 2PbO$

(iv) $6PbO + O_2 \rightarrow 2Pb_3O_4$

(v) $Pb + 2HCl \rightarrow PbCl_2 + H_2$

(vi) $PbCl_2 + 2HCl \rightarrow \underset{\text{Chloroplumbous acid}}{H_2PbCl_4}$

(vii) $Pb+2H_2SO_4(conc.) \rightarrow PbSO_4+SO_2+2H_2O$

(viii) $3Pb+8HNO_3(dil.) \rightarrow 3Pb(NO_3)_2++2NO+4H_2O$

(ix) $Pb+4HNO_3(conc.) \rightarrow Pb(NO_3)_2+2NO_2+2H_2O$

(x) $2Pb+4CH_3COOH \rightarrow 2(CH_3COO)_2Pb+2H_2O$

(xi) $Pb + NaOH \rightarrow Na_2PbO_2 + H_2$

Plumbo Solvancy - Formation of lead hydroxide with H_2O in presence of air is known as plumbo solvancy.

$$2Pb + 2H_2O + O_2 \rightarrow 2Pb(OH)_2$$

Hence lead is readily corroded hard water has no action on lead which forms a protective layer of $PbCO_3$ and $PbSO_4$

Hence hard water can be conveyed through lead pipes.

Uses - In lead accumulators, pigments such as red lead, chrome yellow, chrome red, $(C_2H_5)_4Pb$ as antiknock compound, manufacturing of sulphuric acid.

COMPOUNDS OF LEAD

(i) Lead monooxide (PbO) -

Preparation -

(i) $2Pb(NO_3)_2 \rightarrow 2PbO+4NO_2+O_2$

(ii) $PbCO_3 \rightarrow PbO+CO_2$

(iii) $2Pb+O_2 \xrightarrow{300°C}$

2PbO **(Yellow powder, known as Massicot)**

$2PbO+O_2 \xrightarrow{900°C}$

2PbO **(Reddish yellow, known as Litharge)**

Properties - Insoluble in water and amphoteric in nature.

$$PbO + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O$$
$$PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O$$
$$6PbO + O_2 \xrightarrow{470K} \underset{\text{Red lead}}{2Pb_3O_4} \xrightarrow{775K} 6PbO + O_2$$

Uses - Making glass, pottery, Massicot mixed with glycerine joins glass and stone . As drier in paints and varnishes.

(ii) Lead dioxide (PbO_2 **) -**

Preparation - By any of the methods given below

(i) $Pb_3O_4 + dil.HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O + PbO_2$

(ii) $Pb(OH)_2 + NaOCl \rightarrow PbO_2 + H_2O + NaCl$

(iii) $2Pb(OH)_2 + 2Ca(OCl)_2 \rightarrow 2PbO_2 + 2CaCl_2 + 2H_2O + O_2$

(iv) $Pb(OH)_2 + CaOCl_2 \rightarrow PbO_2 + CaCl_2 + H_2O$(lab method)

(v) $3PbO + KClO_3 \rightarrow 3PbO_2 + KCl$

(vi) $PbO + KNO_3 \rightarrow PbO_2 + KNO_2$

Properties - It is brown solid. Powerful oxidising in nature.

$$PbO_2 + SO_2 \rightarrow PbSO_4$$
$$PbO_2 + 4HCl(conc.) \rightarrow PbCl_2 + 2H_2O + Cl_2$$

Amphoteric in nature

$$PbO_2 + 2NaOH \rightarrow Na_2PbO_3 + H_2O$$
$$2PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O + O_2$$
$$PbO_2 + 2CaO \rightarrow Ca_2PbO_4$$

Uses - Storage batteries and match industry, as oxiding agent.

(iii) Trilead tetraoxide, Red lead, minium or Sindhur -

Preparation - $6PbO + O_2 \rightarrow 2Pb_3O_4$

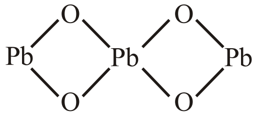
Properties - Red crystalline solid, insoluble in water.

Action of heat $2Pb_3O_4 \rightarrow 6PbO + O_2 \uparrow$

With acids

$$Pb_3O_4 + 8HCl(conc.) \rightarrow 3PbCl_2 + 4H_2O + Cl_2$$
$$2Pb_3O_4 + 6H_2SO_4 \rightarrow 6PbSO_4 + 6H_2O + O_2$$
$$2Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

Structure



Uses - In glass, match and pottery and as red pigment.

(iv) Basic lead carbonate, white lead $[2PbCO_3.Pb(OH)_2]$:

Preparation - Dutch process - It is formed by exposing thin sheets of lead to vapours of acetic acid in presence of horse dung or tan bark .

$$2Pb + O_2 + 2H_2O \rightarrow 2Pb(OH)_2$$

$$Pb(OH)_2 + 2CH_3COOH \rightarrow (CH_3COO)_2Pb + 2H_2O$$

$$Pb(OH)_2 + (CH_3COO)_2Pb \rightarrow \underset{\text{(Basic lead acetate)}}{Pb(CH_3COO)_2.Pb(OH)_2}$$

$$3[Pb(CH_3COO)_2.Pb(OH)_2] + 4CO_2 + 2H_2O \rightarrow \underset{\text{(white lead)}}{2[2PbCO_3.Pb(OH)_2]} + 6CH_3COOH$$

Properties - White crystalline solid, turns black when exposed to H_2S due to PbS formation .It is highly poisonous.

Action of heat

$$2PbCO_3.\,Pb(OH)_2 \rightarrow Pb_3O_4 + H_2O + CO + CO_2$$

Uses - As a white paint.

(v) Halides of lead [Pb(II) halide] :

Preparation - $\underset{\text{(soluble lead salt)}}{Pb^{2+}} + 2X^- \rightarrow PbX_2 (X = F, Cl, Br, I)$

PbI_2 yellow, others are white solids . $PbCl_2$ and PbI_2 are soluble in hot water.

- $PbCl_2$ forms complex with conc. HCl,

  $PbCl_2 + 2HCl \rightarrow H_2[PbCl_4]$ (Soluble)

  $PbCl_2 + Ca(OH)_2$ (lime water) $\rightarrow$

  $\cdot\ Pb(OH)Cl + CaO + HCl$

- Covalent character

  $PbI_2 > PbBr_2 > PbCl_2 > PbF_2$

Pb (IV) halides :

Preparation -

$$PbO_2 + 4HCl(conc.) \xrightarrow{273K} PbCl_4 + 2H_2O$$

Properties - It is covalent liquid and unstable.

$$PbCl_4 \rightarrow PbCl_2 + Cl_2$$

- PbF_4 is ionic solid.
- **Sugar of lead** $(CH_3COO)_2Pb$ -It has sweet taste.
- **Chrome yellow or Lemon chrome** $PbCrO_4$
- **Basic lead Chromate or chrome red**

  $PbCrO_4.Pb(OH)_2$ - It is red pigment.
- **Lead tetra ethyl**

  $Pb + 4C_2H_5Cl + 4Na \rightarrow Pb(C_2H_5)_4 + 4NaCl$

  - Antiknock agent.
- **Lithophone** $(BaSO_4. + ZnS)$ is substitute of white lead.

Fusible Alloys of lead :

1. Type metal	Pb 82% Sb 15% Sn 3 %
2. Wood metal	Bi 50% Pb 25% Sn 12.5% Cd 12.5%
3. Lipowitz	Bi 50% Pb 27% Sn 13% Cd 10%
4. Rose metal	Bi 50% Pb 28% Sn 22%
5. Newton's metal	Bi 50% Pb 31% Sn 19 %

Exercise-1 | NCERT BASED QUESTIONS

Very Short/ Short Answer Questions

1. Explain why silicon shows a higher covalency than carbon?

2. Why is diamond a bad conductor of electricity but a good conductor of heat?

3. Which oxide of carbon is an anhydride of carbonic acid ?

4. Why carbon forms covalent compounds whereas lead forms ionic compounds?

5. What name is given to the compounds formed by more electropositive elements with carbon?

6. What are silicates?

7. Silanes gets hydrolysed by water whereas alkanes do not, why?

8 $(CH_3)_3N$ is basic but $(CF_3)_3N$ is not basic. Explain.

9. (a) CO_2 is a gas while SiO_2 is a solid. Explain.

(b) Give one chemical reaction to show that:

(i) Tin (II) is a reducing agent whereas Pb (II) is not.

(ii) Tin (II) reduces mercuric salt to mercurous salt.

10. (a) Carbon monoxide is readily absorbed by ammonical cuprous chloride solution but carbon dioxide is not. Explain.

(b) Silanes are few in number whereas alkanes are large in number. Explain.

(c) Diamond is covalent, yet it has high melting point. Why?

11. Give reason :

(a) Silicon form compounds with coordination number of 5 and 6.

(b) Si—F bond is stronger than C—F bond although Si is larger in size than C.

12. Arrange the following in increasing order of the property indicated:

(a) CCl_2, $SiCl_2$, $GeCl_2$, $SnCl_2$ and $PbCl_2$ (stability)

(b) CO, SiO, SnO, GeO, PbO (basicity)

(c) SiF_4, $SiCl_4$, SiI_4, $SiBr_4$ (stability)

13. Out of CCl_4 and $SiCl_4$ which one reacts with water?

14. $[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ is not. Give possible reasons.

Long Answer Questions

15. (i) C and Si are almost always tetravalent but Ge, Sn and Pb show bivalency. Why?

Or

Why the tendency to exhibit + 2 oxidation state increases with increasing atomic number in group 14.

Or

+ 2 oxidation of lead is more stable than + 4 oxidation state. Give reasons.

(ii) (a) Why $N(CH_3)_3$ is pyramidal but $N(SiH_3)_3$ is planar?

(b) Why $(SiH_3)_3N$ is a weaker base than $(CH_3)_3N$?

(iii) Account for the following:

PbO_2 is a stronger oxidizing agent than SnO_2.

Or

PbO_2 can act as an oxidizing agent.

16. Glass made up of SiO_2 reacts with HF to form SiF_6^{2-} anion. The analogous CF_6^{2-} anion does not form. Why?

Multiple Choice Questions

17. Which of the following is most stable?

(a) Sn^{2+} (b) Ge^{2+}

(c) Si^{2+} (d) Pb^{2+}

18. Cement, the important building material is a mixture of oxides of several elements. Besides calcium, iron and sulphur, oxides of elements of which of the group (s) are present in the mixture?

(a) Group 2

(b) Groups 2, 13 and 14

(c) Groups 2 and 13

(d) Groups 2 and 14

19. The most commonly used reducing agent is

(a) $AlCl_3$ (b) $PbCl_2$

(c) $SnCl_4$ (d) $SnCl_2$

20. Lead pipes are not suitable for drinking water because

(a) lead forms basic lead carbonate

(b) lead reacts with water containing air to form $Pb(OH)_2$

(c) a layer of lead dioxide is deposited over lipes

(d) lead reacts with air to form litharge

21. Catenation i.e., linking of similar atoms depends on size and electronic configuration of atoms. The tendency of catenation in Group 14 elements follows the order :

(a) $C > Si > Ge > Sn$ (b) $C >> Si > Ge \approx Sn$

(c) $Si > C > Sn > Ge$ (d) $Ge > Sn > Si > C$

22. Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite

(a) is an allotropic form of diamond

(b) has molecules of variable molecular masses like polymers

(c) has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak inter plate bonds

(d) is a non-crystalline substance

23. Which statement is false
(a) Water gas is a mixture of hydrogen and carbon dioxide.
(b) Producer gas is a mixture of CO and nitrogen
(c) Water gas is a mixture of water vapour and hydrogen.
(d) Natural gas consists of methane, ethane and gaseous hydrocarbons.

24. Silicon has a strong tendency to form polymers like silicones. The chain length of silicone polymer can be controlled by adding
(a) $MeSiCl_3$ (b) Me_2SiCl_2
(c) Me_3SiCl (d) Me_4Si

25. Dry ice is
(a) solid NH_3 (b) solid SO_2
(c) solid CO_2 (d) solid N_2

26. Quartz is extensively used as piezoelectric material, it contains __________ .
(a) Pb (b) Si
(c) Ti (d) Sn

Exercise-2 | CONCEPTUAL MCQs

1. Which of the following is most electronegative?
(a) Pb (b) Si
(c) C (d) Sn

2. The most stable +2 oxidation state is exhibited by
(a) Fe (b) Sn
(c) Pb (d) Si

3. The electronic configuration of four different elements is given below. Identify the group 14 element among these
(a) $[He]\,2s^1$ (b) $[Ne]\,3s^2$
(c) $[Ne]\,3s^2 3p^2$ (d) $[Ne]\,3s^2 3p^5$

4. The catenation tendency of C,Si and Ge is in the order Ge <Si<C.The bond energies (in kJ mol^{-1}) of C-C,Si-Si and Ge-Ge bonds, respectively are
(a) 167,180,348 (b) 180,167,348
(c) 348,167,180 (d) 348,180,167

5. Ge(II)compounds are powerful reducing agents whereas Pb(IV)compounds are strong oxidants .It is because
(a) Pb is more electropositive than Ge
(b) ionization potential of lead is less than that of Ge
(c) ionic radii of Pb^{2+} and Pb^{4+} are larger than those of Ge^{2+} and Ge^{4+}
(d) of more pronounced inert pair effect in lead than in Ge

6. Which among CH_4, SiH_4, GeH_4, SnH_4 is most volatile?
(a) CH_4 (b) SiH_4
(c) GeH_4 (d) SnH_4

7. Which of the following halides is the most stable?
(a) CF_4 (b) CI_4
(c) CBr_4 (d) CCl_4

8. Which of the following conceivable structures for CCl_4 will have a zero dipole moment ?
(a) Square planar
(b) Square pyramid (carbon at apex)
(c) Irregular tetrahedron
(d) None of these

9. PbF_4, $PbCl_4$ exist but $PbBr_4$ and PbI_4 do not exist because of
(a) large size of Br^- and I^-
(b) strong oxidising character of Pb^{4+}
(c) strong reducing character of Pb^{4+}
(d) low electronegativity of Br^- and I^-.

10. The element that does not form a monoxide is
(a) lead (b) tin
(c) germanium (d) silicon

11. Pyrosilicate ion is
(a) SiO_2^{2-} (b) SiO_4^{2-}
(c) $Si_2O_6^{7-}$ (d) $Si_2O_7^{6-}$

12. Freon -12 is used as a
(a) refrigerant (b) insecticide
(c) fungicide (d) herbicide

13. Which one of the following allotropic forms of carbon is isomorphous with crystalline silicon?
(a) Graphite (b) Coal
(c) Coke (d) Diamond.

14. The structure and hybridization of $Si(CH_3)_4$ is
(a) Bent, sp (b) Trigonal, sp^2
(c) Octahedral, d^2sp^3 (d) Tetrahedral, sp^3

15. Silicon is an important constituent of
(a) rocks (b) minerals
(c) alloys (d) vegetables.

16. In laboratory, silicon can be prepared by the reaction of
(a) SiO_2 with Mg
(b) by heating C in electric furnace
(c) by heating potassium fluorosilicate with potassium
(d) None of these

17. Silica is soluble in
(a) HCl (b) HNO_3
(c) H_2SO_4 (d) HF

18. Quartz is a crystalline variety of
(a) Si (b) SiO_2
(c) Na_2SiO_3 (d) SiC

19. Carborundum is
(a) $Al_2(SO_4)_3$ (b) $Al_2O_3.\,2H_2O$
(c) $AlCl_3$ (d) SiC

20. Which one of the following is a correct set for SiO_2?
(a) Linear acidic (b) Linear,basic
(c) Tetrahedral, acidic (d) Angular, basic.

21. A pseudo solid is

(a) diamomd (b) glass

(c) rock salt (d) $CaCO_3$

22. Pyrex glass is a mixture of

(a) sodium borosilicate and aluminium borosilicate

(b) sodium silicate and calcium silicate

(c) sodium silicate and lead silicate

(d) sodium silicate and aluminium borosilicate

23. The variety of glass used in making lenses and prisms is

(a) soda glass (b) borosilicate glass

(c) flint glass (d) crooke's glass

24. Cassiterite is an ore of

(a) Mn (b) Ni

(c) C (d) Sn

25. The shape of gaseous $SnCl_2$ is

(a) tetrahedral (b) linear

(c) angular (d) T-shaped

26. Butter of tin is

(a) $SnCl_4.6H_2O$ (b) $SnCl_4.4H_2O$

(c) $SnCl_4.5H_2O$ (d) $SnCl_4.2H_2O$

27. An alloy of Pb and Sn in equal proportion is called

(a) pewter (b) type metal

(c) solder (d) constantan

28. Red lead is

(a) PbO (b) Pb_3O_4

(c) PbO_2 (d) Pb_4O_3

29. An oxide of lead which is used in lead storage battery, in safety matches and is a powerful oxidising agent is

(a) PbO (b) PbO_2

(c) Pb_3O_4 (d) $2PbO.PbO_2$

30. Lead sulphate is soluble in

(a) conc. HNO_3

(b) conc. HCl

(c) solution of ammonium acetate

(d) water

31. The percentage of lead in lead pencil is

(a) zero (b) 20

(c) 80 (d) 70

32. The important ore of lead is

(a) chalcopyrites (b) haematite

(c) galena (d) bauxite

33. Which of the following lead oxides is present in 'Sindhur'?

(a) PbO (b) PbO_2

(c) Pb_2O_3 (d) Pb_3O_4

34. Which of the following reactions occurs at the cathode during the charging of a lead storage battery?

(a) $Pb^{2+} + 2e^- \rightarrow Pb$

(b) $Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

(c) $Pb \rightarrow Pb^{2+} + 2e^-$

(d) $PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

35. White lead is

(a) Pb_3O_4

(b) PbO

(c) $2PbCO_3.Pb(OH)_2$

(d) $Pb(CH_3COO)_2.Pb(OH)_2$

36. The oxide which cannot act as reducing agent is

(a) SO_2 (b) NO_2

(c) CO_2 (d) ClO_2

37. A solid element (symbol Y) conducts electricity and forms two chlorides YCl_n (colourless volatile liquid) and YCl_{n-2} (a colourless solid). To which one of the following groups of the periodic table does Y belong?

(a) 13 (b) 14

(c) 15 (d) 16

38. Which of the following bonds has the most polar character?

(a) C-O (b) C-Br

(c) C-S (d) C-F

39. The ion that can be precipitated by HCl as well as H_2S is

(a) Pb^{2+} (b) Fe^{3+}

(c) Zn^{2+} (d) Cu^{2+}

40. Which of the following is most dense?

(a) Fe (b) Cu

(c) B (d) Pb

41. C and Si have

(a) Same physical properties

(b) Different physical properties

(c) Same physical but different chemical properties

(d) Different chemical and physical properties

42. Mark the oxide which is amphoteric in character

(a) CO_2 (b) SiO_2

(c) SnO_2 (d) CaO

43. Which of the following sulphate is insoluble in water?

(a) $CuSO_4$ (b) $CdSO_4$

(c) $PbSO_4$ (d) $Al_2(SO_4)_3$

44. Which of the following molecule has highest bond energy?

(a) F-F (b) C-C

(c) N-N (d) O-O

45. The metal used for making radiation shield is

(a) Al (b) Fe

(c) Zn (d) Pb

Exercise-3 | PAST COMPETITION MCQs

1. The straight chain polymer is formed by: **[CBSE-PMT 2009]**
(a) hydrolysis of CH_3SiCl_3 followed by condensation polymerisation
(b) hydrolysis of $(CH_3)_4Si$ by addition polymerisation
(c) hydrolysis of $(CH_3)_2SiCl_2$ followed by condensation polymerisation
(d) hydrolysis of $(CH_3)_3SiCl$ followed by condensation polymerisation

4. Name the type of the structure of silicate in which one oxygen 2tom of $[SiO_4]^{4-}$ is shared ? **[CBSE-PMT 2011]**
(a) Linear chain silicate (b) Sheet silicate
(c) Pyrosilicate (d) Three dimensional

3. The basic structural unit of silicates is : **[NEET 2013]**
(a) SiO_4^{4-} (b) SiO_3^{2-}
(c) SiO_4^{2-} (d) SiO

4. Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite **[AIEEE 2003]**
(a) is an allotropic form of diamond
(b) has molecules of variable molecular masses like polymers
(c) has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interplate bonds
(d) is a non-crystalline substance

5. Glass is a **[AIEEE 2003]**
(a) super-cooled liquid (b) gel
(c) polymeric mixture (d) micro-crystalline solid

6. For making good quality mirrors, plates of float glass are used. These are obtained by floating molten glass over a liquid metal which does not solidify before glass. The metal used can be **[AIEEE 2003]**
(a) tin (b) sodium
(c) magnesium (d) mercury

7. The soldiers of Napolean army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White metallic tin buttons got converted to grey powder. This transformation is related to **[AIEEE 2004]**
(a) a change in the partial pressure of oxygen in the air
(b) a change in the crystalline structure of tin
(c) an interaction with nitrogen of the air at very low temperature
(d) an interaction with water vapour contained in the humid air

8. In silicon dioxide **[AIEEE 2005]**
(a) there are double bonds between silicon and oxygen atoms
(b) silicon atom is bonded to two oxygen atoms
(c) each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms
(d) each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms.

9. A metal, M forms chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct? **[AIEEE 2006]**
(a) MCl_2 is more ionic than MCl_4
(b) MCl_2 is more easily hydrolysed than MCl_4
(c) MCl_2 is more volatile than MCl_4
(d) MCl_2 is more soluble in anhydrous ethanol than MCl_4

10. The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence **[AIEEE 2007]**
(a) $PbX_2 << SnX_2 << GeX_2 << SiX_2$
(b) $GeX_2 << SiX_2 << SnX_2 << PbX_2$
(c) $SiX_2 << GeX_2 << PbX_2 << SnX_2$
(d) $SiX_2 << GeX_2 << SnX_2 << PbX_2$.

11. In context with the industrial preparation of hydrogen from water gas ($CO + H_2$), which of the following is the correct statement? **[AIEEE 2008]**
(a) CO is oxidised to CO_2 with steam in the presence of a catalyst followed by absorption of of CO_2 in alkali
(b) CO is removed by absorption in aqueous Cu_2Cl_2 solution
(c) H_2 is removed through occlusion with pd
(d) CO and H_2, are fractionally separated using differences in their densities

12. Among the following substituted silanes the one which will give rise to cross linked silicone polymer on hydrolysis is **[AIEEE 2008]**
(a) R_4Si (b) R_2SiCl_2
(c) $RSiCl_3$ (d) R_3SiCl

13. In view of the signs of $\Delta_r G^\circ$ for the following reactions :

$$PbO_2 + Pb \rightarrow 2PbO, \qquad \Delta_r G^\circ < 0$$
$$SnO_2 + Sn \rightarrow 2SnO, \qquad \Delta_r G^\circ > 0$$

Which oxidation states are more characteristics for lead and tin ? **[AIEEE 2011RS]**
(a) For lead + 2, for tin + 2 (b) For lead + 4, for tin + 4
(c) For lead + 2, for tin + 4 (d) For lead + 4, for tin + 2

14. Name of the structure of silicates in which three oxygen atoms of $[SiO_4]^{4-}$ are shared. **[IIT-JEE 2005 S]**

(a) Pyrosilicate
(b) Sheet silicate
(c) Linear chain silicate
(d) Three dimensional silicate

15. When PbO_2 reacts with conc. HNO_3 the gas evolved is **[IIT-JEE 2005 S]**

(a) NO_2 (b) O_2 (c) N_2 (d) N_2O

16. The species present in solution when CO_2 is dissolved in water are **[IIT-JEE 2006]**

(a) $CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}$
(b) H_2CO_3, CO_3^{2-}
(c) CO_3^{2-}, HCO_3
(d) CO_2, H_2CO_3

Exercise-4 | Applied MCQs

1. On addition of excess of sodium hydroxide solution to stannous chloride solution, we obtain :

(a) $Sn(OH)_2$ (b) $SnO_2.H_2O$
(c) Na_2SnO_2 (d) None of these

2. Lead pipes are readily corroded by

(a) H_2SO_4 (b) HCl
(c) CH_3COOH (d) pure water

3. A salt which gives CO_2 with hot H_2SO_4 and also decolourises acidified $KMnO_4$ on warming is

(a) bicarbonate (b) carbonate
(c) oxalate (d) acetate

4. Which halide is least stable and has doubtful existence

(a) CI_4 (b) GeI_4
(c) SnI_4 (d) PbI_4

5. R_3SiCl on hydrolysis forms

(a) R_3SiOH (b) $R_3Si-O-SiR_3$
(c) $R_2Si=O$ (d) None of these

6. Which melts in boiling water ?

(a) Gun metal (b) Wood's metal
(c) Monel metal (d) Bell metal

7. Incomplete combustion of petrol or diesel oil in automobile engines can be best detected by testing the fuel gases for the presence of

(a) $CO+H_2O$ (b) CO
(c) NO_2 (d) SO_2

8. Which of the following is/ are methanide (s) ?

(a) Be_2C (b) Al_4C_3
(c) Mg_2C_3 (d) Both (a) and (b)

9. Which of the following statements is false?

(a) Water gas is a mixture of hydrogen and carbon monoxide
(b) Producer gas is a mixture of CO and nitrogen
(c) Water gas is a mixture of water vapour and hydrogen
(d) Natural gas consists of methane, ethane and gaseous hydrocarbons.

10. Which gas is essential constituent of almost all fuel gases ?

(a) CO_2 (b) N_2
(c) CO (d) H_2O

11. Which does not exist

(a) $[SnCl_6]^{2-}$ (b) $[GeCl_6]^{2-}$
(c) $[SiCl_6]^{2-}$ (d) $[CCl_6]^{2-}$

12. Newly shaped glass articles when cooled suddenly become brittle, therefore these are cooled slowly, this process in known as

(a) tempering (b) annealing
(c) quenching (d) galvanising

13. Mark the correct statement

(a) Water gas is used in manufacture of methyl alcohol
(b) Water gas has highest calorific value
(c) Water gas burns with luminous flame
(d) The production of water gas is exothermic process.

14. H_2SO_4 is not used for preparation of CO_2 from marble chips because

(a) it does not react
(b) huge amount of heat is evolved
(c) the reaction is vigorous
(d) calcium sulphate is sparingly soluble and gets deposited on marble chips and stops the reaction.

15. CO_2 is used for extinguishing fire because

(a) it has a relatively high critical temperature
(b) in solid state, it is called dry ice
(c) it is neither combustible nor a supporter of combustion
(d) it is a colourless gas

16. Lead pipes are not suitable for drinking water because

(a) lead forms basic lead carbonate
(b) lead reacts with water containing air to form $Pb(OH)_2$
(c) a layer of lead dioxide is deposited over pipes
(d) lead reacts with air to form litharge

17. CO_2 and N_2 are non-supporters of combustion. However for putting out fires CO_2 is preferred over N_2 because CO_2
(a) does not burn
(b) forms non-combustible products with burning substances
(c) is denser than nitrogen
(d) is a more reactive gas

18. When sodium oxide is heated in a current of CO_2 at 360°C we get
(a) sodium formate (b) sodium oxalate
(c) sodium acetate (d) sodium carbonate

19. Tin plague is the
(a) conversion of stannous to stannic
(b) conversion of white tin to grey tin
(c) emission of sound while bending a tin rod
(d) atmospheric oxidation of tin

20. A gas does not turn lime water milky, supports combustion of burning magnesium. It has no smell and is colourless. It extinguishes a glowing splint but under some circumstances reacts with oxygen and hydrogen. It is not poisonous. The gas is likely to be
(a) water vapours (b) nitrogen
(c) CO_2 (d) helium

21. The correct statement with respect to CO is
(a) it combines with H_2O to give carbonic acid
(b) it reacts with haemoglobin in RBC
(c) it is powerful oxidising agent
(d) it is used to prepare aerated drinks

22. Tin cry refers to
(a) conversion of white to grey tin
(b) tin plating
(c) conversion of white tetrahedral tin to white rhombohedral tin
(d) emission of sound while bending a tin rod.

23. Plumbo - solvency means dissolution of lead in
(a) hot water (b) acids
(c) ordinary water (d) alkalies

24. The reducing power of divalent species decreases in the order
(a) Ge > Sn > Pb (b) Sn > Ge > Pb
(c) Pb > Sn > Ge (d) None of these

25. Which is formed when $SiCl_4$ vapours are passed over hot Mg
(a) $SiCl_2 + MgCl_2$ (b) $Si + MgCl_2$
(c) $Mg_2Si + Cl_2$ (d) $MgSiCl_6$

26. Mg_2C_3 possess which of the following characteristics?
(a) Is called magnesium allylide
(b) It contain Mg^{2+} and C_3^{4-} ions
(c) It on hydrolysis gives propyne
(d) All of these

27. Lead is not affected by dil. HCl in cold because
(a) Pb is less electronegative than H
(b) PbO film is formed which resists chemical attack by acid
(c) $PbCl_2$ protective coating gets formed on Pb surface
(d) PbO_2 film is always present on Pb surface, which resist chemical attack

28. Which of the folllowing is not correct?
(a) $Ge(OH)_2$ is amphoteric
(b) $GeCl_2$ is more stable than $GeCl_4$
(c) GeO_2 is weakly acidic
(d) $GeCl_4$ in HCl forms $[GeCl_2]^{2-}$ ion

29. Producer gas, a fuel and also a source of nitrogen is obtained by
(a) passing a mixture of steam and air over incandescent coke.
(b) spraying oil into hot retorts.
(c) restricted supply of air through a bed of incandescent coke.
(d) passing steam over incandescent coke.

30. Which of the following shows bond in silicone :
(a) Si – Si – Si – Si (b) – Si – O – Si – O – Si
(c) Si – C – Si – C – Si (d) Si – C – Si – O – Si

31. Which type of forces bind together the carbon atoms in diamond ?
(a) Coulombic forces (b) van der Waal's forces
(c) Dipole-Dipole forces (d) Covalent forces

32. Which is the best absorbing material for carbon dioxide?
(a) Cold, solid calcium chloride
(b) Heated charcoal
(c) Heated copper oxide
(d) Cold, solid calcium hydroxide.

33. Water gas cannot be prepared by a continuous process because
(a) the reaction ceases when coke is too cool.
(b) it cannot be manufactured without producer gas.
(c) the furnace must be allowed to cool occasionally.
(d) hot coke must be added from time to time.

34. A kettle which becomes furred-up in use has inside it a deposit composed mainly of :
(a) magnesium bicarbonate (b) magnesium sulphate
(c) sodium sulphate (d) calcium carbonate

35. The substance used to impart green colour to glass is :
(a) Cu_2O (b) SnO_2
(c) Cr_2O_3 (d) CdS

36. On doping Ge metal with a little of In, one gets :
(a) insulator (b) rectifier
(c) n-type semiconductor (d) p-type semiconductor.

37. Water gas is produced by :
(a) saturating hydrogen with moisture.
(b) passing steam through a red hot coke bed.
(c) mixing oxygen and hydrogen in the ratio of 1 : 2
(d) heating a mixture of CO_2 and CH_4 in petroleum refineries.

38. Which of the following is similar to graphite
(a) B (b) BN
(c) B_2H_6 (d) B_4C

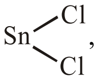
Hints & Solutions

EXERCISE 1

1. Si because of the presence of vacant d–orbitals can show a covalency upto six while C because of the absence of d–orbitals cannot have a covalency of more than four.
3. Since carbonic acid decomposes to give CO_2 and H_2O, therefore, CO_2 is regarded as an anhydride of carbonic acid: $H_2CO_3 \longrightarrow H_2O + CO_2$.
5. Ionic compounds.
6. Silicates are minerals which consist of SiO_4^{4-} units arranged in different ways.
7. Silane gets hydrolysed because silicon has vacant *d*-orbital whereas alkane cannot due to non-availability of vacant *d*-orbital in carbon.

17. (d) 18. (b) 19. (d) 20. (b) 21. (b)
22. (c) 23. (a) 24. (c) 25. (c) 26. (b)

EXERCISE 2

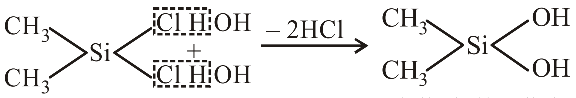
1. **(c)** Electronegativity decreases down the group.
2. **(c)** Inert pair effect increases down the group. Hence for Pb^{2+}, O.S. is most stable.
3. **(c)** Valence shell electronic configuration of group 14 elements is ns^2p^2.
4. **(d)** The more the bond energy, the more is the catenation.
5. **(d)** Ge(II) tends to acquire Ge (IV) state by loss of electrons. Hence it is reducing in nature. Pb (IV) tends to acquire Pb (II) O.S. by gain of electrons. Hence it is oxidising in nature. This is due to inert pair effect.
6. **(a)** The lower the mol. wt. The more is the volatile character.
7. **(a)** Since bond energy of C-F > C-Cl > C-Br > C-I
   Hence CF_4 is most stable.
8. **(d)** CCl_4 is tetrahedral in nature.
9. **(b)** F and Cl are more oxidising in nature and can achieve Pb in (IV) O.S. but Br_2 and I_2 can not achieve Pb in (IV) O.S. secondly Pb^{4+} is strong in oxidising nature and in its presence, Br^- and I^- can not exist.
10. **(d)** Silicon does not form mono oxide.
11. **(d)** $Si_2O_7^{6-}$ ion represent pyrosilicate (see text).
12. **(a)** Freon -12 is used as refrigerant.
13. **(d)** Diamond and crystalline silicon are isomorphous.
14. **(d)** Hybridisation $= \frac{1}{2}(4+4+0-0) = 4$, sp^3 tetrahedral.
15. **(a)** SiO_2, hence silicon, is an important constituent of rocks.
16. **(a)** $SiO_2 + 2Mg \rightarrow MgO + Si$ (lab method).
17. **(d)** $SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$.
18. **(b)** Purest form of SiO_2 is quartz.
19. **(d)** Carborundum is SiC.
20. **(c)** SiO_2 being oxide of non metal is acidic in nature and silicon is bonded to O atoms tetrahedrally. It has giant structure
21. **(b)** Glass is pseudo solid.
22. **(a)** Pyrex glass is a mixture of sodium borosilicate and aluminium borosilicate.
23. **(c)** Flint glass is used for optical (for making lenses) and prism.
24. **(d)** Cassiterite is an ore of tin.
25. **(c)** Shape of $SnCl_2$ is angular  $Sn\begin{smallmatrix}\nearrow Cl\\ \searrow Cl\end{smallmatrix}$, Hybridisation is sp^3.
26. **(c)** Butter of tin is $SnCl_4.5H_2O$.
27. **(c)** Solder (See alloys).
28. **(b)** Red lead is Pb_3O_4.
29. **(b)** PbO_2.
30. **(c)** $PbSO_4 + 2CH_3COONH_4 \rightarrow (CH_3COO)_2Pb + (NH_4)_2SO_4$
31. **(a)** Lead pencils do not contain lead. Lead pencils contain graphite.
32. **(c)** Galena PbS.
33. **(d)** Pb_3O_4 is also known as Sindhur.
34. **(d)** (See chapter on electrochemistry)
35. **(c)** Basic lead carbonate is white lead $2PbCO_3, Pb(OH)_2$.
36. **(c)** CO_2, C is in +4 O.S. which is maximum.
37. **(b)** $SnCl_4$ is colourless volatile liquid and $SnCl_2$ is colourless solid Sn conducts electricity and it belongs to 14 group.
38. **(d)** C-F is most polar due to highest electronegativity difference.
39. **(a)** Pb^{2+} can be precipitated as $PbCl_2$ in cold water and as PbS in II group by H_2S in acid medium.
40. **(d)** Pb is most dense by virtue of its property.
41. **(d)** C and Si have different physical and chemical properties.
42. **(c)** CO_2, SiO_2 are acidic, CaO is basic and SnO_2 is amphoteric.
43. **(c)** $PbSO_4$ is insoluble in water.
44. **(b)**

	F-F	C-C	N-N	O-O
Bond energy	37.0	81.6	39.0	34.9

45. **(d)** Since lead can stop harmful radiation. Hence it is used for making radiation shield.

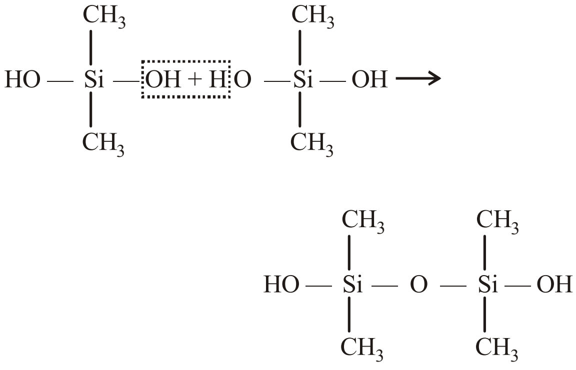
EXERCISE 3

1. **(c)** Hydrolysis of substituted chlorosilanes yield corresponding silanols which undergo polymerisation.



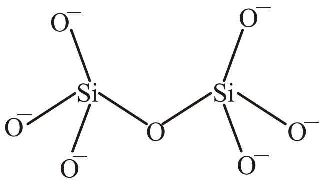
Dialkyl silandiol

Polymerisation of dialkyl silandiol yields linear thermoplastic polymer.



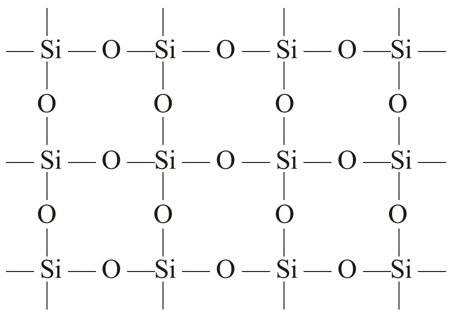
$$HO-Si(CH_3)_2-OH + HO-Si(CH_3)_2-OH \longrightarrow HO-Si(CH_3)_2-O-Si(CH_3)_2-OH$$

2. **(c)**



Pyrosilicate $[Si_2O_7]^{6-}$

3. **(a)** SiO_4^{4-} is basic structural unit of silicates.
4. **(d)** Statement (c) is correct
5. **(a)** Glass is a transparent or translucent super cooled liquid.
6. **(d)** It is because mercury exists as liquid at room temperature.
7. **(b)** Grey tin $\rightleftharpoons$ white tin. Grey tin is brittle and crumbles down to powder in very cold climate.
8. **(d)** In SiO_2 (quartz), each of O-atom is shared between two SiO_4^{4-} tetrahedra.



Structure of SiO_2

9. **(a)** Metal atom in the lower oxidation state forms the ionic bond and in the higher oxidation state the covalent bond because higher oxidation state means small size and great polarizing power and hence greater the covalent character. Hence MCl_2 is more ionic than MCl_4.
10. **(d)** Reluctance of valence shell electrons to participate in bonding is called inert pair effect. The stability of lower oxidation state (+2 for group 14 element) increases on going down the group. So the correct order is

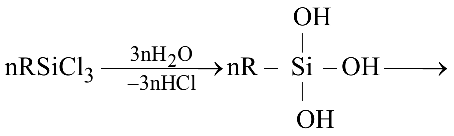
$SiX_2 < GeX_2 < SnX_2 < PbX_2$

11. **(a)** On the industrial scale hydrogen is prepared from water gas according to following reaction sequence

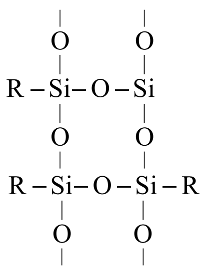
$$\underbrace{CO + H_2}_{\text{water gas}} + H_2O \xrightarrow{\text{catalyst}} CO_2 + 2H_2 \xrightarrow[\text{(alkali)}]{2NaOH} Na_2CO_3 + H_2O$$

From the above it is clear that CO is first oxidised to CO_2 which is then absorbed in NaOH. So the correct answer in option (a)

12. **(c)** The cross linked polymers will be formed by $RSiCl_3$



$$nRSiCl_3 \xrightarrow[-3nHCl]{3nH_2O} nR-Si(OH)_2-OH \longrightarrow$$



(Cross linked polymer)

The correct choice is (c)

13. **(c)** Negative $\Delta_r G^\circ$ value indicates that + 2 oxidation state is more stable for Pb. Also it is supported by inert pair effect that + 2 oxidation state is more stable for Pb and as $\Delta_r G^\circ$ value is positive in second reaction it indicates that + 4 oxidation state is more stable for Sn.

i.e., $Sn^{++} < Pb^{++}$, $Sn^{4+} > Pb^{4+}$

14. **(b)** Two dimensional sheet structures of the formula $(SiO_5)_n^{2n-}$ are formed when tetrahedral are shared.
15. **(b)** PbO_2 is a powerful oxidizing agent and liberate O_2 when treated with acids.

$$2PbO_2 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + 2H_2O + O_2 \uparrow$$

16. **(a)**

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

EXERCISE 4

1. **(d)** $SnCl_2 + 2NaOH \rightarrow Sn(OH)_2 + 2NaCl$

   $Sn(OH)_2 + 2NaOH \rightarrow Na_2SnO_2 + 2H_2O$

2. **(c)** Lead pipes are readily corroded by water containing organic acids.
3. **(c)** Oxalate gives CO and CO_2 with hot H_2SO_4 and decolourises $KMnO_4$

   $$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

4. **(d)** In nature Pb^{4+} is strong oxidant and I^- is strong reductant

   Hence PbI_4 cannot exist.

5. **(b)** $R_3SiCl + HOH \rightarrow R_3SiOH + HCl$

   $R_3SiOH + HOSiR_3 \rightarrow R_3Si-O-SiR_3 + H_2O$

6. **(b)** Wood metal m.p.t. 70°C . (See fusible alloys lead.)
7. **(b)** The exhaust of auto gives CO due to incomplete combustion of petrol or diesel.
8. **(d)** Be_2C and Al_4C_3 give methane with water.
9. **(a)** Water gas is $CO + H_2$
10. **(c)** CO is essential constituent of almost all fuel gases.
11. **(d)** Carbon, due to absence of d-orbitals can not extend its coordination number beyond four.
12. **(b)** Annealing makes the glass soft.
13. **(a)** Methyl alcohol is manufactured using water gas. Patart-process.

    $$(CO + H_2) + H_2 \xrightarrow[300°C]{ZnO+Cr_2O_3+CuO} CH_3OH$$

14. **(d)** Sparingly soluble $CaSO_4$ deposits on marble and stops the reaction.
15. **(c)** CO_2 is incombustible and non supporter of combustion.
16. **(b)** $2Pb + 2H_2O + O_2 \rightarrow 2Pb(OH)_2$
17. **(c)** CO_2 being more dense covers the igniting material more effectively than N_2.
18. **(d)** $CO_2 + Na_2O \rightarrow Na_2CO_3$
19. **(b)** It is the conversion of white tin to grey tin at low temperature which crumbles into powder.
20. **(b)** All mentioned properties are for nitrogen.
21. **(b)** CO react with haemoglobin, forms carboxy haemoglobin and stopes the supply of O_2
22. **(d)** Tin cry is the emission of sound on bending the tin.
23. **(c)** Plumbo- solvency is formation of $Pb(OH)_2$ by Pb with ordinary water.

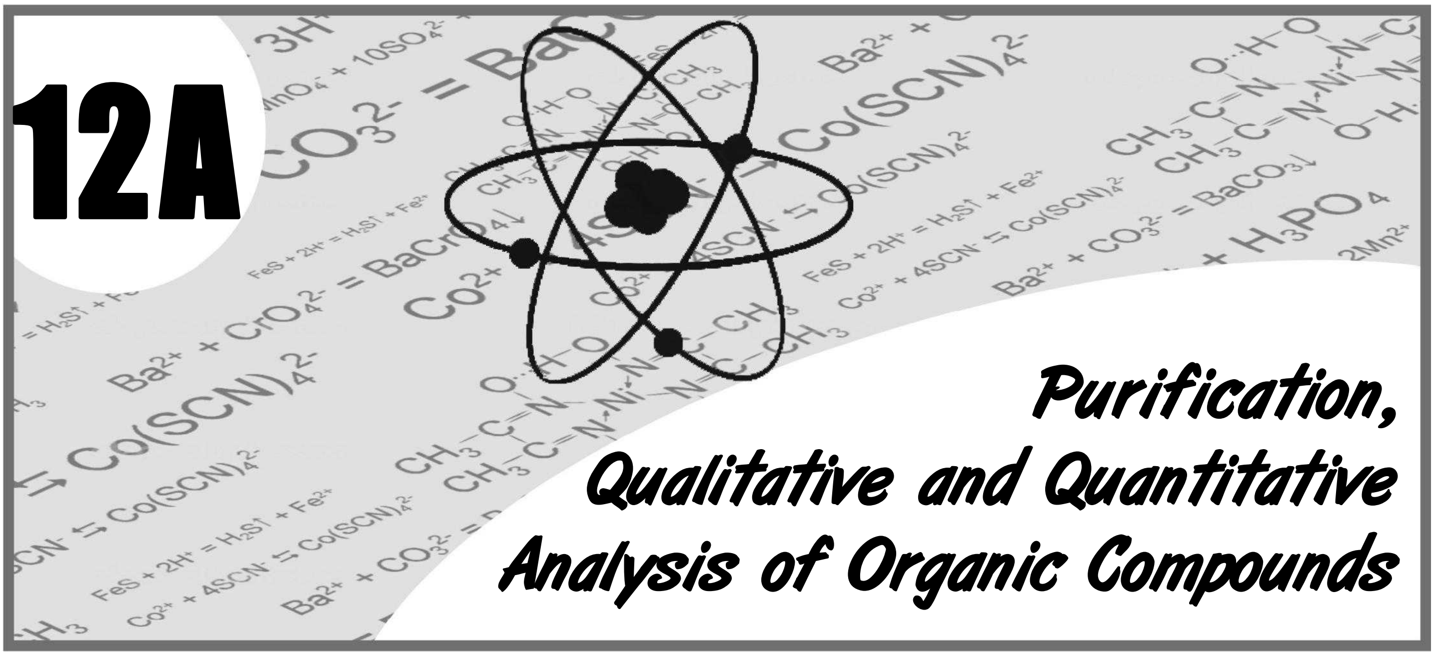
    $2Pb + 2H_2O + O_2 \rightarrow 2Pb(OH)_2$

24. **(a)** The stability of +2O.S. follows the order

    $Pb^{2+} > Sn^{2+} > Ge^{2+}$

    Hence reducing power $Ge > Sn > Pb$

25. **(b)** $SiCl_4 + 2Mg \rightarrow Si + 2MgCl_2$
26. **(d)** $Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + CH_3C \equiv CH$
27. **(c)** Pb with dil HCl forms protective coating of $PbCl_2$
28. **(b)** Ge^{4+} is more stable than Ge^{2+} . Hence $GeCl_4$ is more stable than $GeCl_2$
29. **(c)** Producer gas is mixture of CO + N_2. It is prepared by incomplete combustion of coal in limited supply of air.
30. **(b)** Silicone has $Si-O-Si-O-Si$ linkage.
31. **(d)** In diamond each carbon is sp^3 hybridised and linked to other C-atoms by covalent bonds.
32. **(d)** CO_2 is acidic in nature and it require most basic substance for absorption.
33. **(a)** $CO_2 + H_2 \rightleftharpoons CO + H_2O$ (endothermic process)
34. **(d)** The bicarbonates of Ca and Mg are decomposed to Ca and Mg carbonates by boiling.
35. **(c)** Cr_2O_3 impart green colour to glass.
36. **(d)** Doping of Ge with In produces p-type semiconductor.
37. **(b)** $H_2O\,(steam) + C\,(coke) \longrightarrow CO + H_2$
38. **(b)** Graphite and boron nitride have similar structure.



12A

Purification, Qualitative and Quantitative Analysis of Organic Compounds

The organic compounds obtained from natural sources or synthesised in the lab are often contaminated with impurities. They are purified by specialised methods

METHODS OF PURIFICATION OF SOLIDS

(i) Cystallisation: A saturated solution of impure substance is prepared in hot solvent and is heated with vegetable or animal charcoal which adsorbs the impurities . The solution is filtered while hot through a hot water funnel. The filtrate on cooling deposits crystals of pure compound. Success of the process depends upon the selection of the solvent. The impurities must be least soluble while hot and most-soluble while cold. The quick cooling gives tiny but pure crystals while slow cooling gives bigger but impure crystals. When crystal formation is initiated by adding crystals of substance it is called "***Seeding***".

(ii) Fractional crystallisation : It is based on the differential solubilities of different compounds in a solvent. The compound having less solubility crystallises out first on cooling leaving behind others in solution. Sometimes mixture of two solvents eg. Alcohol & water; Chloroform & Petroleum ether, Alcohol or ether give better results.

(iii) Sublimation*:* Some solids directly pass into vapour when heated and vapour directly pass into solid when cooled without the intermediate formation of liquid. This is known as sublimation. The substances which sublime can be purified by this method provided the impurities present do not sublime.

Camphor, napthalene, anthracene, benzoic acid, phthalic anhydride and anthraquinone are purified by sublimation.

METHODS OF PURIFICATION OF LIQUIDS

(i) Simple distillation: The vapourisation of a liquid by heating and subsequent condensation of vapours by cooling is known as distillation. The liquids boiling under ordinary conditions of temperature and pressure without decomposition and containing non volatile impurities are purified by simple distillation.

(ii) Fractional distillation: It is employed for separating two or more volatile liquids having boiling points close to each other eg. acetone (bpt 60ºC) and methanol (bpt 65ºC). The vapours of the liquids pass through the fractionating column which provides greater space for their cooling. The vapours of high boiling fractions condense and fall back into distillation flask. The process is repeated till fractions of high volatility go up followed by of lower volatility. They are collected separately.

(iii) Distillation under reduced pressure or vacuum distillation: Some liquids decompose when heated to their boiling points eg. glycerol. Such liquids can be purified by distillation under reduced pressure much below their boiling points. The lower the pressure lower is the boiling point and vice versa.

(iv) Steam distillation: The liquids insoluble in water, steam volatile in nature, having high molecular weight and having high vapour pressure are purified by steam distillation provided the impurities present are not steam volatile.

Theory of steam distillation: The liquid boils when its vapour pressure becomes equal to the atmospheric pressure. For a mixture of liquid (pl) and steam (ps) we have at boiling point

$$P = pl + ps \qquad \therefore\ pl = (P - ps)$$

Hence liquid will boil at lower temperature than its normal boiling point. Examples Aniline, *o*-nitrophenol, bromobenzene, salicyaldehyde, essential oils etc.

CHROMATOGRAPHIC METHODS

It was discovered by ***Tswett*** (1906) and developed by ***Kuhn***, ***Winterstein*** and ***Karrer***.

(i) Principle*:* Selective adsorption or distribution of various components of mixture beween the two phases - fixed phase and mobile phase.

(ii) Classification:

(a) ***Adsorption chromatography****:* Fixed phase - Solid or ion exchange resin

Mobile phase - Liquid or gas

Hence it is further known as liquid - solid chromatography, gas-solid chromatography or ion exchange chromatography.

(b) ***Partition Chromatography****:* Fixed phase - liquid supported on inert solid

Mobile phase - liquid or gas

Hence we have liquid - liquid partition chromatography and liquid gas partition chromatography

Paper chromatography is the example of partition chromatography

(iii) Column chromatography:

Example of Adsorption chromatography

Adsorbents used are*:* alumina, silica gel, cellulose powder, sucrose, animal charcoal, magnesium oxide or keiselguhr etc.

Liquid Solvents used are *:* benzene, petrolium ether, chloroform, alcohol etc.

When the solvent is poured over the mixture present at the top of a column packed with adsorbent the components are separated into number of layers called ***Zones***, ***bands*** or ***chromatograms*** due to preferential adsorption. The process being known as development.

Elution *:* The continuous pouring of solvent from the top of column is known as elution or running of column.

Solvent *:* It is known as ***eluent***.

The most weakly adsorbed component is eluted first by least polar solvent while more strongly adsored component is eluted later by highly polar solvents.

CHEMICAL METHODS

The substance to be purified is treated with a suitable chemical reagent to form a stable derivative (impurities being unreacted). It is then separated by suitable method and decomposed to get the pure compound. Examples:

(i) Mixture of amines (1°, 2° and 3°) is separated by ***Hinsberg's method*** and ***Hoffmann's method***.

(ii) Acetic acid from pyroligneous acid is separated by forming Ca salt.

(iii) Acids are separated by forming Na derivatives with $NaHCO_3$.

(iv) Commercial benzene contains thiophene which is removed by forming sulphonic acid derivative.

(v) Carbonyl compounds are purified by forming bisulphite derivative.

(vi) Absolute alcohol is obtained from rectified spirit by quick lime process and azeotropic distillation.

EXTRACTION

The process of removing a substance from its aqueous solution by shaking with a suitable solvent is known as extraction. (partition law) The greater the number of operations the greater is the recovery of substance. Soxhlet extractor is used for continuous extraction.

DRYING OF ORGANIC SUBSTANCES

Stable solids may be dried in a steam or air oven; by heating on a free flame. In a vacuum desicator using anhy. $CaCl_2$, conc H_2SO_4 or P_2O_5 etc.

Alcohols are dried over : Quick lime, anhy. K_2CO_3, $MgSO_4$ or Na_2SO_4

Aldehydes and Ketones : Anhy. $MgSO_4$, Na_2SO_4 or $CaCl_2$

Organic acids: Anhy. $MgSO_4$, Na_2SO_4 or P_2O_5

Organic bases: Solid KOH, Quick lime or Soda lime

CRITERIA OF PURITY

(i) Mixed melting point: The purified substance is mixed with pure substance (100%) and melting point is taken. If it is sharp the substance is pure otherwise not. Impurities lower the melting point.

(ii) Boiling Point : The boiling point of a liquid is defined as the temperature at which its vapour pressure becomes equal to atomospheric pressure. Sharp and concordant boiling point is the criteria of purity of organic substance. Impurities increase the boiling point.

DETECTION OF CARBON AND HYDROGEN

$$\text{(C) organic compound} + CuO \xrightarrow[\Delta]{\text{Strong}}$$

$$CO_2 \xrightarrow[\text{Colourless}]{Ca(OH)_2} \underset{\text{milky}}{CaCO_3 \downarrow} H_2O$$

$$\text{(H) organic compound} + CuO \xrightarrow[\Delta]{\text{Strong}}$$

$$H_2O \xrightarrow[\text{Colourless}]{\text{Anhy. } CuSO_4} \underset{\text{blue}}{CuSO_4.5H_2O}$$

DETECTION OF NITROGEN

(i) Soda-lime test:

organic compound + NaOH → smell of $NH_3 \uparrow$

(Not reliable since $–NH_2$, $–NO_2$ and $– N = N$-groups do not respond).

(ii) Lassaigne's test: Common for N, S and X (halogens)

Lassaigne's filtrate or sodium extract is prepared by fusing the organic compound with Na in ignition tube. Fused mass is dissolved in water, boiled and filtered. The filtrate is sodium extract which contains

$Na + C + N \rightarrow$ NaCN sodium cyanide

$2Na + S \rightarrow$ Na_2S Sodium sulphide

$Na + X \rightarrow$ NaX (Sodium halide)

$Na + C + N + S \rightarrow$ NaCNS

Sodium Sulphocyanide

Test for nitrogen : Sod. extract + freshly prepared $FeSO_4$ solution + $FeCl_3$ solution + dil. H_2SO_4 → green or blue colouration or sometimes blood red colour

$$2\,NaCN + FeSO_4 \rightarrow Fe(CN)_2 + Na_2SO_4$$

$$4\,NaCN + Fe(CN)_2 \rightarrow Na_4[Fe(CN)_6]$$

$$3\,Na_4[Fe(CN)_6] + 4\,FeCl_3 \rightarrow \underset{\text{(prussian blue)}}{\underset{\text{ferric ferocyanide}}{Fe_4[Fe(CN)_6]_3}} + 12NaCl$$

$$FeCl_3 + 3\,NaCNS \rightarrow \underset{\text{(Blood red)}}{\underset{\text{Ferric sulphocyanide}}{Fe(CNS)_3}} + 3NaCl$$

($NH_2.NH_2$ and diazo compounds do not give this test, diazo compounds are decomposed to give N_2 and $NH_2.NH_2$ does not contain C)

Test for sulphur :

$$Na_2S + \underset{\text{Sodium nitropruside}}{Na_2[Fe(CN)_5NO]} \rightarrow \underset{\text{Purple coloured complex}}{Na_4[Fe(CN)_5NOS]}$$

$$Na_2S + (CH_3COO)_2Pb \rightarrow \underset{\text{black ppt.}}{PbS} + 2CH_3COONa$$

Test for halogens:

Sod. extract + Conc. HNO_3 + $AgNO_3$ Solution

(i) If white precipitate soluble in NH_4OH → Cl^- present

$$NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$$

$$AgCl + 2NH_4OH \rightarrow \underset{\text{Soluble Complex}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

(ii) If light yellow precipitate sparingly soluble in NH_4OH → Br^- present

$$NaBr + AgNO_3 \rightarrow AgBr\downarrow + NaNO_3$$

$$AgBr + 2NH_4OH \rightarrow \underset{\text{Complex}}{\underset{\text{Sparingly Soluble}}{[Ag(NH_3)_2]Br}} + 2H_2O$$

(iii) If yellow precipitate insoluble in NH_4OH → I^- present

$$NaI + AgNO_3 \rightarrow AgI\downarrow + NaNO_3$$

$$AgI + NH_4OH \rightarrow \text{No Complex}$$

(a) ***Function of Conc. HNO_3*** : It decomposes NaCN and Na_2S to avoid their interference

$$NaCN + HNO_3 \rightarrow NaNO_3 + HCN\uparrow$$

$$Na_2S + 2HNO_3 \rightarrow 2NaNO_3 + H_2S\uparrow$$

$$NaCN + AgNO_3 \rightarrow \underset{\text{white ppt.}}{AgCN\downarrow} + NaNO_3$$

$$Na_2S + 2AgNO_3 \rightarrow \underset{\text{Black ppt.}}{Ag_2S} + 2NaNO_3$$

(b) ***Layer test for bromine and iodine***:

Sod. extract + dil. HNO_3 + $CHCl_3$ or CCl_4 or CS_2

$$+ Cl_2 \text{ water} \xrightarrow{\text{Shake}} \text{Brown layer Br}$$

$$\rightarrow \text{Violet layer I}$$

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$$

$$Br_2 + \text{Solvent} - \text{Brown layer}$$

$$2NaI + Cl_2 \rightarrow 2NaCl + I_2$$

$$I_2 + \text{Solvent} - \text{Violet layer}$$

(c) ***Beilstein's test***:

Organic compounds containing halogens when heated over Cu wire loop, give blue or green colour flame due to formation of volatile copper halides.

(Not reliable since thiourea, urea, pyridine and organic acids also give this test)

DETECTION OF PHOSPHOROUS

Organic compound + fusion mixture (Na_2CO_3 + KNO_3) or Na_2O_2 $\xrightarrow{\Delta}$ fused mass $\xrightarrow{H_2O}$ water extract + conc. HNO_3 + ammonium molybdate → yellow ppt.

$$Na_3PO_4 + 3HNO_3 \rightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + \underset{\text{Amm. molybdate}}{12\,(NH_4)_2MoO_4} + 21\,HNO_3 \rightarrow$$

$$\underset{\text{Amm. phosphomolybdate (yellow ppt.)}}{(NH_4)_3PO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

ESTIMATION OF ELEMENTS

(i) Estimation of carbon and hydrogen (Liebig's method)

$$C_xH_y + O_2 \xrightarrow{CuO} x\,CO_2 + y/2\,H_2O$$

By knowing the amount of CO_2 and H_2O from known weight of organic compound, the percentage of carbon and hydrogen can be calculated.

- The water is absorbed in anhydrous $CaCl_2$ or anhydrous magnesium perchlorate
- The carbon dioxide is absorbed in Saphnolite (a resion) or Ascarite (NaOH on asbestos) or KOH
- When organic compound contains nitrogen, oxides of nitrogen (NO and N_2O etc) are formed and absorbed by caustic potash. These are removed by the use of bright copper gauge

$$4Cu + 2NO_2 \rightarrow 4CuO + N_2$$

$$Cu + N_2O \rightarrow CuO + N_2$$

Nitrogen is not absorbed by KOH solution.

- When organic compound contains halogens they are removed by using silver gauge by forming non volatile silver halide
- When sulphur is present, it is removed by forming lead sulphate by using fused lead chromate and halogens form lead halides.

- Percentage of carbon

$$= \frac{12}{44} \times \frac{\text{Wt. of } CO_2 \times 100}{\text{Wt. of organic substance}}$$

- Percentage of hydrogen

$$= \frac{2}{18} \times \frac{\text{Wt. of } H_2O \times 100}{\text{Wt. of organic substance}}$$

(ii) Estimation of nitrogen: It is estimated by Dumas or *Kjeldahl's* method

(a) ***Duma's Method**:* This method can be applied to all nitrogenous compounds. Though tedious better than *Kjeldahl's* method.

$$C_xH_yN_z \xrightarrow[CO_2]{CuO} x.CO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + \text{traces of oxides of Nitrogen} \xrightarrow{Cu}$$

$$4Cu + 2NO_2 \rightarrow 4CuO + N_2$$

$$2Cu + 2NO \rightarrow 2CuO + N_2$$

$$Cu + N_2O \rightarrow CuO + N_2$$

The mixture of gases is passed in KOH all gases except N_2 are absorbed. Nitrogen is collected over KOH and its volume at NTP is measured.

Percentage of Nitrogen

$$= \frac{28 \times \text{volume of } N_2 \text{ at NTP} \times 100}{22400 \times \text{wt. of organic compound}}$$

$$= \frac{\text{wt of nitrogen} \times 100}{\text{wt. of organic substance}}$$

(b) ***Kjeldahl's method**:*

Organic compound + Conc H_2SO_4 + (small amount of K_2SO_4 and $CuSO_4$ or Hg) $\rightarrow (NH_4)_2SO_4$

$$\xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$$

Ammonia is passed into H_2SO_4 or HCl of known volume and normality. The volume of acid neutralised by NH_3 is calculated by neutralising the acid left by NaOH solution.

$$\text{Percentage of Nitrogen} = \frac{1.4 \times N \times V}{\text{wt. of organic compound}}$$

N = normality of acid, V = volume of acid in ml. neutralised by ammonia

In practice K_2SO_4 is added to raise the bpt of H_2SO_4 and $CuSO_4$ or Hg is added to catalyse the reaction)

Kjeldahl's method is not reliable. The results obtained are generally low. It cannot be applied to compounds in which nitrogen is directly linked to oxygen such as **nitro, nitroso, azo** and nitrogen present as in **pyridine**. It is used for estimating nitrogen in food , fertilizers and agricultural products.

(iii) Estimation of halogens (Carius method)

(a) Organic compound + Fuming HNO_3 + $AgNO_3$ $\rightarrow$ AgX.

It is estimated gravimetrically

Percentage of halogen

$$= \frac{\text{wt. of halogen atom} \times \text{wt. of AgX} \times 100}{\text{Mol. wt. of AgX} \times \text{wt. of organic compound}}$$

(b) Schiff's and Piria method :

organic compound (small amount)

$$+ (CaO + Na_2CO_3) \xrightarrow[\Delta \text{ Strong}]{\text{Pt Crucible}} \text{cooled} +$$

$$\text{dil } HNO_3 \xrightarrow{\text{Filter}} \text{Filtrate} + AgNO_3 \rightarrow AgX$$

AgX is estimated as in Carius method

This method is not suitable for volatile halides for iodides only Na_2CO_3 is used as lime froms calcium iodate which is insoluble in water.

(c) Stepanov's method:

$$R - X + C_2H_5OH + Na \xrightarrow{\text{Reflux}} RH + NaX + C_2H_5ONa$$

Excess of alcohol distilled off and solution treated with 6N HNO_3 and filtered. AgX is precipitated by adding $AgNO_3$ which is filtered, washed and weighted.

(iv) Estimation of sulphur: sulphur can be estimated by (a) ***Messenger's method***, (b) ***Carius method*** or (c) ***Asboth's method***.

Organic compound + oxidising agent (fuming HNO_3 in ***Carius method***) $\rightarrow$ $H_2SO_4 \xrightarrow{BaCl_2} BaSO_4$. It is estimated gravimetrically (Alk.$KMnO_4$ in ***Messenger's*** method)

($Na_2O_2 + Na_2CO_3$ in ***Asboth's*** method)

$$\text{Percentage of Sulphur} = \frac{32 \times \text{wt. of } BaSO_4 \times 100}{233 \times \text{wt. of organic compound}}$$

(v) Estimation of phosphorous: By Carius method

Organic Compound + Fuming nitric acid $\rightarrow$ H_3PO_4

$$\xrightarrow[\substack{\text{mixture} \\ (MgSO_4+NH_4OH+NH_4Cl)}]{\text{Magnesia}} Mg\,NH_4PO_4$$

$$\xrightarrow{\text{ignition}} Mg_2\,P_2O_7 \text{ (Magnesium phyrophosphate)}$$

Percentage of phosphorous

$$= \frac{62 \times \text{wt. of } Mg_2P_2O_7 \times 100}{222 \times \text{wt. of organic compound}}$$

DETERMINATION OF MOLECULAR WEIGHT

(A) Physical methods

- (i) Vapour Density method: by (a) Victor's Meyer, (b) Dumas and (c) Hofmann's
- (ii) Freezing point
- (iii) Boiling method.

(i) Vapour Density method: by (a) Victor's Meyer, (b) Dumas and (c) Hofmann's

(a) ***Victor Meyer's method****:* for volatile substances: A known weight of the volatile substance is vaporised by heating in Victor Meyer's tube and the equivalent volume of the air displaced is calculated at NTP after proper correction of aqueous tension. Vapour density is given by following relation.

$$\text{V.D.} = \frac{\text{Weight of certain volume of vapour}}{\text{Weight of same volume of hydrogen}}$$

At N.T.P. 22.4 Litre of Hydrogen = 2 g.

$$\text{M. Wt} = 2 \times \text{VD}$$

(b) ***Duma's method*** *:* Weight of known volume of the vapour of the substance in a glass bulb at an elevated temperature is noted.

(c) ***Hofmann's method****: (i)* A known weight of the substance is vaporised above a mercury column in a barometric tube and volume of the vapours formed is noted.

In Dumas and Hofmann method the calculations are same as Victor Meyer's method.

(ii) Freezing point method or cryoscopic method*:*

$$M = \frac{K_f \times w \times 1000}{\Delta T_f \times W}$$

M = molecular weight of the substance

K_f = molal depression constant

w = Weight of the substance

ΔT_f = depression in freezing point

W = weight of the Solvent

(iii) Boiling point method or Ebulioscopic method*:*

$$M = \frac{K_b \times w \times 1000}{\Delta T_b \times W}$$

M = molecular weight of the substance

K_b = molal elevation constant

w = weight of the substance

W = weight of solvent

ΔT_b = Elevation in boiling point

(B) Chemical methods:

- (i) Silver Salt method for Acids
- (ii) Platinichloride method for Bases
- (iii) Volumetric method for Acids and Bases

(i) Silver salt method for acids*:* Mol. wt. of an acid is given by the following expression

Mol. wt. of acid = Equivalent wt × basicity

$$\text{Mol. wt. of acid} = n\left(\frac{\text{wt. of silver salt} \times 108}{\text{wt. of silver}} - 107\right)$$

n = basicity of the acid

(ii) Platinichloride method for bases*:* Mol wt. of a base is given by the following expression

Mol. wt. of base = Eq. wt. of base × Acidity

$$\text{Mol. wt. of base} = \frac{n}{2}\left(\frac{\text{wt. of Pt. salt} \times 195}{\text{wt. of Pt.}} - 410\right)$$

n = Acidity of the base

(iii) Molecular weight of an Acid and a Base by Volumetric method*:*

Equivalent weight of an acid is that weight of acid which is neutralised by 1 geq. of a base Equivalent weight of a base is that weight of base which is neutralised by 1 geq of an acid

$$\text{geq of acid or base} = \frac{N \times V}{1000}$$

where N = Normality of acid of base

V = Volume of acid or base in ml.

EMPIRICAL AND MOLECULAR FORMULA

(i) Empirical formula: It represents the relative number of atoms of each element present in one molecule of the compound.

(ii) Molecular formula: It represents the actual number of atoms of each element present in one molecule of the compound.

CALCULATION OF EMPIRICAL FORMULA

- (i) Divide the percentage of each element by the atomic weight of the element.
- (ii) Divide all the numbers by lowest number obtained in the first step.
- (iii) Convert them in whole numbers if obtained in fractions by multiplying them by common factor.

CALCULATION OF MOLECULAR FORMULA

$$\text{Molecular formula} = \frac{\text{Mol. wt.}}{\text{Empirical wt.}}(\text{Empirical formula})$$

EUDIOMETRY

Determination of molecular formula of gaseous hydrocarbon by exploding with excess of oxygen in a eudiometer is known as Eudiometry.

Hydrocarbon (known volume) + O_2 (Exces known volume)

$$\xrightarrow{\text{(i) Exploded}} \begin{matrix} CO_2 \\ H_2O \\ O_2\,\text{(unreacted)} \end{matrix} \xrightarrow{\text{(ii)Cool}} \xrightarrow[\text{gives volume of } H_2O]{\text{Contraction in volume}} \xrightarrow[\text{volume gives volume of } CO_2]{\text{(iii) KOH contraction in}} \xrightarrow[\text{volume is of uncreated } O_2]{\text{(iv) Remaining}}$$

It is absorbed by alkaline pyrogallol. Hence volume of O_2 reacted can be known and molecular formula can be calculated with the help of following equation

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow XCO_2 + \frac{y}{2}H_2O$$

DENTIFICATION OF SOME ORGANIC COMPOUNDS

(i) **Aldehydes :** Give silver mirror with Tollen's reagent and red precipitate with Fehling soln. and pink colour with Schiffs reagent.
Remember benzaldehyde do not respond to Fehling solution.

(ii) **Ketones :** Give orange ppt with 2, 4 dinitrophenyl hydrazine solution.

(iii) **Acids :** Give effervescence with $NaHCO_3$

(iv) **Alcohols :** Give wine red colour with cerric ammonium nitrate.

(v) **Phenols :** Give deep colour change with 1% $FeCl_3$ sol.

(vi) **Ethers :** with conc. HI give alcohol and alkyl iodide. With excess HI, RI is the product.

(vii) **Methyl ketones :** Give iodoform with I_2 and NaOH.

(viii) **Esters :** When added to very dil soln. of NaOH containing phenolphthalein, the pink colour is discharged.

(ix) **Aliphatic 1° amines :** Give alcohols with $NaNO_2$ and HCl.

(x) **Aromatic 1° amines :** Give diazo compound with $NaNO_2$ and HCl.
(Note : NH_2 must be linked to benzene nucleus)

(xi) **2° amines :** Give highly nitrosamine with $NaNO_2$ and HCl.

(xii) **3° amines :** Salt only salt with $NaNO_2$ and HCl

(xiii) **Cyanides :** On reduction with Na + C_2H_5OH give 1° amines. On hydrolysis give acids

(xiv) **Isocyanide :** On reduction with Na + C_2H_5OH give 2° amines. On acid hydrolysis give 1° amine and formic acid.

(xv) **1° amine :** Give isocyanides with $CHCl_3$ + NaOH, which have unpleasant odour.

(xvi) **Nitro compounds :** Give 1° amine with Sn + HCl.

(xvii) **Amides :** Give NH_3 when heated with NaOH.

(xviii) **Anilides :** They are hydrolysed to 1° amines.

Miscellaneous Solved Examples

1. 0.280 gm. of an organic substance gave on combustion 0.560 gm. of carbon dioxide and 0.14 gm. of water. Calculate the percentage of carbon, hydrogen and oxygen present in the compound.

Sol. Percentage of carbon

$$= \frac{12}{44} \times \frac{\text{Wt. of } CO_2 \times 100}{\text{Wt. of substance}} = \frac{12 \times 0.560 \times 100}{44 \times 0.280} = 54.54\%$$

Percentage of hydrogen

$$= \frac{2}{18} \times \frac{\text{Wt. of } H_2O \times 100}{\text{Wt. of substance}} = \frac{2 \times 0.14 \times 100}{18 \times 0.280} = 5.55\%$$

Percentage of oxygen = 100 – (54.54 + 5.55)

= (100 – 60.09) = 39.91%

2. 0.300 gm. of an organic substance gave 37.9 ml. of dry N_2 at 17°C and 770 mm of Hg pressure. Calculate the percentage of N_2 in the compound.

Sol. Convert the volume of N_2 at NTP

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2};\ \frac{770 \times 37.9}{(273+17)} = \frac{760 \times V_2}{273};\ \therefore V_2 = 36.14 \text{ ml}$$

Percentage of N_2 =

$$\frac{28}{22400} \times \frac{\text{Vol. of } N_2 \text{ at NTP} \times 100}{\text{Wt. of substance}}$$

$$= \frac{28 \times 36.14 \times 100}{22400 \times 0.300} = 15.06\%$$

3. 0.4422 gm. of an organic substance was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 cc of 1N H_2SO_4. The residual acid required 65.5 cc of N/2 alkaline solution. Find the percentage of nitrogen in the compound.

Sol. M_{eq} of the acid taken = 50 × 1 = 50

M_{eq} of the acid neutralised by alkaline solution =

$$65.5 \times \frac{1}{2} = 32.75$$

M_{eq} of the acid neutralised by ammonia

= 50 – 32.75 = 17.25

Percentage of nitrogen

$$= \frac{1.4 \times N \times V}{\text{Wt. of substance}} = \frac{1.4 \times 17.25}{0.4422} = 54.61\%$$

4. 0.147 gm. of an organic compound containing chlorine was heated with nitric acid and silver nitrate which gave 0.287 gm. of silver chloride. Calculate the percentage of chlorine in the compound.

Sol. Percentage of chlorine

$$= \frac{35.5 \times \text{Wt. of AgCl} \times 100}{143.5 \times \text{Wt. of substance}} = \frac{35.5 \times 0.287 \times 100}{143.5 \times 0.147} = 48.29\%$$

5. 0.2595 gm. of an organic compound when treated by Carius method gave 0.35 gm. of $BaSO_4$. Calculate the percentage of sulphur in the compound.

Sol. Percentage of Sulphur

$$= \frac{32}{233} \times \frac{\text{Wt. of } BaSO_4 \times 100}{\text{Wt. of substance}} = \frac{32 \times 0.35 \times 100}{233 \times 0.2595} = 18.52\%$$

6. 0.35 gm of an organic compound was Kjeldahlised and ammonia evolved was absorbed in 100 ml. of N/5 H_2SO_4. The residual acid required 154 ml. of N/10 NaOH for neutralisation. Calculate the percentage of nitrogen in the compound.

Sol. Percentage of nitrogen $= \dfrac{1.4 \times N \times V}{\text{Wt. of substance}}$

where N V = M_{eq} of acid neutralised by ammonia

Total M_{eq} of acid taken = N.V. = $\dfrac{1}{5} \times 100 = 20$

M_{eq} of NaOH used to neutralise acid = $\dfrac{1}{10} \times 154 = 15.4$

M_{eq} of acid neutralised by ammonia = 20.0 – 15.4 = 4.6

Percentage of nitrogen = $\dfrac{1.4 \times 4.6}{0.35} = 18.4\%$

7. 0.6 gm. of the silver salt of a dibasic acid when ignited gave a residue of 0.370 gm. of metallic silver. Find its molecular weight.

Sol. Molecular weight of an acid

$$= \text{Basicity}\left(\frac{\text{Wt. of silver salt} \times 108}{\text{Wt. of silver}} - 107\right)$$

$$= 2\left(\frac{0.60 \times 108}{0.37} - 107\right) = 136.24$$

8. 0.596 gm. of chloroplatinate of a monoacidic base gave on ignition 0.195 gm. of Platinum. Find the molecular weight of the base.

Sol. Molecular weight of a base

$$= \frac{\text{Acidity}}{2}\left(\frac{\text{Wt. of platinum salt} \times 195}{\text{Wt. of platinum}} - 410\right)$$

$$= \frac{1}{2}\left(\frac{0.596 \times 195}{0.195} - 410\right) = 93$$

9. 0.22 gm. of a substance when vaporised by Victor Meyer's method displaced 45.0 ml. of air measured over water at 20°C and 755 mm pressure. Calculate the molecular weight of the substance (vapour pressure of water at 20°C is 17.4 mm).

Sol. Calculation of volume at NTP

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2};\ \frac{(755 - 17.4) \times 45}{(273 + 20)} = \frac{760 \times V_2}{273}$$

$\therefore V_2 = 40.70$ ml.

Wt. of 40.7 ml. of vapour at NTP = 0.22 gm.

$\therefore$ Wt. of 22400 ml. of vapour at NTP

$$= \frac{0.22}{40.7} \times 22400 = 121.1 \text{ gm.}$$

Hence molecular weight of the substance = 121.1

10. The molal freezing point constant of benzene is 4.90 and its melting point is 5.51°C. A solution of 0.816 g of a compound A dissolved in 7.5 g of benzene freezes at 1.59°C. Calculate the molecular weight of compound A.

Sol. $\Delta T_f = 5.51°C - 1.59°C = 3.92°C$

$$m = \frac{K_f \times w \times 1000}{\Delta T_f \times W} = \frac{4.9 \times 0.816 \times 1000}{3.92 \times 7.5} = 136$$

11. The boiling point of pure acetone is 56.38°C at normal pressure. When 0.707 gm. of a substance is dissolved in 10 gm. acetone, the solution boils at 56.88°C. Calculate the molecular weight of the substance. Ebullioscopic constant K_b for acetone is 1.67.

Sol. Molecular weight M

$$= \frac{K_b \times w \times 1000}{\Delta T_b \times W} = \frac{1.67 \times 0.707 \times 1000}{(56.88 - 56.38) \times 10} = 236.13$$

12. 0.177 gm. of a monobasic acid requires 30 cc of N/10 NaOH for complete neutralisation. Calculate the molecular weight of the acid.

Sol. geq. of NaOH used = $30 \times \frac{1}{10} \times \frac{1}{1000} = 0.003$

geq. of acid neutralised by NaOH = 0.003

$0.003 \text{ geq.} \equiv 0.177 \text{ g. of acid}$

$1 \text{ geq.} \equiv \frac{0.177}{0.003} = 59$ g of acid,

Hence equivalent of acid = 59

Since the acid is monobasic. Therefore molecular weight of acid = 59 × 1 = 59.

13. 20 ml. of gaseous hydrocarbon was exploded with excess of oxygen in an eudiometer tube. On cooling volume was reduced by 50 ml. On further treatment with KOH solution there was further contraction of 40 ml. What is the molecular formula of hydrocarbon ?

Sol. $C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$

$$1 \text{ vol.} \quad \left(x + \frac{y}{4}\right) \text{vol.} \quad x \text{ vol.} \quad \frac{y}{2}\text{vol.}$$

$$20 \text{ vol.} \quad 20\left(x + \frac{y}{4}\right)\text{vol.} \quad 20x \text{ vol.}$$

CO_2 produced is 40 ml. Therefore $20x = 40 \Rightarrow x = 2$

Contraction produced on explosion and cooling

$$20 + 20\left(x + \frac{y}{4}\right) - 20x$$

Contraction on explosion as given in question is 50.

$$\therefore 20 + 20\left(x + \frac{y}{4}\right) - 20x = 50$$

$$20 \times \frac{y}{4} = 30 \qquad \therefore y = 6$$

Hence formula of hydrocarbon = C_2H_6.

14. A dibasic acid gave the following results on analysis

(a) 0.177 gm. of acid gave on combustion 0.2642 gm. of CO_2 and 0.081 gm. of water.

(b) 0.2988 gm. of its Ag salt left 0.1944 gm. of Ag on ignition. Determine the molecular formula of the acid and write down the structural formula of its possible isomers.

Sol. % of C = $\frac{12}{44} \times \frac{0.2642 \times 100}{0.177} = 40.70$

% of H = $\frac{2}{18} \times \frac{0.081 \times 100}{0.177} = 5.07$

% of O = $100 - (40.70 + 5.07) = 54.23$

Element	**%**	**At. wt.**	**Relative no. of atoms**	**Simple ratio**
C	40.70	12	$\frac{40.70}{12} = 3.39$	$\frac{3.39}{3.39} = 1 \times 2 = 2$
H	5.07	1	$\frac{5.07}{1} = 5.07$	$\frac{5.07}{3.39} = 1.5 \times 2 = 3$
O	54.23	16	$\frac{54.23}{16} = 3.39$	$\frac{3.39}{3.39} = 1 \times 2 = 2$

Empirical formula of dibasic acid = $C_2H_3O_2$

Empirical formula weight of the acid = 59

$$\text{Mol. wt. of acid} = \text{basicity} \times \left(\frac{\text{Wt. of Ag Salt} \times 108}{\text{Wt. of Ag}} - 107\right)$$

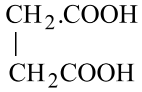
$$= 2\left(\frac{0.2988 \times 108}{0.1944} - 107\right) = 118$$

Molecular formula =

$$\frac{\text{Molecular weight}}{\text{Empirical formula weight}}(\text{Empirical formula})$$

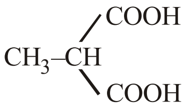
$$= \frac{118}{59}(C_2H_3O_2) = C_4H_6O_4$$

Since the acid is dibasic it must contain two –COOH groups which may be present on the same or different C-atoms.



$CH_2.COOH$ | CH_2COOH

Succinic acid



Methyl malonic acid

15. 0.56 g of an organic compound gave 0.589 g of silver iodide. Calculate the % of I in the compound.

Sol. $\% I = \frac{127}{235} \times \frac{\text{wt. of AgI}}{\text{wt. of organic compound}} \times 100$

$$= \frac{127}{235} \times \frac{0.589}{0.56} \times 100 = 56.84$$

16. 2.79 g of an organic compound was heated in a Carius tube with conc HNO_3 and H_3PO_4 formed was converted into Mg NH_4PO_4 ppt. The precipitate on heating gave 1.332 g of $Mg_2P_2O_7$. What is the % of P in the compound?

Sol. $\% P = \frac{62}{222} \times \frac{\text{wt. of } Mg_2P_2O_7}{\text{wt. of organic compound}} \times 100$

$$= \frac{62}{222} \times \frac{1.332}{2.79} \times 100 = 13.33\%$$

17. A dibasic acid contain C = 32%, H = 4%. 0.91 g silver salt of the acid gives 0.54 g silver on ignition. Determine the molecular formula of the compound.

Sol.

Element	**%**	**At. wt.**	**Relative no. of atoms**	**Simple ratio**
C	32.0	12	$\frac{32}{12}$=2.66	$\frac{2.66}{2.66} = 1 \times 2 = 2$
H	4.0	1	$\frac{4.0}{1}$=4.0	$\frac{4.0}{2.66} = 1.50 \times 2 = 3$
O	64.0	16	$\frac{64}{16}$=4.0	$\frac{4.0}{2.66} = 1.50 \times 2 = 3$

Empirical formula = $C_2H_3O_3$

Mol. wt. of acid

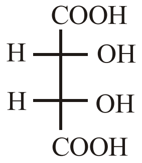
$$= \text{Basicity} \cdot \left(\frac{\text{Wt. of Silver salt} \times 108}{\text{Wt. of Silver}} - 107\right)$$

$$= 2 \times \left(\frac{0.91 \times 108}{0.54} - 107\right) = 150$$

$$n = \frac{\text{Mol. wt}}{\text{Empirical wt}} = \frac{150}{75} = 2$$

Molecular formula = $(C_2H_3O_3)_2 = C_4H_6O_6$

The compound is Tartaric acid



18. 0.236 g organic compound on combustion gives 0.528 g CO_2 and 0.324 g H_2O. 0.295 g compound gives 56 cc N_2 by Dumas method. The compound is monoacidic base and its platinichloride contains 36.89% platinum. Find the mol. formula of the compound.

Sol. $\% C = \frac{12}{44} \times \frac{0.528}{0.236} \times 100 = 61.02$

$$\% H = \frac{2}{18} \times \frac{0.324}{0.236} \times 100 = 15.25$$

$$\% N = \frac{28}{22400} \times \frac{56 \times 100}{0.295} = 23.74$$

Element	**%**	**At. wt.**	**Relative no. of atoms**	**Simple ratio**
C	61.02	12	$\frac{61.02}{12}$=5.08	$\frac{5.08}{1.69} = 3$
H	15.25	1	$\frac{15.25}{1}$=15.25	$\frac{15.25}{1.69} = 9$
N	23.74	14	$\frac{23.74}{14} = 1.69$	$\frac{1.69}{1.69} = 1$

Empirical formula of compound C_3H_9N.

Mol. wt. of compound

$$= \frac{\text{Acidity}}{2}\left(\frac{\text{wt. of Pt salt} \times 195}{\text{wt. of Pt}} - 410\right)$$

$$= \frac{1}{2}\left(\frac{100 \times 195}{36.89} - 410\right) = 59$$

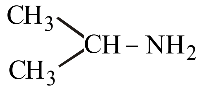
$$n = \frac{\text{Mol. wt}}{\text{Empirical wt.}} = \frac{59}{59} = 1$$

∴ Mol. formula of compound = C_3H_9N

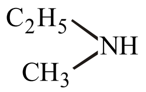
It can have any one of the following structures :

$CH_3CH_2CH_2NH_2$

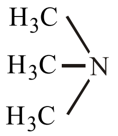
n propylamine



Isopropylamine



Ethylmethylamine



Trimethylamine

19. Find the molecular formula of the compound from the following data

C = 16.27%, H = 0.677%, Cl = 72.20%

In victor Meyer's method 0.2950 g of compound displaces 50.44 ml moist air at 24°C and 735.7 mm pressure. The aqueous tension at 24°C is 22.2 mm

Sol.

Element	%	At. wt.	Relative no. of atoms	Simple ratio
C	16.27	12	$\frac{16.27}{12}=1.356$	$\frac{1.356}{0.677}=2$
H	0.677	1	$\frac{0.677}{1}=0.677$	$\frac{0.677}{0.677}=1$
Cl	72.20	35.5	$\frac{72.20}{35.5}=2.03$	$\frac{2.03}{0.677}=3$
O	10.853	16	$\frac{10.853}{16}=0.678$	$\frac{0.678}{0.677}=1$

Empirical formula of compound C_2HCl_3O

Mol. wt. of compound by victor Meyer's method

$$=\frac{2\times W}{V_0\times 0.00009}$$

Where W = wt. of organic compound

V_0 = volume of dry air at NTP

$$V_0=\frac{273}{760}\times\frac{(753.7-22.2)}{24+273}\times 50.44=44.62$$

$$\text{M. wt.}=\frac{2\times 0.2950}{44.62\times 0.00009}=146.9$$

$$n=\frac{\text{Mol. wt.}}{\text{Emperical wt.}}=\frac{146.9}{147.5}=1$$

Molecular formula of organic compound = C_2HCl_3O

The compound is $Cl_3C.CHO$ chloral.

SOME PRACTICE PROBLEMS ON THE ESTIMATION OF ELEMENTS

1. 0.4950 g of CO_2 and 0.2025 g of H_2O were obtained by combustion of 0.275 g of an organic compound. Find the percentage of C and H (Ans C = 54.54%, H = 9.09%)
2. 0.236 g of an organic compound gave 0.528 g CO_2 and 0.324 g H_2O on complete combustion. Determine the % of C and H in the organic compound. (Ans C = 61.02 %, H = 15.25%)
3. 1 g of an organic compound was analysed by Kjeldahl's method. Ammonia evolved was absorbed in 80 ml $\frac{N}{5}$ H_2SO_4. The residual acid required 35 ml $\frac{N}{10}$ NaOH for neutralisation. Calculate the % N in the compound. (Ans 17.64%)
4. In Duma's experiment 0.204 g of an organic compound gave 18.6 ml moist N_2 at 17°C and 756 mm pressure. Calculate the % N in the compound. (Aq. tension at 17°C = 14.5 mm) (Ans 10.468%)
5. 0.2046 g of an organic compound in Dumas experiment gave 30.4 ml N_2 at 15°C and 732 mm pressure. Aq. tension at 15°C is 12.7 mm. Find the % N in the compound. (Ans 16.68%)
6. Ammonia obtained in Kjeldahl's method neutralised 20 ml $\frac{N}{10}$ H_2SO_4. What is the % N in the compound. (Ans 14.0%)
7. In carius method 0.378 g of an organic compound gave 0.64 g of AgBr. Calculate the % Br in the compound. (Ag = 108, Br = 80) (Ans 73.60%)
8. 0.75 g of an organic compound containing phosphorous was heated with conc HNO_3 in the carius tube. The H_3PO_4 formed was precipitated with Magnesia mixture as $MgNH_4PO_4$. The latter when ignited after washing and drying left a residue of 1.2545 g of $Mg_2P_2O_7$. Calculate the % P in the compound (Mg = 24, P = 31, O = 16). (Ans 46.71%)
9. 0.32 g of an organic compound containing sulphur gave after suitable treatment 0.2334 g of $BaSO_4$. Calculate the % S in the compound. (Ba = 137.4 , S = 32, O = 16) (Ans 10 %)
10. An organic compound containing C, H, N and O gave following results on analysis.
    (i) 0.50 g of the compound gave 0.726 g CO_2 and 0.450 g H_2O.
    (ii) Same compound gave 62.4 ml N_2 at NTP. Find the percentage of all the elements presents in the compound.
    (Ans C = 39.6%, H = 10.0%, N = 15.6%, O = 34.8%)

Exercise-1 | NCERT BASED QUESTIONS

Very Short/ Short Answer Questions

1. Two volatile compounds A and B differ in their boiling points by 15K. Suggest a suitable method for their separation.

2. How will you separate a mixture of *o*– and *p*– nitrophenols?

3. Name two methods which can be safely used to purify aniline.

4. What type of organic compounds cannot be Kjeldahlised?

5. Name the process of separating benzoic acid and naphthalene.

6. What is the suitable adsorbent in the process of column chromatography?

7. What is the value of 'x' in an organic compound with molecular formula C_xH_{12} with vapour density 42?

8. Why are melting point and refractive index used as the criteria of purity of organic compounds?

9. It is advisable to prepare Lassaigne's extract in distilled water. Why?

10. Explain why an organic liquid vapourizes at a temperature below its boiling point in its steam distillation?

11. What type of compounds are purified by sublimation?

12. What are the advantages of using the chromatography method over other methods of separation?

13. In Carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 of AgBr. Find the percentage of bromine in the compound.

14. A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.5 MH_2SO_4. The residual acid required 60 ml of 0.5 M solution of NaOH for neutralization. Find the percentage composition of nitrogen in the compound.

Long Answer Questions

15. (i) On combustion, 0.3650 g of compound (A) gave 0.88 g CO_2 and 0.495 g H_2O. Further, 0.1186 g of the same compound gave, on combustion by Dumas' method, 20 ml of nitrogen measured at 27°C and 779 mm Hg pressure. (Aqueous tension at 27°C = 19 mm Hg). What is the percentage composition of the compound?

(ii) A 3.87 mg sample of organic compound give 5.80 mg CO_2 and 1.58 mg H_2O on combustion. What is the percentage composition of this compound? The organic compound contains only C, H and O.

16. (i) Give reaction for test of sulphur with sodium nitroprusside in organic compound.

(ii) What is the role of

(a) K_2SO_4 in Kjeldahl solution during digestion.

(b) Dil. HNO_3 in Lassaigne's extract.

Multiple Choice Questions

17. The principle involved in paper chromatography is

(a) Adsorption (b) Partition

(c) Solubility (d) Volatility

18. The fragrance of flowers is due to the presence of some steam volatile organic compounds called essential oils. These are generally insoluble in water at room temperature but are miscible with water vapour in vapour phase. A suitable method for the extraction of these oils from the flowers is:

(a) Distillation

(b) Crystallisation

(c) Distillation under reduced pressure

(d) Steam distillation

19. During hearing of a court case, the judge suspected that some changes in the documents had been carried out. He asked the forensic department to check the ink used at two different places. According to you which technique can give the best results?

(a) Column chromatography

(b) Solvent extraction

(c) Distillation

(d) Thin layer chromatography

20. Styrene can be purified by

(a) Simple distillation (b) Fractional distilation

(c) Steam distillation (d) Vacuum distillation

21. In Kjeldahl's method for the estimation of nitrogen, the foumula used is

(a) $\%N = \frac{1.4VW}{N}$ (b) $\%N = \frac{1.4VW}{V}$

(c) $\%N = \frac{VNW}{1.8}$ (d) $\%N = \frac{1.4\ VN}{W}$

22. Chromatography is a valuable method for the separation, isolation, purification and identification of the constituents of a mixture and it is based on general principle of

(a) phase rule (b) phase distribution

(c) interphase separation (d) phase operation

23. In Carius method 0.099 g organic compound gave 0.287 g AgCl. The percentage of chlorine in the compound will be

(a) 28.6 (b) 71.7 (c) 35.4 (d) 64.2

24. Which of the following compounds gives blood red colouration when its Lassaigne's extract is treated with alkali and ferric chloride ?

(a) Thiourea (b) Diphenyl sulphide

(c) Phenyl hydrazine (d) Benzamide

Exercise-2 | CONCEPTUAL MCQs

1. For the separation of two immiscible liquids which method (or apparatus) is used?
(a) chromatography (b) fractionating column
(c) fractional distillation (d) separating funnel

2. A mixture of benzene and chloroform is separated by
(a) sublimation (b) separating funnel
(c) crystallization (d) distillation

3. Which of the following has molecular weight of 92 ?
(a) Toluene (b) Benzene
(c) Methylene (d) Propene

4. Aniline is usually purified by
(a) chromatographic technique
(b) steam distillation
(c) by addition of oxalic acid
(d) fractional crystallization

5. An organic compound contains 49.3% carbon, 6.84% hydrogen and its vapour density is 73. Empirical formula of the compound is
(a) $C_3H_5O_2$ (b) $C_6H_{10}O_4$
(c) $C_3H_{10}O_2$ (d) $C_4H_{10}O_4$

6. Distillation under reduced pressure is employed for
(a) C_6H_6
(b) petrol
(c) $CH_2OHCHOHCH_2OH$
(d) organic compounds used in medicine

7. Impure glycerine is purified by
(a) steam distillation (b) simple distillation
(c) vacuum distillation (d) None of these

8. Absolute alcohol is prepared by
(a) fractional distillation (b) Kolbe's method
(c) azeotropic distillation (d) vacuum distillation

9. The latest technique used for purification of organic compounds is
(a) chromatography (b) vacuum distillation
(c) fractional distillation (d) crystallization

10. In paper chromatography
(a) moving phase is liquid and stationary phase in solid
(b) moving phase is liquid and stationary phase is liquid
(c) moving phase is solid and stationary phase is solid
(d) moving phase is solid and stationary phase is liquid

11. A is a lighter phenol and B is an aromatic carboxylic acid. Separation of mixture of A and B can be carried out easily by using a solution of
(a) sodium hydroxide (b) sodium sulphate
(c) calcium chloride (d) sodium bicarbonate

12. In sodium fusion test of organic compounds, the nitrogen of the organic compound is converted into
(a) sodamide (b) sodium cyanide
(c) sodium nitrite (d) sodium nitrate

13. The Lassaigne's extract is boiled with dil. HNO_3 before testing for halogens because
(a) silver halides are soluble in HNO_3
(b) Na_2S and NaCN are decomposed by HNO_3
(c) Ag_2S is soluble in HNO_3
(d) AgCN is soluble is HNO_3

14. Which of the following compounds does not show Lassaigne's test for nitrogen ?
(a) Urea (b) Hydrazine
(c) Phenylhydrazine (d) Azobenzene

15. When pieces of human hair are heated strongly with soda-lime, smell of ammonia can be detected. Which one of the following conclusion can be drawn form this observation?
(a) Ammonia is present in the human hair
(b) Ammonium salt is present in hair
(c) Hair contains amino acids
(d) None of the above

16. Which of the following is the best scientific method to test presence of water in a liquid ?
(a) Smell
(b) Taste
(c) Use of litmus paper
(d) Use of anhydrous copper sulphate

17. Liebig's method is used for the estimation of
(a) nitrogen (b) sulphur
(c) carbon and hydrogen (d) halogens

18. 0.765 g of an acid gives 0.535 g of CO_2 and 0.138 g of H_2O. Then the ratio of the percentage of carbon and hydrogen is
(a) 19 : 2 (b) 18 : 11
(c) 20 : 17 (d) 1 : 7

19. Nitrogen in an organic compound can be estimated by
(a) Kjeldahl's method only (b) Duma's method only
(c) Both (a) and (b) (d) Neither (a) nor (b)

20. Duma's method involves the determination of nitrogen content in the organic compound in form of
(a) NH_3 (b) N_2
(c) NaCN (d) $(NH_4)_2SO_4$

21. Molecular mass of a volatile substance may be obtained by

(a) Kjeldahl's method (b) Duma's method
(c) Victor-meyer's method (d) Liebig's method

22. The percentage of sulphur in an organic compound whose 0.32 g produces 0.233 g of $BaSO_4$ [At. wt. Ba = 137, S = 32] is

(a) 1.0 (b) 10.0
(c) 23.5 (d) 32.1

23. If 0.2 gram of an organic compound containing carbon, hydrogen and oxygen on combustion, yielded 0.147 gram carbon dioxide and 0.12 gram water. What will be the content of oxygen in the substance ?

(a) 73.29% (b) 78.45%
(c) 83.23% (d) 89.50%

24. If a compound on analysis was found to contain C = 18.5%, H = 1.55%, Cl = 55.04% and O = 24.81.%, then its empirical formula is

(a) $CHClO$ (b) CH_2ClO
(c) C_2H_2OCl (d) $ClCH_2O_2$

25. An organic compound contains C = 40%, H = 13.33% and N = 46.67%. Its empirical formula would be

(a) CHN (b) C_2H_2N
(c) CH_4N (d) C_3H_7N

26. Two elements X (atomic weight = 75) and Y (atomic weight = 16) combine to give a compound having 75.8% X. The formula of the compound is

(a) XY (b) X_2Y
(c) X_2Y_2 (d) X_2Y_3

27. On analysis, a saturated hydrocarbon is found to contain 83.70% carbon and 16.30% hydrogen. The empirical formula will be (at wt. of C= 12; at. wt. of H= 1)?

(a) C_3H_6 (b) C_3H_8
(c) C_3H_4 (d) C_6H_{12}

28. Empirical formula of a hydrocarbon containing 80% carbon and 20% hydrogen is

(a) CH (b) CH_2
(c) CH_3 (d) CH_4

29. An organic compound with C = 40% and H = 6.7% will have the empirical formula

(a) CH_4 (b) CH_2O
(c) $C_3H_6O_3$ (d) $C_2H_4O_2$

30. In a hydrocarbon, mass ratio of hydrogen and carbon is 1:3, the empirical formula of hydrocarbon is

(a) CH_4 (b) CH_2
(c) C_2H (d) CH_3

31. 0.24 g of a volatile liquid on vaporization gives 45 ml of vapours at NTP. What will be the vapour density of the substance ? (Density of H_2 = 0.089 g L^{-1})

(a) 95.39 (b) 39.95
(c) 99.53 (d) 59.93

32. 0.1914 g of an organic acid is dissolved in about 20 ml of water. 25 ml of 0.12 N NaOH is required for the complete neutralization of the acid solution. The equivalent weight of the acid is

(a) 65.0 (b) 64.0
(c) 63.8 (d) 62.5

33. The equivalent weight of an acid is equal to

(a) Molecular weight × acidity
(b) Molecular weight × basicity
(c) Molecular weight/basicity
(d) Molecular weight/acidity

34. Simple distillation can be used to separate liquids which differ in their boiling points at least by

(a) 5ºC (b) 10ºC
(c) 30º – 50ºC (d) 100ºC

35. Empirical formula of a compound is CH_2O. If its vapour density is 90, then the molecular formula of the compound is

(a) $C_5H_{10}O_5$ (b) $C_3H_6O_3$
(c) $C_6H_{12}O_6$ (d) $C_4H_8O_4$

36. The empirical formula of an acid is CH_2O_2, the probable molecular formula of the simplest acid may be

(a) CH_2O (b) CH_2O_2
(c) $C_2H_4O_4$ (d) $C_3H_6O_6$

37. A gaseous hydrocarbon has 85% carbon and vapour density of 28. The possible formula of the hydrocarbon will be

(a) C_3H_6 (b) C_2H_4
(c) C_2H_2 (d) C_4H_8

38. A hydrocarbon has C= 85.72% and remaining H. The hydrocarbon is

(a) C_2H_4 (b) C_2H_6
(c) C_2H_2 (d) CH_4

39. An organic compound containing carbon, hydrogen and oxygen contains 52.2% carbon and 13.04% hydrogen. Vapour density of the compound is 23. Its molecular formula will be

(a) C_2H_6O (b) C_3H_8O
(c) C_4H_8O (d) $C_5H_{10}O$

40. Percentage of Se(at. wt. = 78.4) in peroxidase anhydrase enzyme is 0.5% by weight, then minimum molecular weight of peroxidase anhydrase enzyme is

(a) 1.568×10^4 (b) 1.568×10^3
(c) 15.68 (d) 2.136×10^4

41. The empirical formula of a compound is CH_2. One mole of the compound has a mass of 42 g, its molecular formula is

(a) CH_2 (b) C_2H_2
(c) C_3H_6 (d) C_3H_8

42. In a compound, C, H and N atoms are present in 9 :1: 3.5 by weight . If molecular weight of the compound is 108, then molecular formula of the compound is

(a) $C_2H_6N_2$ (b) C_3H_4N
(c) $C_6H_8N_2$ (d) $C_9H_{12}N_3$

43. The following is the percentage composition of a compound : Na = 16.08%, C = 4.19%, O = 16.78% and H_2O = 62.95%. Its molecular formula is

(a) Na_2CO_3 (b) $Na_2CO_3H_2O$
(c) $Na_2CO_3.10H_2O$ (d) $Na_2CO_3.5H_2O$

Exercise-3 | PAST COMPETITION MCQs

1. Lassaigne's test is used in qualitative analysis to detect **[CBSE-PMT 1989]**

(a) Nitrogen (b) Sulphur
(c) Chlorine (d) All of these

2. Kjeldahl's method is used in the estimation of **[CBSE-PMT 1990]**

(a) Nitrogen (b) Halogens
(c) Sulphur (d) Oxygen

3. In sodium fusion test of organic compounds, the nitrogen of the organic compound is converted into **[CBSE-PMT 1991]**

(a) Sodamide (b) Sodium cyanide
(c) Sodium nitrite (d) Sodium nitrate

4. A is a lighter phenol and B is an aromatic carboxylic acid. Separation of a mixture of A and B can be carried out easily by using a solution of **[CBSE-PMT 1992]**

(a) Sodium hydroxide
(b) Sodium sulphate
(c) calcium chloride
(d) Sodium bicarbonate

5. The most suitable method for separtion of a 1 : 1 mixture of ortho and para nitrophenols is **[CBSE-PMT 1994]**

(a) Sublimation (b) Chromatography
(c) Crystallization (d) Steam distillation

6. The first organic compound, synthesized in the laboratory, was **[CBSE-PMT 1995]**

(a) alcohol (b) acetic acid
(c) urea (d) none of these

7. The best method for the separation of naphthalene and benzoic acid from their mixture is: **[CBSE-PMT 2005]**

(a) distillation (b) sublimation
(c) chromatography (d) crystallisation

8. The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is **[AIEEE-2004]**

(a) $Fe_4[Fe(CN)_6]_3$ (b) $Na_3[Fe(CN)_6]$
(c) $Fe(CN)_3$ (d) $Na_4[Fe(CN)_5NOS]$

9. In a compound C, H and N atoms are present in 9 : 1 : 35 by weight. Molecular weight of compound is 108. Molecular formula of compound is **[AIEEE 2002]**

(a) $C_2H_6N_2$ (b) C_3H_4N
(c) $C_6H_8N_2$ (d) $C_9H_{12}N_3$.

10. The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 mL of 0.1 M sulphuric acid. The excess of acid required 20 mL of 0.5 M sodium hydroxide solution for complete neutralization. The organic compound is **[AIEEE 2004]**

(a) urea (b) benzamide
(c) acetamide (d) thiourea

11. Sodium nitroprusside, when added to an alkaline solution of sulphide ions, produces purple colour ion due to the formation of **[IIT 1995, Orissa JEE 2008]**

(a) $Na[Fe(H_2O)_5 NOS]$ (b) $Na_2[Fe(H_2O)_5 NOS]$
(c) $Na_3[Fe(CN)_5NOS]$ (d) $Na_4[Fe(CN)_5NOS]$

Exercise-4 | Applied MCQs

1. In Kjeldahl's method nitrogen present is estimated as
(a) N_2 (b) NH_3
(c) NO_2 (d) None of these

2. Lassaigne's test for the detection of nitrogen will fail in case of
(a) NH_2CONH_2 (b) $H_2NCONHNH_2.HCl$
(c) $H_2N.NH_2.2HCl$ (d) $H_6C_5NHNH_2.2HCl$

3. The most suitable method of separation of 1:1 mixture of ortho and para nitrophenols is
(a) distillation (b) crystallisation
(c) sublimation (d) chromatography

4. In kjeldahl's method of estimation of nitrogen, K_2SO_4 acts as
(a) oxidising agent (b) catalytic agent
(c) hydrolysing agent (d) boiling point elevator

5. For detection of sulphur in an organic compound sodium nitroprusside is added to the sodium extract. A violet colour is obtained due to formation of
(a) $Fe(CN)_2$ (b) $K_3Fe(CN)_5NS$
(c) $Na_4[Fe(CN)_5NOS]$ (d) $Na_4Fe(CN)_6$

6. Which of the following reagents is useful for separating aniline and nitrobenzene?
(a) $NaOH(aq)$ (b) H_2O
(c) $NaHCO_3$ (d) $HCl(aq)$

7. 0.5g of an organic compound containing nitrogen on Kjeldahlising required 29 mL of N/5 H_2SO_4 for complete neutralization of ammonia. The percentage of nitrogen in the compound is
(a) 34.3 (b) 16.2
(c) 21.6 (d) 14.8

8. Kjeldahl's method cannot be used for the estimation of nitrogen in
(a) pyridine (b) nitro compounds
(c) azo compounds (d) All of these

9. A compound contains 38.8% C, 16% H and 45.2% N. The formula of compound would be :
(a) CH_3NH_2 (b) CH_3CN
(c) C_2H_5CN (d) $CH_2(NH_2)_2$

10. 0.22 g of organic compound C_xH_yO which occupied 112 ml at NTP and on combustion gave 0.44 g CO_2. The ratio of x to y in the compound is
(a) 1 : 1 (b) 1 : 2
(c) 1 : 3 (d) 1 : 4

11. Liquid benzene burns in oxygen according to $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(g)$. How many litre of O_2 at STP are needed to complete the combustion of 39g of liquid benzene:
(a) 11.2 litre (b) 22.4 litre
(c) 84 litre (d) 74 litre

12. 0.75 g platinic chloride of a mono- acidic base on ignition gives 0.245 g platinum. The molecular weight of the base is
(a) 75.0 (b) 93.5
(c) 100 (d) 80.0

13. An organic compound has C and H percentage in the ratio 6 : 1 and C and O percentage in the ratio 3:4 the compound is
(a) HCHO (b) CH_3OH
(c) CH_3CH_2OH (d) $(COOH)_2$

14. Before testing halogens the sodium extract is boiled with conc. HNO_3 to
(a) bring common ion effect
(b) make solution clear
(c) destroy CN^- and S^{--} ions
(d) make the solution acidic

15. The sodium extract prepared from sulphanilic acid, contains SCN^-. It gives blood red colouration with
(a) a mixture of Na_2S and CS_2
(b) $FeCl_3$
(c) $FeSO_4$
(d) Na_2SO_3

16. An organic compound is treated with $NaNO_2$ and dil. HCl at 0°C. The resulting solution is added to an alkaline solution of β-naphthol where by a brilliant red dye is produced. It shows the presence of
(a) $-NO_2$ group (b) aromatic $-NH_2$ group
(c) $-CONH_2$ group (d) aliphatic $-NH_2$ group

17. Methanol and ethanol can be distinguished by
(a) iodoform reaction (b) Esterification
(c) Victor Meyer test (d) Acrolein test

18. 0.532 g of the chloroplatinate of an organic base (M. wt. 264) gave 0.190 g of Pt on ignition. Then the number of nitrogen atoms per molecule of the base is
(a) 4 (b) 3
(c) 1 (d) 2

19. 0.59 g of an organic substance when treated with caustic soda evolved ammonia which required 20 cc of N/2 sulphuric acid for neutralisation. The percentage of nitrogen is

(a) 26.32% (b) 40%
(c) 53.6% (d) 63.6%

20. Which of the following compounds will give foul odour of isocyanide when heated with chloroform and alcoholic KOH ?

(a) Sulphanilic acid (b) Para toluidine
(c) Glycine (d) Anthranilic acid

21. 10.0 ml mixture of methane and ethylene was exploded with 30 ml (excess) of oxygen. After cooling the volume was 21.0 ml. On treatement with KOH solution the volume was reduced to 7.0 ml. The amount of methane and ethylene in the mixture respectively are

(a) 5 ml CH_4 + 5 ml C_2H_4
(b) 3 ml CH_4 + 7 ml C_2H_4
(c) 6 ml CH_4 + 4 ml C_2H_4
(d) 4 ml CH_4 + 6 ml C_2H_4

22. In steam distillation the vapour pressure of volatile organic compound is

(a) equal to atmospheric pressure
(b) double the atmospheric pressure
(c) less than atmospheric pressure
(d) more than atmospheric pressure

23. Which of the following compounds will give orange red ppt. with 2, 4-dinitrophenylhydrazine reagent ?

(a) C_6H_5OH (b) CH_3CH_2COOH
(c) $CH_3COOC_2H_5$ (d) CH_3COCH_3

24. Beilstein's test is given by which of the following?

(a) Halogens (b) Thiourea
(c) Pyridine (d) All of these

25. The molecular mass of an organic compound which contains only one nitrogen atom can be

(a) 152 (b) 146
(c) 76 (d) 73

26. Which of the following observations is correct and useful in identifying carboxylic acids ?

(a) Carboxylic acids liberate CO_2 gas from $NaHCO_3$ solution
(b) Acids liberate I_2 from a mixture of KIO_3 and KI
(c) They produce fruity smell of esters when heated with alcohol in presence of conc. H_2SO_4
(d) All of these

27. To detect iodine in presence of bromine, the sodium extract is treated with $NaNO_2$ + glacial acetic acid + CCl_4. Iodine is detected by the appearance of

(a) yellow colour of CCl_4 layer
(b) purple colour of CCl_4
(c) brown colour in the organic layer of CCl_4
(d) deep blue colour in CCl_4

28. Which of the following compounds will give silver mirror test ?

(a) CH_3COOH (b) HCOOH
(c) $CH_3CO.COOH$ (d) None of these

29. Benzaldehyde and acetone can be distinguished by

(a) $NaHSO_3$ test (b) nitropruside test
(c) Fehling solution test (d) iodoform test

30. In the estimation of carbon and hydrogen by combustion method which of the following is/are correct ?

I. A spiral of copper is introduced at the right extreme of combustion tube if the organic compound contains nitrogen.
II. A spiral of silver is introduced if the organic compound contains halogens.
III. The copper oxide in the combustion tube is replaced by lead chromate if the organic compound contains sulphur.

(a) I and II are correct (b) I and III are correct
(c) II and III are correct (d) All are correct

31. In Kjeldahl's method for the estimation of N_2, potassium sulphate and copper sulphate are used. On the basis of their functions which of the following statement(s) is/are correct?

I. Potassium sulphate raises the bpt. and ensures complete reaction.
II. Copper sulphate acts as catalyst.
III. Potassium sulphate acts as catalyst and copper sulphate raises the bpt.

(a) Only III is correct (b) I and II are correct
(c) Only II is correct (d) None is correct

32. 2.79 g of an organic compound when heated in Carius tube with conc. HNO_3 and H_3PO_4 formed converted into $MgNH_4.PO_4$ ppt. The ppt. on heating gave 1.332 g of $Mg_2P_2O_7$. The percentage of P in the compound is

(a) 23.33% (b) 13.33%
(c) 33.33% (d) 26.66%

Hints & Solutions

EXERCISE 1

1. By fractional distillation.

2. o–nitrophenol is steam volatile while *p*–nitro phenol is not and hence these can be separated by steam distillation.

3. Vacuum distillation and steam distillation.

5. Fractional crystallisation using benzene as a solvent.

6. Al_2O_3 (alumina).

7. V.D. is 42, Mol. wt. = 2 × V.D. = 2 × 42 = 84 therefore, molecular formula is C_6H_{12}.

8. Every pure substance has fixed melting point and refractive index. Impurities reduce the melting point and change refractive index.

9. Tap water usually contains dissolved chlorine which gives test for halogens.

13. Percentage of Br = 34.04%

14. Percentage of nitrogen = 56%

17. **(b)** **18.** **(d)** **19.** **(d)** **20.** **(d)**

21. **(d)** **22.** **(b)** **23.** **(b)** **24.** **(a)**

EXERCISE 2

1. (d)

2 (d) Benzene (b.p. 80ºC) and chloroform (b.p. 61.5ºC) have different boiling points.

3. (a) Mol. wt. of toluene, $C_6H_5CH_3 = 72 + 5 + 12 + 3 = 92$

4. (b) Aniline is miscible in steam and has b.p. lower than water, hence it is collected as distillate along with steam.

5. (a) % of O = 100 – (49.3 + 6.84) = 43.86

$$\text{Relative ratio of C : H : O} = \frac{49.3}{12} : \frac{6.84}{1} : \frac{43.86}{16}$$

$$= 4 : 6.84 : 2.74$$

$$= 1.49 : 2.49 : 1$$

$$= 3 : 5 : 2 \ \text{(multiplying by 2)}$$

∴ Empirical formula = $C_3H_5O_2$

6. (c) Glycerol decomposes at its boiling point, hence it should be purified by distillation under reduced pressure.

7. (c) Vaccum distillation means distillation under reduced pressure.

8. (c) Since alcohol and water form a constant boiling mixture (azeotrope).

9. (a) **10. (b)**

11. (d) Carboxylic acids dissolve in sodium bicarbonate, while phenol does not.

12. (b)

13. (b) Na_2S and NaCN, formed during fusion with metallic sodium, must be removed before adding $AgNO_3$, otherwise black ppt. due to Na_2S or white precipitate due to AgCN will be formed and thus white precipitate of AgCl will not be identified easily.

$$Na_2S + 2AgNO_3 \longrightarrow 2NaNO_3 + \underset{\text{Black}}{Ag_2S\downarrow}$$

$$NaCN + AgNO_3 \longrightarrow NaNO_3 + \underset{\text{White}}{AgCN\downarrow}$$

$$NaCl + AgNO_3 \longrightarrow NaNO_3 + \underset{\text{white}}{AgCl\downarrow}$$

$$Na_2S + 2HNO_3 \xrightarrow{\text{boil}} 2NaNO_3 + H_2S\uparrow$$

$$NaCN + HNO_3 \xrightarrow{\text{boil}} NaNO_3 + HCN\uparrow$$

14. (b) Hydrazine (NH_2NH_2) does not contain carbon and hence on fusion with Na metal, it cannot form NaCN; consequently hydrazine does not show Lassaigne's test for nitrogen.

15. (c) Hair contains amino acids which upon fusion with soda lime (NaOH + CaO) evolve NH_3.

16. (d) Hydrated $CuSO_4$ is blue in colour, while anhydrous is white.

$$\underset{\text{White}}{CuSO_4} + 5H_2O \longrightarrow \underset{\text{Blue}}{CuSO_4.5H_2O}$$

17. (c)

18. (a) $$\%\text{ of C} = \frac{12}{44} \times \frac{0.535}{0.765} \times 100 = 19.07\,\%$$

$$\%\text{ of H} = \frac{2}{18} \times \frac{0.138}{0.765} \times 100 = 2.004\,\%$$

Ratio of C : H = 19 : 2

19. (c) **20. (b)** **21. (c)**

22. (b) $$\%\text{ of S} = \frac{32}{233} \times \frac{0.233}{0.32} \times 100 = 10\,\%$$

23. (a) $$\%\text{ of C} = \frac{12}{44} \times \frac{0.147}{0.2} \times 100 = 20.045\,\%$$

$$\%\text{ of H} = \frac{2}{18} \times \frac{0.12}{0.2} \times 100 = 6.666\,\%$$

$$\%\text{ of O} = 100 - (20.045 + 6.666) = 73.29\,\%$$

24. (a) Relative ratio of wts.

C	H	Cl	O
$\frac{18.5}{12}$	$\frac{1.55}{1}$	$\frac{55.04}{35.5}$	$\frac{24.81}{16}$
= 1.55	= 1.55	= 1.55	= 1.55

∴ Relative No. of atoms

1	1	1	1

Hence empirical formula is CHClO

25. (c) As in above question,

$$C = \frac{40}{12} = 3.33;\ H = \frac{13.33}{1} = 13.33;\ N = \frac{46.67}{14} = 3.34$$

Relative No. of atoms,

$$C=\frac{3.33}{3.33}=1;\ H=\frac{13.33}{3.33}=4;\ N=\frac{3.34}{3.33}=1$$

∴ Empirical formula = CH_4N

26. (d) Relative No. of atoms : $X=\frac{75\ .8}{75}=2\ ;\ Y=\frac{24\ .2}{16}=3$

∴ Empirical formula = X_2Y_3

27. (b) Relative No. of atoms

C	H
$\frac{83.70}{12}=7$	$\frac{16.30}{1}=16.30$
or $\frac{7}{7}=1$	$\frac{16.30}{7}=2.33$
or $1\times3=3$	$2.33\times3=8$

∴ Empirical formula = C_3H_8

28. (c) C : H or $\frac{80}{12}=6.66\ ;\ \frac{20}{1}=20$ or $\frac{6.66}{6.66}=1\ ;\ \frac{20}{6.66}=3$

∴ Empirical formula = CH_3

29. (b) % of O = 100 – (40 + 6.7) = 53.33

$$C:H:O=\frac{40}{12}:\frac{6.7}{1}:\frac{53.33}{16}=3.33:6.7:3.33=1:2:1$$

∴ Empirical formula = CH_2O

30. (a) Mass ratio of H : C = 1 : 12

However, given mass ratio of H : C = 1 : 3

Therefore, for every C atom, there are 4 H atoms, hence empirical formula = CH_4

31. (d) $\text{V.D.}=\frac{\text{Wt. of 45 ml. of vapours at NTP}}{\text{Wt. of 45 ml. of } H_2 \text{ at NTP}}$

$$=\frac{0.24\,g}{45\,ml.\times0.000089\,g\ ml^{-1}}=59.93$$

32. (c) 25 ml of 0.12 N NaOH = 0.1914 g of acid

$$1000\text{ ml of 1 N NaOH}=\frac{0.1914\times1000}{25\times0.12}=63.8$$

∴ Eq. wt. of the acid = 63.8

33. (c) **34. (c)**

35. (c) Mol. wt. = 2 × V.D. = 2 × 90 = 180

Empirical formula wt. = 12 + 2 + 16 = 30

$$\therefore \text{Molecular formula}=\frac{\text{Mol. wt.}}{\text{EF wt.}}\times\text{empirical formula}$$

$$=\frac{180}{30}\times CH_2O=C_6H_{12}O_6$$

36. (b) The simplest acid is HCOOH whose mol. formula is CH_2O_2 which coincides with the given empirical formula.

37. (d) $C:H=\frac{85}{12}:\frac{15}{1}=7:15\approx1:2$

∴ Empirical formula = CH_2

Mol. wt. = 2 × 28 = 56

$$\text{Mol. Formula}=\frac{56}{12+2}\times CH_2=C_4H_8$$

38. (a) $C:H=\frac{85.72}{12}:\frac{14.28}{1}=7.15:14.28=1:2$

∴ Empirical formula = CH_2

From the give options, simple multiple of CH_2 is only C_2H_4

39. (a) % of O = 100 – (52.2 + 13.04) = 34.76%

Relative ratio of

C	H	O
$\frac{52.2}{12}$	$\frac{13.04}{1}$	$\frac{34.76}{16}$
4.35	13.04	2.17
2	6	1

∴ Empirical formula = C_2H_6O

$$\text{Mol. formula}=\frac{2\times23}{24+6+16}\times C_2H_6O=C_2H_6O$$

40. (a) $\%\text{ of Se}=\frac{\text{At. wt. of Se}}{\text{Min. mol.wt.}}\times100$

$$\therefore \text{Min. mol. wt.}=\frac{\text{At. wt. of Se}}{\%\text{ of Se}}\times100$$

$$=\frac{78.4\times100}{0.5}=1.568\times10^4$$

41. (c) Mol. wt. of the compound

= Mass of 1 mole of the compound = 42

empirical formula wt. of CH_2 = 12 + 2 = 14

$$\therefore \text{Molecular formula}=CH_2\times\frac{42}{14}=C_3H_6$$

42. (c) Relative ratio of wts. of C : H : N = 9 : 1 : 3.5

Relative No. of atoms $\frac{9}{12}:\frac{1}{1}:\frac{3.5}{14}=0.75:1:0.25=3:4:1$

∴ Empirical formula = C_3H_4N

Mol. wt.(given) = 108

$$\therefore \text{Mol. formula}=\frac{108}{36+4+14}\times C_3H_4N=C_6H_8N_2$$

43. (c) Relative No. of atoms or molecule

$$Na:C:O:H_2O=\frac{16.08}{23}:\frac{4.19}{12}:\frac{16.78}{16}:\frac{62.95}{18}$$

$=0.70:0.35:1:3.50$

$=2:1:3:10$

∴ Empirical formula = $Na_2CO_3.10H_2O$

EXERCISE 3

1. (d) Nitrogen, sulphur and halogens are tested in an organic compound by Lassaigne's test. The organic compound is fused with sodium metal as to convert these elements into ionisable inorganic substances,

$$Na+C+N\longrightarrow NaCN$$

$$2Na+S\longrightarrow Na_2S$$

$$2Na+X_2\longrightarrow 2NaX$$

The cyanide, sulphide or halide ions can be confirmed in aqueous solution by usual test.

2. **(a)** Kjeldahl's method is suitable for estimating nitrogen in those compounds in which nitrogen is linked to carbon and hydrogen. The method is not used in case of nitro, azo and azoxy compound. This method is basically used for estimating nitrogen in food fertilizers and agricultural products.

3. **(b)** Sodium cyanide ($Na + C + N \rightarrow NaCN$).
(Lassaigne's test)

4. **(d)** Carboxylic acids dissolve in $NaHCO_3$ but phenols do not.

$$RCOOH \xrightarrow{NaHCO_3} RCOONa + H_2O + CO_2$$

by evolving CO_2 gas.

5. **(d)** The boiling point of o-nitrophenol is less than para-nitrophenol due to presence of intramolecular hydrogen bonding. Since p-nitrophenol is less volatile in than o-nitrophenol due to presence of inter molecular hydrogen bonding hence they can be separated by steam distillation.

6. **(c)**

7. **(b)** Among the given compounds naphthelene is volatile but benzoic acid is non-volatile (it forms a dimer). So, the best method for their separation is sublimation, which is applicable to compounds which can be converted directly into the vapour phase from its solid state on heating and back to the solid state on cooling. Hence it is the most appropriate method.

8. **(a)** Prussian blue $Fe_4[Fe(CN)_6]_3$ is formed in lassaigne test for nitrogen.

$$3Na_4[Fe(CN)_6 + Fe^{3+} \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_4]_3} + 12Na^+$$

9. **(c)** According to given molecular weight.

10. **(a)** H_2SO_4 is dibasic.

$0.1\,MH_2SO_4 = 0.2NH_2SO_4$

M_{eq} of H_2SO_4 taken = $= 100 \times 0.2 = 20$

M_{eq} of H_2SO_4 neutralised by NaOH $= 20 \times 0.5 = 10$

M_{eq} of H_2SO_4 neutralised by NH_3 $= 12 - 10 = 10$

$$\%\text{ of } N_2 = \frac{1.4 \times M_{eq} \text{ of acid neutrialised by } NH_3}{\text{wt. of organic compound}}$$

$$= \frac{1.4 \times 10}{0.3} = 46.6$$

$$\%\text{ of nitrogen in urea} = \frac{14 \times 2 \times 100}{60} = 46.6$$

11. **(d)** $Na_2[Fe(CN)_5NO] + S^{2-} \rightarrow \underset{\substack{\text{Sodium thio-nitroprusside}\\ \text{(violet)}}}{Na_4[Fe(CN)_5NOS]}$

EXERCISE 4

1. **(b)** In Kjeldahl's method nitrogen is converted into $(NH_4)_2\,SO_4$, then to NH_3

2. **(c)** For detection of nitrogen by Lassaigne's method, the compound must contain C and N both to form NaCN.

3. **(a)** o- nitrophenol is more volatile due to intramolecular H-bonding . p - nitrophenol is less volatile due to intermolecular H-bonding

4. **(d)** To increase the bpt of H_2SO_4,K_2SO_4 is added

5. **(c)** $\underset{\text{Sodium nitroprusside}}{Na_2S + Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{Sodium thionitroprusside}}{Na_4[Fe(CN)_5NOS]}$

6. **(d)** $C_6H_5NH_2 + HCl \rightarrow \underset{\text{Soluble salt}}{C_6H_5\overset{+}{N}H_3\overset{-}{Cl}}$

Nitrobenzene remains unaffected

7. **(b)** $$N\% = \frac{1.4 \times N \times V}{\text{wt. of organic compound}} = \frac{1.4 \times 29 \times 1/5}{0.5} = 16.24\%$$

8. **(d)** Kjeldahl's method is not suitable for heterocylclic ring with N atom, azo, azoxy and nitro compounds

9. **(a)**

	% of element	Relative no. of atoms	Simple ratio
C	38.8	$\frac{38.8}{12} = 3.2$	1
H	16.0	$\frac{16}{1} = 16.0$	5
N	45.28	$\frac{45.28}{14} = 3.2$	1

10. **(b)** $$\text{M.wt of compound} = \frac{0.22 \times 22400}{112} = 44$$

$$\%\text{ of C} = \frac{12}{44} \times \frac{0.44 \times 100}{0.22} = 54.54$$

$$\text{Amount of C in compound} = \frac{44 \times 54.54}{100} = 24$$

$\therefore$ molecular formula is C_2H_yO or C_2H_4O
It corresponds to M.wt 44. Hence x : y is 1 : 2

11. **(c)** 2×78 g C_6H_6 requires 15×22.4 litre O_2

$$\therefore\ 39\text{ g } C_6H_6 \text{ will require} = \frac{15 \times 22.4 \times 39}{2 \times 78} = 84 \text{ litre}$$

12. **(b)** Apply the formula M.wt

$$= \frac{\text{Acidity}}{2}\left(\frac{\text{wt of Pt salt} \times 195}{\text{wt of Pt}} - 410\right)$$

$$\therefore \text{M.wt} = \frac{1}{2}\left(\frac{0.75 \times 195}{0.245} - 410\right) = 93.5$$

13. **(a)** % ratio of C : H is 6 : 1 and C : O is 3 : 4 or 6 : 8
$\therefore$ % ratio of C : H : O is $6 : 1 : 0$ (Total = 15)

$\%\text{ of C} = \frac{6}{15} \times 100 = 40 \qquad 40/12 = 3.33 = 1$

$\%\text{ H} = \frac{1}{15} \times 100 = 6.6 \qquad 6.6/1 = 6.6 = 2$

$\%\text{ O} = \frac{8}{15} \times 100 = 53.3 \qquad 53.3/16 = 3.3 = 1$

simple ratio CH_2O

$\therefore$ The compound is H.CHO

14. (c) It decomposes NaCN and Na_2S to avoid their interference

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN\uparrow$$

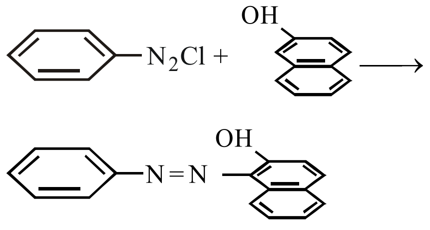
$$Na_2S + 2\,HNO_3 \longrightarrow 2\,NaNO_3 + H_2S\uparrow$$

$$NaCN + AgNO_3 \longrightarrow AgCN\downarrow + NaNO_3$$

$$Na_2S + 2\,AgNO_3 \longrightarrow Ag_2S\downarrow + 2\,NaNO_3$$

15. (b) $SCN^- + Fe^{+++} \longrightarrow Fe(SCN)_3$ blood red ppt.

16. (b)



Red dye

17 (a) $CH_3COCH_3 \xrightarrow{I_2/NaOH} CHI_3$ (iodoform)

18. (a) The equivalent wt. of base

$$E = \frac{1}{2}\left(\frac{0.532}{0.190}\times 195 - 410\right) = 68$$

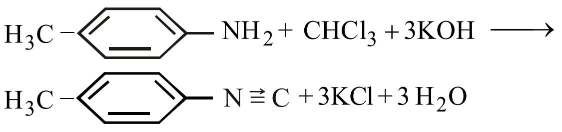
$$\text{Acidity} = \frac{264}{68} = 4$$

Acidity of base = number of N atoms per molecule of base = 4

19. (a) Percentage of nitrogen by Kjeldahl's method

$$= \frac{1.4\times N\times V}{\text{Wt. of organic compound}} = \frac{1.4\times 20}{0.532}\times\frac{1}{2} = 26.32\%$$

20. (b)



Isocyanides have foul odour.

21. (c) Let the vol. of CH_4 be = a ml

$\therefore$ Vol. of $C_2H_4 = (10-a)$ ml

Equation for combustion of CH_4 and C_2H_4

$$\underset{a\text{ ml}}{CH_4} + \underset{2a\text{ ml}}{2\,O_2} \longrightarrow \underset{a\text{ ml}}{CO_2} + \underset{\text{negligible volume}}{2\,H_2O\ (\text{liquid})}$$

$$\underset{(10-a)\text{ ml}}{C_2H_4} + \underset{3(10-a)\text{ ml}}{3\,O_2} \longrightarrow \underset{2(10-a)\text{ ml}}{2\,CO_2} + \underset{\text{negligible}}{2\,H_2O}$$

Vol. of CO_2 produced + O_2 left = 21 ml

Vol. of CO_2 produced = 21 – 7 = 14 ml

CO_2 produced is

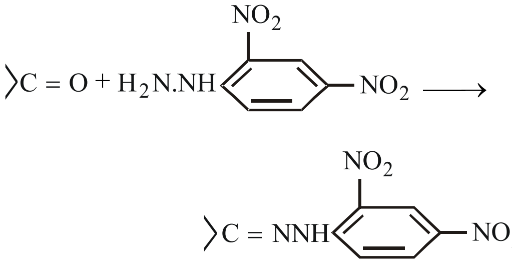
$a + 2(10-a) = 14$

$\therefore\quad a = 6$

$\therefore$ Vol. of CH_4 = 6 ml and vol. of C_2H_4 = 4 ml

22. (d)

23. (d)



orange red ppt.

24. (d) Pyridine and thiourea form volatile cupric cyanide and also give bluish green flame like volatile cupric halides.

25. (d) The compounds with odd number of N-atoms have odd masses and with even number of N-atoms have even masses. This is "nitrogen rule".

26. (d) All the points are correct.

27. (b) $2NaI + 2\,NaNO_2 + 4\,CH_3COOH \longrightarrow$

$I_2 + 2NO + 4\,CH_3COONa + 2\,H_2O$

28. (b) HCOOH is reducing in nature

$$Ag_2O + HCOOH \longrightarrow \underset{\text{silver mirror}}{2Ag} + H_2O + CO_2$$

29. (d) Benzaldehyde does not give iodoform test while acetone forms CHI_3.

30. (d) When organic compound contains nitrogen, upon combustion it will produce oxides of nitrogen soluble in KOH solution. The copper will convert them into N_2

$$2NO + 2Cu \longrightarrow 2CuO + N_2$$

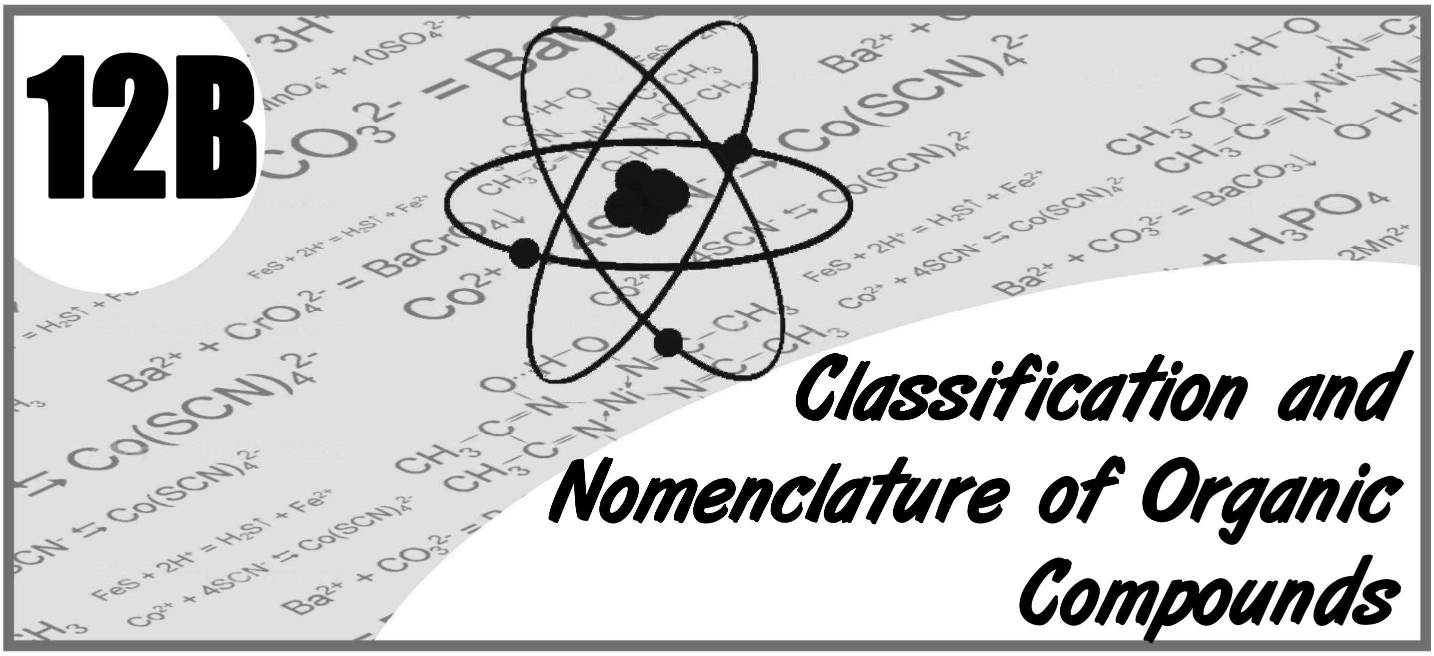
$$2\,NO_2 + 4Cu \longrightarrow 4CuO + N_2 \text{ etc.}$$

Halogens will be removed as AgX. In case of sulphur SO_2 formed will be removed as $PbSO_4$.

31. (b) K_2SO_4 raises bpt. and $CuSO_4$ acts as catalyst.

32. (b) $$\text{Percentage of P} = \frac{62}{222}\times\frac{\text{wt. of } Mg_2P_2O_7}{\text{wt. of compound}}\times 100$$

$$= \frac{62}{222}\times\frac{1.332}{2.79}\times 100 = 13.33\%$$

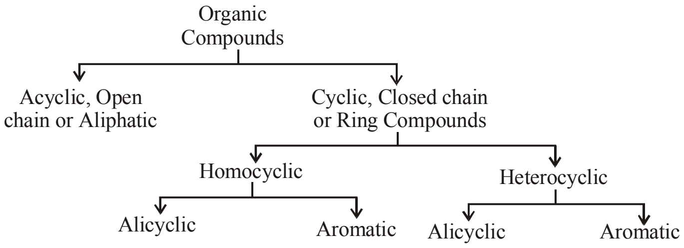


12B

Classification and Nomenclature of Organic Compounds

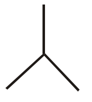
CLASSIFICATION OF ORGANIC COMPOUNDS

The ability of carbon to combine with large number of elements especially O, N, S, X etc, to undergo catenation to form chains of varying lengths and shapes and existance of isomers has led to the formation of more than five million organic compounds. These have been classified into the following main groups



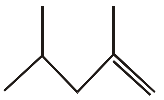
(i) Acyclic or open chain compounds : For example

n-Butane



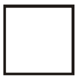
Isobutane

n-Butanol

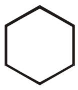


2, 4-Dimethyl pent-1-ene

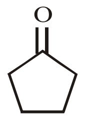
(ii) Cyclic or closed chain compounds.: For example



Cyclobutane



Cyclohexane



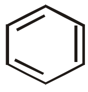
Cyclopentanone

(iii) Homocyclic : The ring system is made up of one type of atoms generally carbon

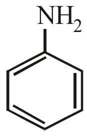
(a) ***Alicyclic*** *:* The cyclic compounds resembling open chain aliphatic compounds.

For example: Cycloalkanes

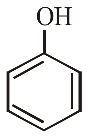
(b) ***Aromatic*** *:* The benzene, napthalene and their derivatives etc are homocyclic aromatic compounds



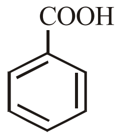
Benzene



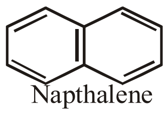
Aniline



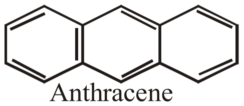
Phenol



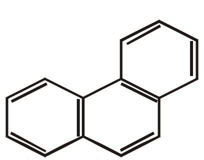
Benzoic acid



Napthalene

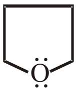


Anthracene

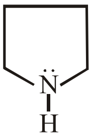


Phenanthrene

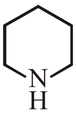
(iv) Heterocyclic : The ring system is made up of two or more than two types of atoms. They may be *(a)* ***Alicyclic*** : eg.



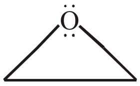
Tetrahydrofuran



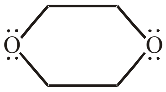
Pyrrolidine



Piperidine

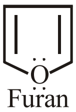


Oxirane or Epoxyethane

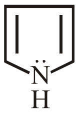


1,4-Dioxane

(b) ***Aromatic*** : eg.

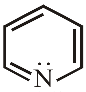


Furan

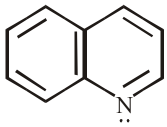


Pyrrole

Thiophene



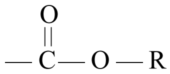
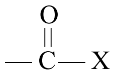
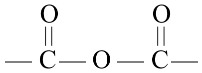
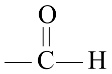
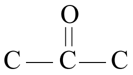
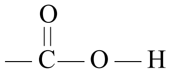
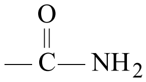
Pyridine



Quinoline

CLASSIFICATION BASED ON FUNCTIONAL GROUPS

On the basis of functional groups which confer characteristic properties on them, the organic compounds have been classified as follows

Class	*Functional group*
Halides	X (Cl, Br, I) Halo
Esters	 $-\overset{O}{\overset{\parallel}{C}}-O-R$
Olefins Alkenes	$>C=C<$
Acid halides	 $-\overset{O}{\overset{\parallel}{C}}-X$
Acetylenes / Alkynes	$-C\equiv C-$
Anhydrides	 $-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-$
Alcohols	—OH (Hydroxy)
Amines	$-NH_2$
Aldehydes	 $-\overset{O}{\overset{\parallel}{C}}-H$
Ketones	 $C-\overset{O}{\overset{\parallel}{C}}-C$
Sulphonic acid	$-SO_3H$
Acids	 $-\overset{O}{\overset{\parallel}{C}}-O-H$
Amides	 $-\overset{O}{\overset{\parallel}{C}}-NH_2$

HOMOLOGOUS SERIES

A group of a particular class of compounds where a preceeding or succeeding member differ by one–CH_2. The members of the series are known as homologues. The homologues

- *(i)* have the same general formula C_nH_{2n+2} or $C_nH_{2n+1}X$
- *(ii)* molecular weight differing by 14 of two successive members
- *(iii)* can be prepared by general methods of preparation
- *(iv)* have almost similar chemical properties
- *(v)* show regular gradation in physical properties such as mpt, bpt, density etc

NOMENCLATURE

The most widely accepted and the latest system of naming organic compounds is IUPAC ***(International Union of Pure and Applied Chemists)*** system, according to which the name essentially consists of three parts.

(i) **Word root** : It indicates the nature of the basic carbon skeleton. From C_1 to C_4 common names have been retained and from C_5 upwards Greek number roots have been used

Chain length	*Word root*	*Chain length*	*Word root*
C_1	Meth-	C_7	Hept-
C_2	Eth-	C_8	Oct-
C_3	Prop-	C_9	Non-
C_4	But-	C_{10}	Dec-
C_5	Pent-	C_{11}	Undec-
C_6	Hex-	C_{12}	Dodec

The generic word root for any carbon chain is **"*alk*"**.

(ii) **Suffix** : These are of two types

(a) ***Primary suffix*** *:* It is added to the word root to designate saturation or unsaturation in a carbon chain

Type of Carbon chain	*Primary Suffix*	*Generic name*
Saturated	- ane	Alkane
Unsaturated with one C=C	- ene	Alkene
Unsaturated with one $C\equiv C$	- yne	Alkyne

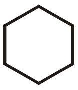
(b) ***Secondary suffix*** *:* It is added to indicate the functional group present in the compound. The terminal 'e' is dropped, if secondary suffix begins with a vowel (**a, e, i, o, u, y**) but it is retained if the secondary suffix begins with a consonant.

Functional group	*Secondary suffix*	*Generic name*
–OH	– ol	Alkanol
–CHO	– al	Alkanal
>C=O	– one	Alkanone
–COOH	– oic acid	Alkanoic acid
–COX	– oyl halide	Alkanoyl halide
$-CONH_2$	– amide	Alkanamide

$-COOR$	– alkyl – – oate	Alkyl alkanoate
$-(CO)_2O$	– oic anhydride	Alkanoic anhydride
$-CN$	– nitrile	Alkane nitrile
$-SH$	– thiol	Alkanethiol
$-NH_2$	– amine	Alkanamine

(iii) **Prefix** : They are of two types

(a) ***Primary prefix*** *:* It is for cyclic nature of the compound and primary prefix ***cyclo*** is used immediately before the word root. eg.:



Primary prefix	*Word* root	*Prim.* suffix	*Sec.* suffix	*IUPAC* name
Cyclo	hex	ane	–	Cyclohexane

(b) ***Secondary prefix*** *:* The certain atoms and groups which are not considered as functional groups but are treated as substituents are called secondary prefixes. They are added before the word root in case of acyclic compounds and before the primary prefix in case of cyclic compounds in alphabetical order.

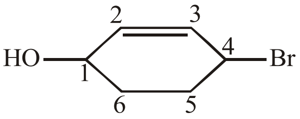
The important secondary prefixes are

Substituent	***Sec. prefix***
$-X$ (F, Cl, Br, I)	Halo
$-NO_2$	Nitro
$-NO$ Nitroso	
$-\overset{+}{N}\equiv\overset{..}{N}$	Diazo
$-OR\left(\begin{matrix}R=\\ CH_3, C_2H_5, C_3H_7, \text{etc.}\end{matrix}\right)$	Alkoxy
$-R$ (CH_3, C_2H_5, C_3H_7, etc)	Alkyl

Thus the complete IUPAC name of an organic compound consists of the following parts

Sec. prefix	Prim. prefix
word root	Prim. suffix
Sec. suffix	

For example:



4-Bromo-cyclo-Hex-2-ene-1-ol

IUPAC name is 4-Bromocyclohex-2-ene-1-ol or 4-Bromo-2-Cyclohexenol

word root = hex
Prime suffex = ene
Sec. suffex = ol
Prime prefex = Cyclo
Sec. prefex = 4bromo

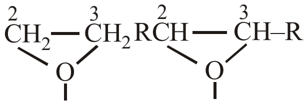
ALKYL GROUPS :

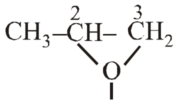
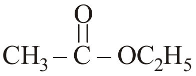
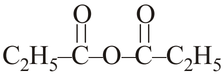
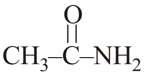
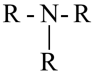
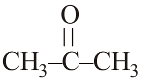
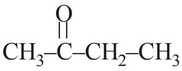
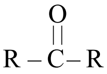
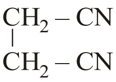
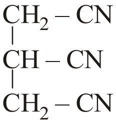
Univalent groups formed by the removal of one hydrogen atom from an alkane are known as alkyl groups or alphyl groups. Their names are obtained by changing the suffix **–ane** of parent hydrocarbon by **–yl**.

Alkane	*Group*	*Short-hand notation*	*IUPAC name*
Methane	Methyl CH_3-	Me	Methyl
Ethane	ethyl C_2H_5-	Et	Ethyl
Propane	n-propyl $CH_3CH_2CH_2-$	n-P_r, P_r^{α} or P_r	1-propyl
	Iso propyl $CH_3-\overset{\vert}{C}H-CH_3$	Iso-P_r, P_r^{β}, P_r^{i}	2-propyl
Butane	n-butyl $CH_3CH_2-CH_2-CH_2-$	–n-Bu, Bu^{α} or Bu	1-butyl
	s-butyl $CH_3CH_2-\overset{\vert}{C}H-CH_3$	s-Bu, Bu^{β} or Bu^{S}	1-methyl propyl
	Iso-butyl $(CH_3)_2CH-CH_2-$	Iso-Bu, or Bu^i	2-methyl propyl
	t-butyl $(CH_3)_3C-$	t-Bu, Bu^t	1,1-dimethyl ethyl

NOMENCLATURE OF SIMPLE ALIPHATIC COMPOUNDS

	Class	*Formula*	*General formula*	*Common name*	*IUPAC group name*	*IUPAC*
1.	Alkanes or paraffins	CH_4 C_2H_6	C_nH_{2n+2}	Methane Ethane	Alkane	Methane Ethane
2.	Alkenes or Olefins	C_2H_4 C_3H_6	C_nH_{2n}	Ethylene Propyline	Alkene	Ethene Propene

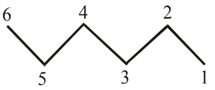
3.	Alkynes or Acetylenes	C_2H_2 C_3H_4	C_nH_{2n-2}	Acetylene Methyl acetylene	Alkyne	Ethyne Propyne
4.	Alkyl halides	CH_3Cl C_2H_5Cl	R–X	Methyl chloride Ethyl chloride	Haloalkanes	Chloromethane Chloroethane
5.	Dihalogen derivatives	CH_2Cl | CH_2Cl (vicinal)	$C_nH_{2n}X_2$ (Alkylene halide)	Ethylene chloride		1,2-dichloroethane
		$CHCl_2$ | CH_3 Geminal		Ethylidine Chloride		1,1-dichloroethane
6.	Trihalogen derivatives	$CHCl_3$	$C_nH_{2n-1}X_3$	Chloroform		1,1,1-trichloromethane
7.	Tetra halogen derivatives	CCl_4	$C_nH_{2n-2}X_4$	Carbon tetra chloride		1,1,1,1-tetra-chloromethane
8.	Alcohols (Monohydric)	CH_3OH	$C_nH_{2n+1}OH$	Methyl alcohol	Alkanol	Methanol
	Dihydric	CH_2OH | CH_2OH	$C_nH_{2n}(OH)_2$	Ethylene glycol		Ethane-1, 2-diol
	Trihydric	CH_2OH | $CHOH$ | CH_2OH	$C_nH_{2n-1}(OH)_3$	Glycerol		Propane-1,2,3-triol
9.	Monocarboxylic Acids or Fatty acids	$HCOOH$ CH_3COOH $C_3H_7.COOH$ $C_4H_9.COOH$	R–COOH	Formic Acid Acetic acid Butyric acid Valeric acid	Alkanoic acid	Methanoic acid Ethanoic acid Butanoic acid Pentanoic acid
	Dicarboxylic acids	$CH_2<\begin{matrix}COOH\\COOH\end{matrix}$	$C_nH_{2n}(COOH)_2$	Malonic acid		Propane-1, 3 dioic acid
		CH_2COOH | CH_2COOH		Succinic acid acid		Butane-1, 4-dioic
		$CH_2<\begin{matrix}CH_2COOH\\CH_2COOH\end{matrix}$		Glutaric acid		Pentane-1,5-dioic acid
		$CH_2.CH_2COOH$ | CH_2CH_2COOH		Adipic acid		Hexane-1,6-dioic acid
		$COOH$ | $COOH$		oxalic acid		Ethane-1,2-dioic acid
10.	Ethers	$CH_3OC_2H_5$	R–O–R'	Ethyl methyl ether	Alkoxy alkane	Methoxyethane
		$CH_3OCH_2–CH_2–CH_3$		Methyl Propyl ether		1-methoxypropane
	Epoxides			Alkene Oxides	Oxirane or Epoxyalkane	Oxirane or (Ethylene Oxide)

				Propylene Oxide		2-methyl Oxirane 1,2-Epoxypropane
11.	Acid chlorides	CH_3COCl	$R–COCl$	Acetyl chloride	Alkanoyl halide	Ethanoyl chloride
12.	Esters	 $CH_3-\overset{O}{\overset{\parallel}{C}}-OC_2H_5$	$RCOOR'$	Ethyl acetate	Alkyl alkanoate (here alkyl attached to oxygen)	Ethyl ethanoate
13.	Anhydrides Propanoic anhydride	 $C_2H_5-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-C_2H_5$		$(RCO)_2O$	Propionic anhydride	Alkanoic anhydride
14.	Amides	 $CH_3-\overset{O}{\overset{\parallel}{C}}-NH_2$	$RCONH_2$	Acetamide	Alkanamide	Ethanamide
15.	Amines					
(a)	1° Amine	CH_3NH_2	RNH_2	Methyl amine	Alkanamine	Methanamine
(b)	2° Amine	$(CH_3)_2NH$	$RNHR$	Dimethyl amine	N-alkylalkan-amine	N-methyl-methanamine
(c)	3° Amine	$(CH_3)_3N$	 $R-\underset{\underset{R}{\vert}}{N}-R$	Trimethyl amine	N,N-dialkyl alkanamine	N,N-dimethyl methanamine
16.	Aldehydes	CH_3CHO $CH_3–CH_2CHO$  $\begin{array}{l}CHO\\ \vert\\ CHO\end{array}$	$RCHO$	Acetaldehyde Propional-dehyde Glyoxal	Alkanal	Ethanal Propanal Ethan-1, 2-dial
17.	Ketones	 $CH_3-\overset{O}{\overset{\parallel}{C}}-CH_3$  $CH_3-\overset{O}{\overset{\parallel}{C}}-CH_2-CH_3$	 $R-\overset{O}{\overset{\parallel}{C}}-R$	Acetone Ethylmethyl ketone	Alkanone	Propan-2-one Butan-2-one
18.	Cyanides	$HC \equiv N$ $CH_3C \equiv N$  $\begin{array}{l}CH_2-CN\\ \vert\\ CH_2-CN\end{array}$  $\begin{array}{l}CH_2-CN\\ \vert\\ CH-CN\\ \vert\\ CH_2-CN\end{array}$	$R–CN$	Hydrogen cyanide Methyl cyanide	Alkanenitrile	Methanenitrile Ethanenitrile Butan-1, 4 dinitrile Propanl-1, 2, 3-tricarbonitrile

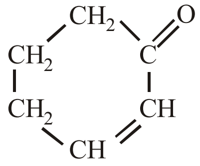
LINE ANGLE FORMULA

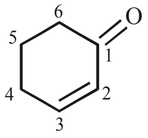
Bonds are represented by lines, carbon atoms are assumed to be present at the start and finish of a line. Nitrogen, oxygen and halogens are labelled, but hydrogens are only shown when bonded to a drawn atom. Each atom is assumed to have sufficient hydrogen atoms around it to make it neutral. For example:

n-Hexane $CH_3(CH_2)_4CH_3$

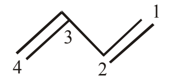


2-Cyclohexenone

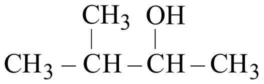




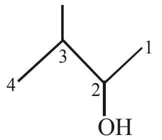
But-1, 3-diene $CH_2=CH-CH=CH_2$



3-methyl but-2-ol



$$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{OH}{|}}{CH}-CH_3}$$



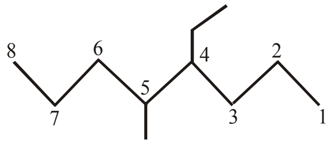
NOMENCLATURE OF COMPLEX HYDROCARBONS

The following rules are followed

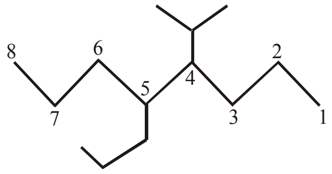
(i) **Longest chain rule :** The longest continuous chain of carbon atoms is picked up which forms the base name of the compound.

(ii) **Numbering :** The longest chain is numbered by arabic numerals beginning with the end nearest a substituent.

(iii) If two or more side chains are in equivalent positions, then the one cited first in the name is assigned the lower number.

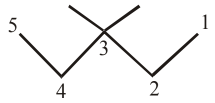


4-Ethyl-5-methyloctane
(not 4-Methyl-5-ethyloctane)



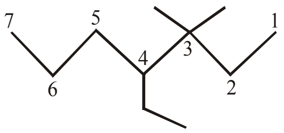
4-isopropyl-5-propyl octane
(not 5-Isopropyl-4-propyloctane)

(iv) If two or more of the same alkyl groups are present, use the prefixes di, tri etc to avoid repetition



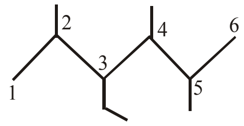
3, 3-Dimethylpentane

(v) **Alphabetical order** : The side chains are cited in alphabetical order



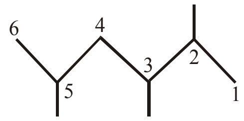
4-Ethyl-3, 3-dimethylheptane

(vi) **Longest chain with maximum number of side chains** : If two or more chains of the same length are possible, choose the one with maximum number of side chains.



3-Ethyl-2,4,5-trimethylhexane
(not 4-Isopropyl-2,3-dimethylhexane)
(not 3-Isopropyl-4,5-dimethylhexane)

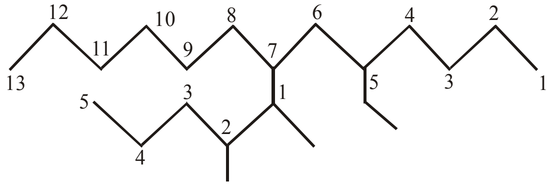
(vii) **Locant sum *:*** Sum of the locants must be minimum. But out of two sets of the sum of the locants, the set having the lowest number when compared by term is preferred. For example out of (2+6+7=15) and (3+4+7=14), the first set is correct.



2,3, 5-Trimethylhexane (not 2,4,5-Trimethylhexane)

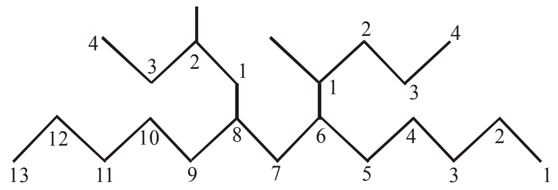
(viii) **The name of a complex radical** is considered to begin with the first letter of its complete name

i.e. including the ***numerical affix*** (di, tri, tetra etc are numerical affix) for alphabetical order.



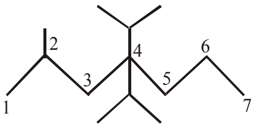
7-(1,2-Dimethyl pentyl)-5-ethyl tridecane

(ix) When the side chains have the identical name the priority is given to side chain having lowest locant



6-(1-Methylbutyl)-8-(2-methyl butyl) tridecane
(not 6-(2-Methylbutyl)-8-(1-Methylbutyl) tridecane)

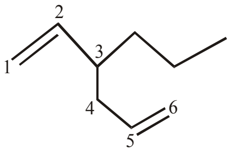
(x) The numerical prefixes bis, tris tetrakis are used to indicate the multiplicity of substituted substituent



2-Methyl-4-bis(1-methylethyl)heptane

Nomenclature of complex alkenes and alkynes :

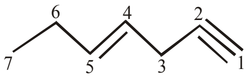
(i) Selection of longest chain containing maximum number of double or triple bonds (sometimes longest chain rule is violated)



3-n-propylhexa-1,5-diene

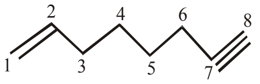
It contains longest chain of 7C atoms, but both the double bonds are not included. Hence longest chain of 6C catoms is picked up)

(ii) If both, the double and triple bonds, are present the compound is regarded as derivative of alkyne. In such cases the terminal 'e' of -ene is dropped if it is followed by suffix starting with a,i,o,u,y. For example :



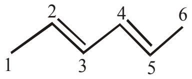
Hept-4-en-1-yne
(not Hept-4-ene-1-yne)

(iii) If double and triple bonds are at equidistance from either side, the preference is given to double bond.

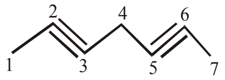


oct-1-en-7-yne
(not oct-7-en-1-yne)

(iv) If the compound contains two or more double or triple bonds a terminal "a" is added to the word root.

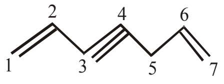


Hexa-2,4-diene
(not Hex-2,4-diene)

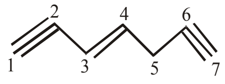


Hepta-2,5-diyne
(not Hept-2,5-diyne)

(v) The terminal 'a' is not added to the word root when the complete primary suffix do not start with a ***numerical affix***



Hepta-1,6-dien-3-yne



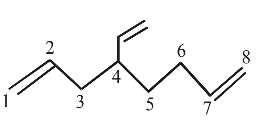
Hept-3-ene-1,6-diyne

(Note that di, tri, tetra.. are numerical affix)

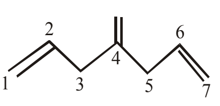
(vi) Side chains containing multiple bonds are named as follows

$CH_2= CH_2=CH–CH_2–$ Allyl
$CH_3–CH=$ Ethylidene
$CH_2=CH–$ Vinyl

Examples :



4-Vinylocta-1,7-diene

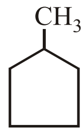


4-Methylidenhepta-1,6-diene

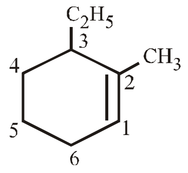
NOMENCLATURE OF CYCLOALKANES : (Alicyclic Compounds)

(i) The base name is decided by the number of carbon atoms which the cyclic or acyclic portion contains. If the ring contains more or equal number of carbon atoms as alkyl then it is regarded as derivative of cycloalkane

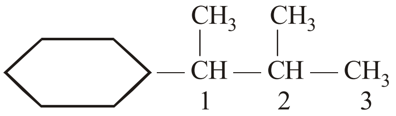
(ii) Carbons are numbered to give lowest numbers to substituted carbons. For example



methyl cyclo pentane

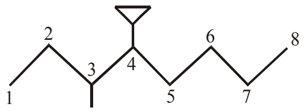


3–Ethyl–2–methyl cyclohex-1-ene



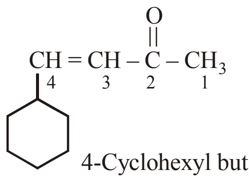
(1, 2-dimethyl propyl) cyclohexane

(iii) When there are more acyclic than cyclic carbons the cyclic part becomes cycloalkyl substituent



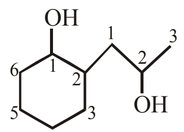
4-Cyclopropyl-3-methyloctane

(iv) When acyclic portion contains a multiple bond or a functional group, the cyclic portion is treated as substituent.



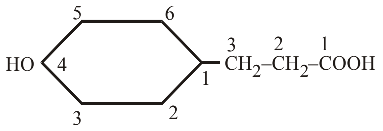
4-Cyclohexyl but-3-en-2-one

(v) In case when both contain the same functional group, the base name is decided by the number of c-atoms.



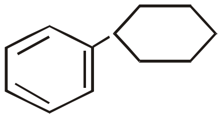
2-(2-Hydroxy propyl) cyclohexan-1-ol

(vi) When both contain the different functional groups, the base name is decided by principal characteric group



3-(4-Hydroxycyclohexyl)propanoic acid

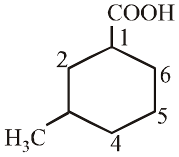
(vii) When the acylic ring is directly attached to benzene ring, it is named as derivative of benzene



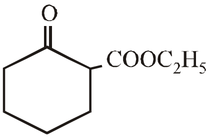
Cyclohexyl benzene

(viii)Presence of certain groups

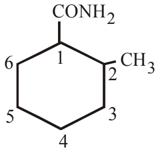
Functional gp.	Suffix
$-COOH$	Carboxylic acid
$-COOR$	Alkyl carboxylate
$-COX$	Carbonyl halide
$-CONH_2$	Carboxamide
$-C \equiv N$	Carbonitrile
$-CHO$	Carbaldehyde



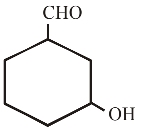
3-Methyl Cyclohexane Carboxylic acid



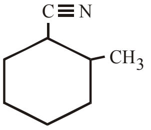
Ethyl 2-Oxo, cyclohexane 1-carboxylate



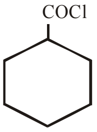
2-Methylcyclohexane-1-carboxamide



3-hydroxy cyclohexane carbaldehyde



2-Methyl cyclohexane carbonitrile

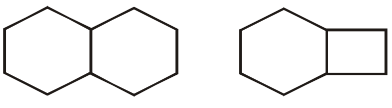


cyclohexane-1-carbonyl chloride

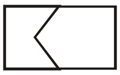
NOMENCLATURE OF POLYCYCLIC ALKANES

There are three ways that rings can be joined.

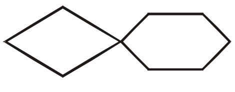
(i) Fused rings



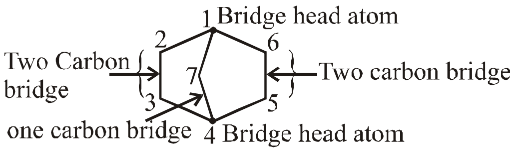
(ii) Bridged rings

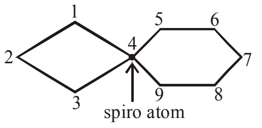


(iii) Spirocyclic compounds



The carbon atoms common to both the rings are called ***bridge head atoms.*** The chain of carbon atoms connecting the bridge head atoms is called a bridge.

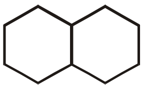




Numbering of C-atoms in fused rings and bridge rings : The numbering starts from bridge head carbon, proceeds along the longest bridge passing through the second bridge head atom, proceeds to the next longest bridge and completed along the shortest path.

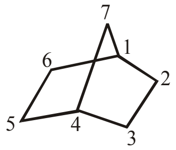
Numbering of C-atoms in spiro compounds : The numbering starts from the carbon atom, next to spiro atom, present in the smaller ring giving minimum number to atoms containing functional groups.

(i) Fused Rings : Fused rings share two adjacent carbon atoms and the bond between them eg. :



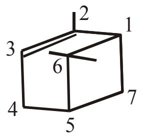
Bicyclo [4.4.0]decane

(ii) Bridged Rings : These share two non adjacent carbon atoms (the bridgehead carbons) and one or more carbon atoms between them

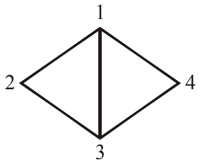


Bicyclo [2.2.1]heptane

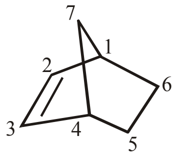
More examples of bridge Compounds



2, 6, 6-Trimethyl bicyclo[3.1.1]hept-2-ene

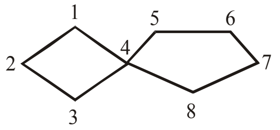


Bicyclo [1.1.0] butane



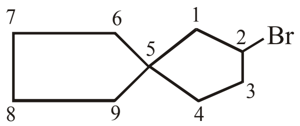
Bicyclo[2.2.1]hept-2-ene

(iii) Spirocyclic Compounds : The two rings share one carbon atom

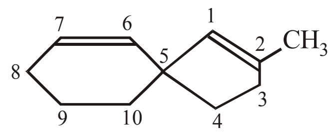


Spiro [4.3] octane

More examples of spiro Compounds



2-Bromo spiro[4.4] nonane

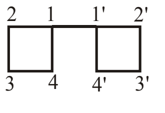


2-methyl spiro[4.5]deca-1, 6-diene

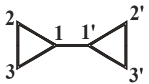
Nomenclature of compounds containing identical cyclic units joined by a single bond

No. of cyclic hydrocarbon units	Two	Three	Four
Prefix	bi	ter	quarter

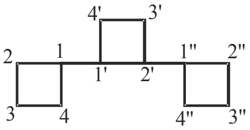
Numbering of C-atoms : The numbering starts from the C-atom joining the rings.



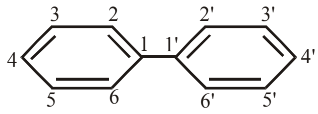
1,1'-Bicyclobutane



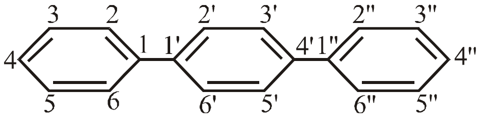
1,1'-Bicyclopropane



1,1',2',1"-Tercyclobutane



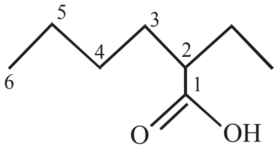
1,1'-Biphenyl



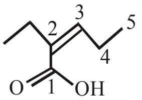
1,1',4',1"-Terphenyl

NOMENCLATURE OF COMPOUNDS CONTAINING TERMINATING FUNCTIONAL GROUPS

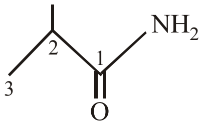
If only one group such as –COOH, –CHO, –COOR, –CONH$_2$, –COCl or $-C\equiv N$ is present in the molecule it is always given number 1 and 1 is never writen when there is no ambiguity.



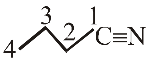
2-Ethylhaxenoic acid



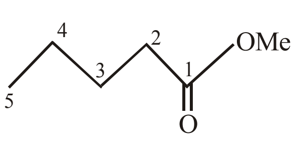
2-Ethylpent-2-enoic acid



2-Methylpropanamide



Butane nitrile
(e is retained as it
comes before n)

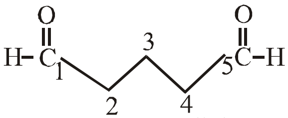


Methylpentanoate

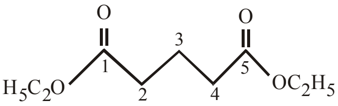
Pent-2-enal
(terminal e of ene is removed
as it comes before a)

Nomenclature of compounds containing two or more than two similar terminal groups

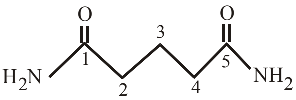
(i) **Presence of only two similar terminal groups :** The carbon atoms of such groups are included in the principal chain. For example



Pentanedial



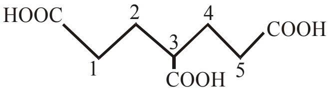
Diethyl pentanedioate



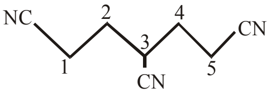
Pentanediamide

(ii) **Presence of more than two similar terminal groups attached to the main principal chain :** In this case special suffixes are used and carbons of terminal groups are not counted in the principal chain

Functional groups	**Suffix**
–COOH	- Carboxylic acid
–CHO	- Carbaldehyde
–COX	- Carbonylhalide
–CONH$_2$	- Carboxamide
–COOR	- Alkyl carboxylate
–CN	- Carbonitrile

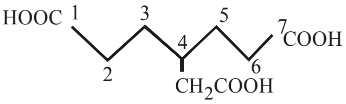


Pentane-1,3,5-tricarboxylic acid

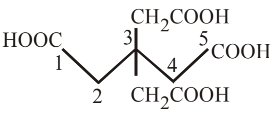


Pentane-1,3,5-tricarbonitrile

Presence of more than two similar terminal groups not directly attached to the principal chain : In such case the longest chain with two similar terminal groups is selected and carbons of groups are counted in the principal chain.



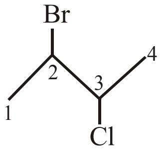
4-(Carboxymethyl)heptanedioic acid



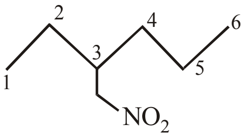
3,3-Bis(Carboxymethyl)
pentanedioic acid

NOMENCLATURE OF COMPOUNDS

containing substituents (not regarded principal functional groups)



2-Bromo-3-Chlorobutane
(follow alphabetical order)



3- Nitromethylhexane

NOMENCLATURE OF COMPOUNDS CONTAINING MORE THAN ONE TYPE OF FUNCTIONAL GROUPS

In such case the compound is regarded as derivative of senior funtional group and the other functional groups are regarded as substituents. The numbering of the parent chain is done in such a way so that the functional group of highest priority gets the lower number and the chain contains the maximum number of functional groups.

The seniority of functional groups (highest prirority) follow the following order

Group	*Prefix name*	*2ᵒ Suffix name*
$-SO_3H$	Sulpho	Sulphonic acid
$-COOH$	Carboxy	Oic acid
$-COOR$	alkoxy carbonyl	Oate
$-COX$	Halo carbonyl/Haloformyl	–oyl halide
$-CONH_2$	Carbamoyl	amide
$-CHO$	Aldo or formyl	al
$-CN$	Cyano	nitrile
$-NC$	Isocyano	Isonitrile
$>C=O$	Keto or oxo	one
$-OH$	Hydroxy ol	
$-SH$	Mercapto	thiol
$-NH_2$	Amino	Amine
$-OR$	Alkoxy	–
$\underset{\diagdown O \diagup}{>C-C<}$	Epoxy	–
$>C=C<$	–	ene
$-C\equiv C-$	–	yne
$-N=N$	Azo	–
$-NO_2$	Nitro	–
$-NO$	Nitroso	–
$-X$ (Cl, Br, I)	Halo (Cl, Br, I)	

The terminal e of the primary suffix is replaced by the suffix name of functional group.

Alphabetical order for substituents : These should be placed in alphabetical order.

Naming of substituted substituents : In this case the subsidiary substituents are named as prefixes. For example

$-CH_2-CHO$
Formyl methyl

$=CH-CH_3$
Ethylidene

$\equiv C-CH_2-CH_3$
Propylidyne

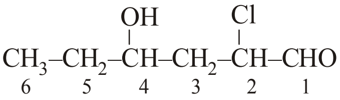
$-CH_2-COOH$
Carboxymethyl

$-CH_2Cl$
Chloromethyl

$-CH_2-C\equiv N$
Cyanomethyl

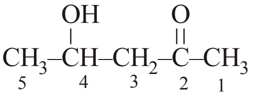
$-CH_2-CH_2-CO-NH_2$
Carbomoylethyl

Examples :

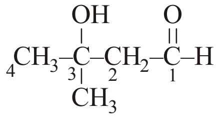
1.


$\underset{6}{CH_3}-\underset{5}{CH_2}-\underset{4}{\overset{\overset{OH}{|}}{CH}}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{Cl}{|}}{CH}}-\underset{1}{CHO}$

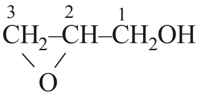
2-Chloro-4-hydroxyhexanal

2.


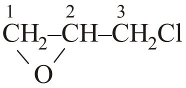
$\underset{5}{CH_3}-\underset{4}{\overset{\overset{OH}{|}}{CH}}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{1}{CH_3}$ 4-hydroxypentan-2-one

3.


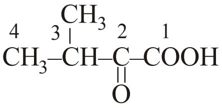
${}_4CH_3-\underset{\underset{CH_3}{3|}}{\overset{\overset{OH}{|}}{C}}-\underset{2}{CH_2}-\underset{1}{\overset{\overset{O}{\|}}{C}}-H$ 3-hydroxy-3-methylbutan-1-al

4.


$\underset{\diagdown O \diagup}{\overset{3}{CH_2}-\overset{2}{CH}}-\overset{1}{CH_2}OH$ 2,3-epoxypropan-1-ol

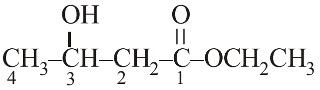
5.


$\underset{\diagdown O \diagup}{\overset{1}{CH_2}-\overset{2}{CH}}-\overset{3}{CH_2}Cl$ 3-Chloro-1, 2-epoxypropane

6.


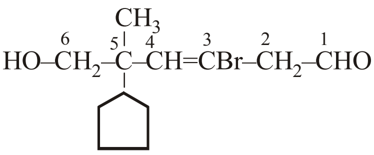
$\overset{4}{CH_3}-\overset{\overset{CH_3}{3|}}{CH}-\underset{\underset{O}{\|}}{\overset{2}{C}}-\overset{1}{COOH}$ 3-methyl-2-oxobut-1-oic acid

7. $NC-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{COOH}$ 3-cyanoprop-1-oic acid

8.


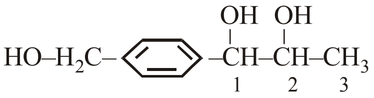
$\underset{4}{CH_3}-\underset{3}{\overset{\overset{OH}{|}}{CH}}-\underset{2}{CH_2}-\underset{1}{\overset{\overset{O}{\|}}{C}}-OCH_2CH_3$

Ethyl-3-hydroxybutanoate

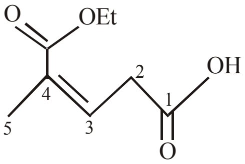
9.


$HO-\overset{6}{CH_2}-\overset{\overset{CH_3}{5|}}{C}-\overset{4}{CH}=\overset{3}{C}Br-\overset{2}{CH_2}-\overset{1}{CHO}$

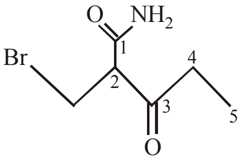
3-Bromo-5-cyclopentyl-6-hydroxy-5-methylhex-3-en-1-al

10.


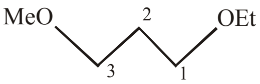
1-(p-hydroxymethylphenyl)prop-1, 2-diol

11.


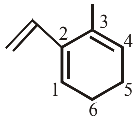
4-Carbethoxypent-3-en-1-oic acid

12.


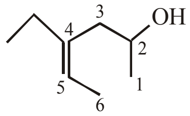
2-(Bromomethyl)-3-oxopentanamide

13.


1-ethoxy-3-methoxypropane

14.


2-Ethenyl-3-methylcyclohexa-1, 3-diene

15.


4-ethylhex-4-en-2-ol

NOMENCLATURE OF AROMATIC COMPOUNDS

Generally Benzene and its derivatives are known as aromatic compounds. They are of two types

(i) **Nuclear substituted :** The functional group is directly attached to the benzene nucleus e.g. phenol, toluene, chlorobenzene etc.

(ii) **Side chain substituted :** The functional group is present in the side chain e.g. Benzyl alcohol, Benzylamine etc.

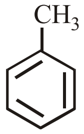
In the first case the compounds are named as derivatives of benzene and in the second case as derivatives of aliphatic compounds (except arenes).

The IUPAC name of benzene is cyclohex-1,3, 5-triene, but now aromatic compounds have their popular common name adopted by IUPAC. In IUPAC system the position of functional groups are indicated by arabic numerals i.e. 1, 2, 3 instead of *o*, *m* and *p*.

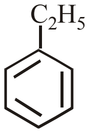
Aromatic hydrocarbons (Arenes).

(i) Containing one ring:

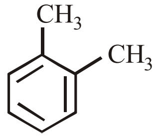
Benzene



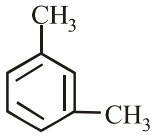
Methyl benzne (Toluene)



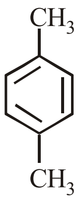
Ethyl benzne



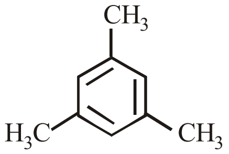
1, 2-dimethylbenzene (o-xylene)



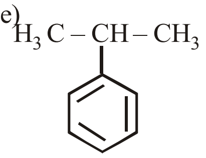
1, 3-dimethylbenzene (m-xylene)



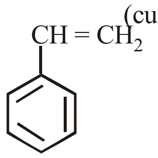
1, 4-dimethylbenzene (p.xylene)



1, 3, 5-trimethylbenzene (mesitylene)

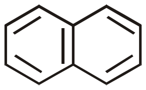


2-propylbenzene (cummene)

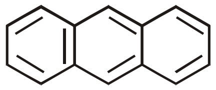


ethenylbenzene (styrene, vinyl benzene)

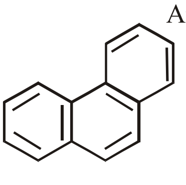
(ii) Containing more than one ring



Naphthalene

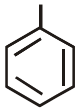


Anthracene

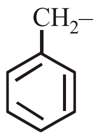


Phenanthrene

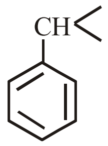
(iii) ***Aryl groups:***



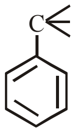
Phenyl



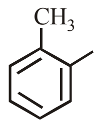
Benzyl



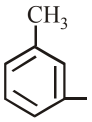
Benzal



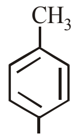
Benzo



2-Tolyl or
o-Tolyl

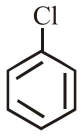


3-Tolyl (m-Tolyl)

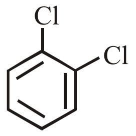


4-Tolyl (p-Tolyl)

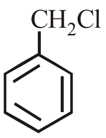
(iv) ***Halogen dervivatives:***



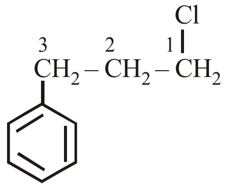
Chlorobenzene



1, 2-dichlorobenzene
(o-dichlorobenzene)



phenylchloro methane
(Benzyl chloride)

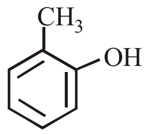


1-chloro-3-phenyl propane
(γ-phenylpropyl chloride)

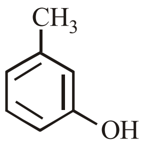
(v) ***Phenols-***

(a) Nuclear substituted hydroxy derivatives are known as phenols

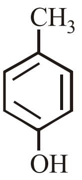
Phenol



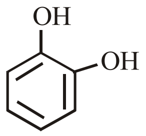
2-methylphenol
(o-cresol)



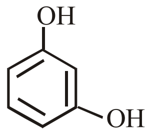
3-methylphenol
(m-cresol)



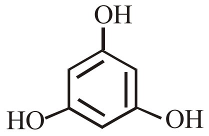
4-methylphenol
(p-cresol)



1, 2-dihydroxy benzene
(Catechol)

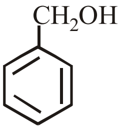


1, 3-dihydroxybenzene
(Resorinol)

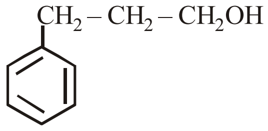


1, 3, 5-trihydroxybenzne
(Phloroglucinol)

(b) Side chain substituted hydroxy derivatives are known as alcohols

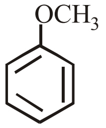


Phenylmethanol
(Benzyl alcohol)

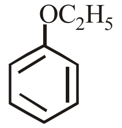


3-phenyl prop-1-ol

(vi) ***Aromatic ethers:***

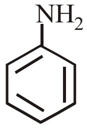


Methoxybenzene
(Anisole)

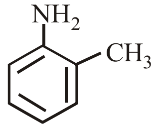


Ethoxybenzene
(phenetole)

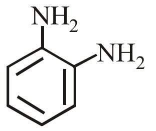
(vii) Amines:



Benzenamine
(Aniline)

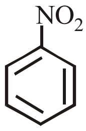


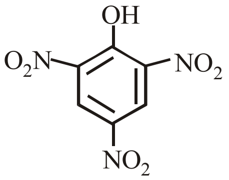
2-methylbenzenamine
(o-Toluidine)

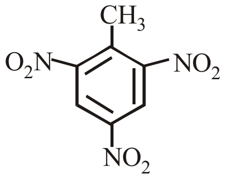


Benzene-1, 2-diamine
(o-Phenylenediamine)

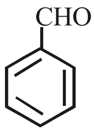
(viii) Nitro compounds:

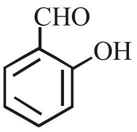

Nitro benzene


2, 4, 6-trinitrophenol
(Picric acid)

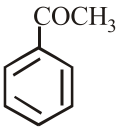

2, 4, 6-trinitrotoluene
(T.N.T.)

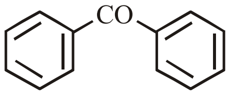
(ix) Aldehydes:


Benzaldehyde

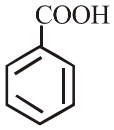

2-hydroxybenzaldehyde
(Salicyaldehyde)

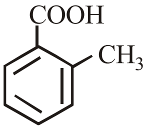
(x) Ketones:

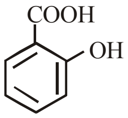

Methyl phenyl Ketone
(Acetophenone)

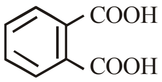

Diphenyl Ketone
(Benzophenone)

(xi) Acids:

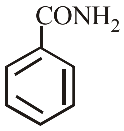

Benzoic acid

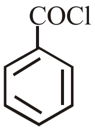

2-methylbenzoic acid
(o-Toluic acid)

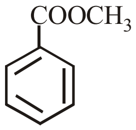

2-Hydroxybenzoic acid
(Salicylic acid)

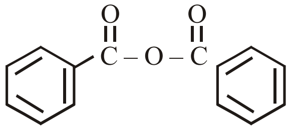

Benzene-1, 2-dicarboxylic acid
(Phthalic acid)

(xii)Acid derivatives:

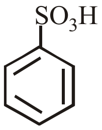

Benzamide


Benzoyl chloride


Methyl benzoate


Benzoic anhydride

(xiii)Sulphonic acids:


Benzene sulphonic acid

Exercise-1 | NCERT BASED QUESTIONS

Very Short/ Short Answer Questions

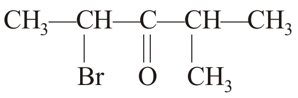
1. Write the metamer of diethyl ether. What is its IUPAC name?

2. What is the functional group of (i) an aldehyde and (ii) a nitro compound?

3. What primary and secondary suffixes are as applied to IUPAC nomenclature?

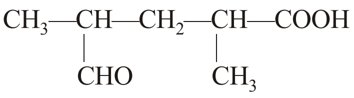
4. Give the IUPAC name of the compound: $CH_2=CH-CH(CH_3)_2$

5. Give the IUPAC names of the following compound:



$CH_3-\underset{\substack{|\\Br}}{CH}-\underset{\substack{\|\\O}}{C}-\underset{\substack{|\\CH_3}}{CH}-CH_3$

6. Write the IUPAC name of

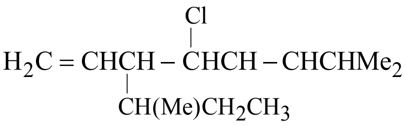


$CH_3-\underset{\substack{|\\CHO}}{CH}-CH_2-\underset{\substack{|\\CH_3}}{CH}-COOH$

7. Write IUPAC names for

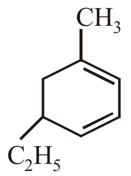
(i) $CH_3-CH=C(NO_2)\,CH_2CH_3$

(ii)



$H_2C=CH\underset{\substack{|\\CH(Me)CH_2CH_3}}{CH}-\overset{\substack{Cl\\|}}{C}HCH-CHCHMe_2$

(iii)



(iv) $(H_2C=CH)_2\,CHCH_2CH=CHCH_3$

8. Write the condensed structural formula of

(a) 4-ethyl-3-methyl heptane

(b) 3, 3-dimethyl octane

9. Write the structural formula of

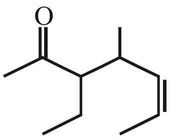
(i) o-methoxyethylbenzene

(ii) 2,3-dibromo-1-phenylpentane

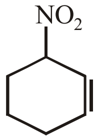
(iii) 4-ethyl-1-fluoro-2-nitrobenzene

10. Name the compounds whose line formulae are given below:

(i)



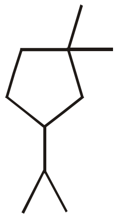
(ii)



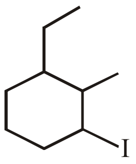
Long Answer Questions

11. Name each of the following :

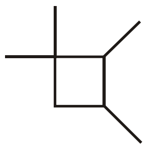
(i)



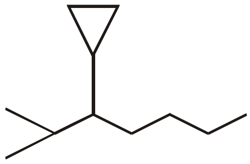
(ii)



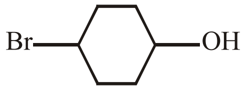
(iii)



(iv)

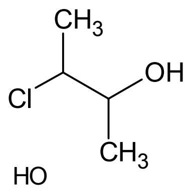


(v)

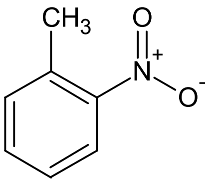


12. Give IUPAC names of

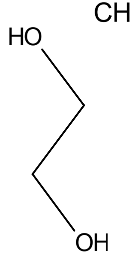
(a)



(b)

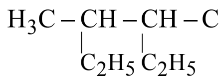


(c)



Multiple Choice Questions

13. Correct IUPAC name of



$H_3C-\underset{\substack{|\\C_2H_5}}{CH}-\underset{\substack{|\\C_2H_5}}{CH}-CH_3$ is ————— .

(a) 2 –ethyl-3-methylpentane

(b) 3,4-dimethylhexane

(c) 2-sec-butylbutane

(d) 2, 3-dimethylbutane

14. Which of the following is the correct IUPAC name?

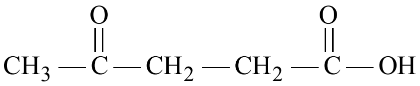
(a) 3-Ethyl-4, 4-dimethylheptane

(b) 4,4-Dimethyl-3-ethylheptane

(c) 5-Ethyl-4, 4-dimethylheptane

(d) 4, 4-Bis(methyl)-3-ethylheptane

15. The IUPAC name for


$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$

is ___.

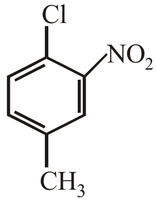
(a) 1-hydroxypentane-1, 4-dione

(b) 1,4-dioxopentanol

(c) 1-carboxybutan-3-one

(d) 4-oxopentanoic acid

16. The IUPAC name for



(a) 1-Chloro-2-nitro-4-methyl benzene

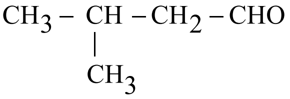
(b) 1-Chloro-4-methyl-2-nitrobenzene

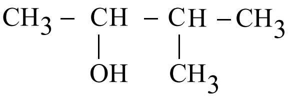
(c) 2-Chloro-1-nitro-5-methyl benzene

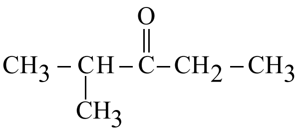
(d) *m*-Nitro-*p*-chlorotoluene

17. Which of the following compounds has wrong IUPAC name?

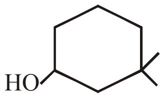
(a) $CH_3-CH_2-CH_2-COO-CH_2CH_3$ → ethyl butanoate

(b) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CHO \rightarrow$ 3-methyl-butanal

(c) 
$CH_3-\underset{OH}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3 \rightarrow$ 2-methyl-3-butanol

(d) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \rightarrow$ 2-methyl-3-pentanone

18. The IUPAC name of the compound is



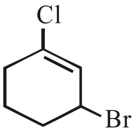
(a) 3, 3-dimethyl - 1- cyclohexanol

(b) 1, 1-dimethyl-3-hydroxy cyclohexane

(c) 3, 3-dimethyl-1-hydroxy cyclohexane

(d) 1, 1-dimethyl-3-cyclohexanol

19. The IUPAC name of the compound shown below is :



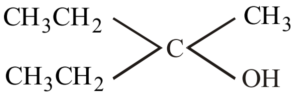
(a) 3-bromo-1-chlorocyclohexene

(b) 1-bromo-3-chlorocyclohexene

(c) 2-bromo-6-chlorocyclohex-1-ene

(d) 6-bromo-2-chlorocyclohexene

20. Name of the following compound is :



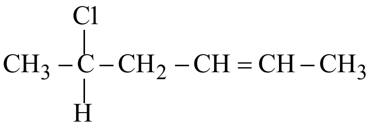
(a) 2-ethylbutan-2-ol

(b) 1-ethyl-1-methylpropan-1-ol

(c) 3-methyl pentan-3-ol

(d) diethylethanol

21. The IUPAC name for


$CH_3-\underset{H}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-CH_2-CH=CH-CH_3$ is

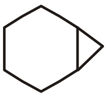
(a) 5–chlorohex–2–ene

(b) 2–chlorohex–5–ene

(c) 1–chloro–1–methylpent–3–ene

(d) 5–chloro–5–methylpent–2–ene

22. The correct name for the following hydrocarbon is

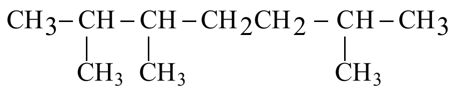


(a) Tricyclo [4.1.0] heptane (b) Bicyclo [5.2.1] heptane

(c) Bicyclo [4.1.0] heptane (d) Bicyclo [4.1.0] hextane

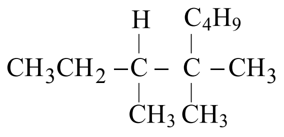
Exercise-2 | CONCEPTUAL MCQs

1. The kind of valency that exists in CaH_2 & C_2H_2 is
   (a) electrovalency in CaH_2 and covalency in C_2H_2
   (b) electrovalency in both
   (c) covalency in CaH_2 and electrovalency in C_2H_2
   (d) covalency in both
2. The compound which has one isopropyl group is
   (a) 2, 2, 3, 3 - Tetramethylpentane
   (b) 2, 2 - Dimethylpentane
   (c) 2, 2, 3- Trimethylpentane
   (d) 2- Methypentane
3. Which of the following statements is false for isopentane ?
   (a) It has three CH_3 groups
   (b) It has one CH_2 group
   (c) It has one CH group
   (d) It has a carbon which is not bonded to hydrogen
4. Which of the following IUPAC names is correct?
   (a) 2-Methyl-3-ethylpentane
   (b) 3-Ethyl-2-methylpentane
   (c) 2-Ethyl-3-methylpentane
   (d) 3-Methyl-2-ethylpentane
5. The correct IUPAC name of the compound with molecular formula, $(CH_3)_3C-CH_3$ is
   (a) Pentane
   (b) 1, 1, 1 -trimethylethane
   (c) 2, 2- dimethylpropane
   (d) Neopentane
6. The IUPAC name of



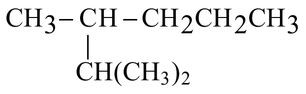
$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$$

   (a) 2, 5, 6- trimethylhexane
   (b) 2, 3, 6- trimethylheptane
   (c) 2, 3, 6- trimethylhexane
   (d) 2, 5, 6- trimethylheptane
7. The IUPAC name of



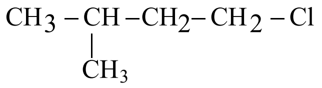
$$CH_3CH_2-\overset{H}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{C_4H_9}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3 \quad \text{is}$$

   (a) 3, 4, 4- trimethylheptane
   (b) 3, 4, 4- trimethyloctane
   (c) 2- butyl -2-methyl-3-ethylbutane
   (d) 2-ethyl-3, 3- dimethylheptane
8. The IUPAC name of this compound



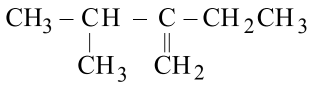
$$CH_3-\underset{CH(CH_3)_2}{\underset{|}{CH}}-CH_2CH_2CH_3 \quad \text{is}$$

   (a) 2- isopropylpentane (b) 2, 3 -dimethylhexane
   (c) Isononane (d) 2, 4- dimethylhexane
9. The IUPAC name of the compound



$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-Cl$$

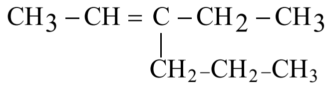
   (a) 1-chloro -3- methylbutane
   (b) 2- methyl-4- chlorobutane
   (c) 2-methyl-4-chlorobutane
   (d) 1-chloropentane
10. IUPAC name of the given compound will be $(CH_3)_2C(CH_2CH_3)CH_2CH(Cl)CH_3$
   (a) 5-chloro-3-, 3-dimethylhexane
   (b) 4-chloro-2-ethyl-2-methylpentane
   (c) 2-chloro-4-ethyl-4-methylpentane
   (d) 2-chloro-4, 4- dimethylhexane
11. The IUPAC name of $(CH_3)_3C-CH=CH_2$ is
   (a) 2 , 2- dimethylbut -3-ene
   (b) 2, 2- dimethylpent -4-ene
   (c) 3, 3- dimethylbut - 1- ene
   (d) Hex -1-ene
12. The IUPAC name of the following $CH_3C(CH_3)_2CH_2CH=CH_2$ is
   (a) 2, 2- dimethyl -4- pentene
   (b) 4, 4- dimethyl -1- pentene
   (c) 1, 1, 1- trimethyl -3- butene
   (d) 4, 4, 4- trimethyl -1- butene
13. The IUPAC name of the compound



$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_2}{\underset{\|}{C}}-CH_2CH_3$$

   (a) 2- ethyl -3- methylbut -1- ene
   (b) 2- isopropylbut -1- ene
   (c) 2- methyl - 3 ethyl - 3- butene
   (d) 2- (1- methylethyl) but -1- ene
14. $CH_3CH_2CH_2CH(CH=CH_2)CH_2CH_2CH_3$ is
   (a) 4-ethenylheptane
   (b) 3-n-propyl-1-hexene
   (c) 4-ethenylhexane
   (d) 3-ethenylheptane

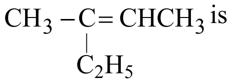
15. IUPAC name of the following compound will be



$CH_3-CH=\underset{CH_2-CH_2-CH_3}{\underset{|}{C}}-CH_2-CH_3$

(a) 3-propyl-3-hexene (b) 3-propyl-2-hexene
(c) 3-ethyl-2-hexene (d) 4-ethyl-4-hexene

16. The IUPAC name of

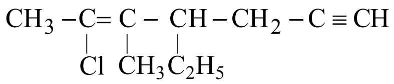


$CH_3-\underset{C_2H_5}{\underset{|}{C}}=CHCH_3$ is

(a) 2-ethylbutene (b) 2-ethylbut-2-ene
(c) 3-methylpent-2-ene (d) 2-ethylpent-2-ene

17. The IUPAC name of $CH_3-C\equiv C-CH(CH_3)_2$ is
(a) 4- methyl -2-pentyne
(b) 4, 4 - dimethyl -2 butyne
(c) Isopropylmethylacetylene
(d) 2-Methyl-4-pentyne

18. The IUPAC name of



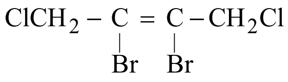
$CH_3-\underset{Cl}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-\underset{C_2H_5}{\underset{|}{CH}}-CH_2-C\equiv CH$ is

(a) 6-chloro-4-ethyl-5-methylhept-5-en-1-yne
(b) 6-chloro-4-ethyl-5-methylhept-1-yn-5-ene
(c) 2-chloro-4-ethyl-3-methylhept-2-en-6-yne
(d) 2-chloro-4-ethyl-3-methylhept-6-yn-2-ene

19. The IUPAC name of $CH_3OC_2H_5$ is
(a) Methyl ethyl ether (b) Ethyl methyl ether
(c) Methoxyethane (d) Ethoxymethane

20. Which of the following represents the correct IUPAC name of the compound $CH_2=CH-CH_2Cl$?
(a) Allyl chloride (b) 1- chloro -3- propene
(c) 3- chloro-1- propene (d) Vinyl chloride

21. The name of

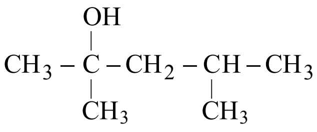


$ClCH_2-\underset{Br}{\underset{|}{C}}=\underset{Br}{\underset{|}{C}}-CH_2Cl$ according to IUPAC nomenclature system is

(a) 2, 3- dibromo -1, 4- dichlorobutene-2
(b) 1, 4- dichloro-2, 3- dibromobutene-2
(c) Dichlorodibromobutene
(d) Dichlorodibromobutane

22. IUPAC name of $(C_2H_5)_2CHCH_2OH$ is
(a) 2- ethylbutanol - 1 (b) 2- methylpentanol -1
(c) 2- ethylpentanol -1 (d) 3- ethylbutanol -1

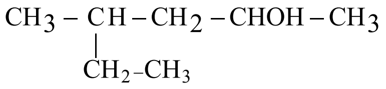
23. The IUPAC name of



$CH_3-\underset{CH_3}{\underset{|}{\overset{\overset{OH}{|}}{C}}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$ is

(a) 2, 4- dimethylpentanol -2
(b) 2, 4- dimethylpentanol -4
(c) 2, 2- dimethylbutanol-2
(d) Butanol -2

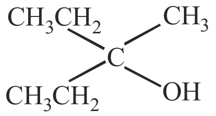
24. IUPAC name of the compound



$CH_3-\underset{CH_2-CH_3}{\underset{|}{CH}}-CH_2-CHOH-CH_3$ is

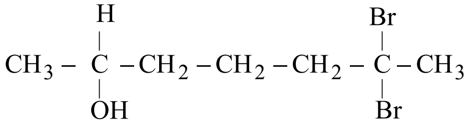
(a) 4- methyl -3- hexanol (b) Heptanol
(c) 4- methyl - 2- hexanol (d) None of these

25. The correct nomenclature (IUPAC) for the following alcohol is



(a) 2-ethyl-2-butanol
(b) 3-methyl-3-pentanol
(c) 3-ethyl-3-methyl-3-pentanol
(d) 1, 1 - diethylethanol

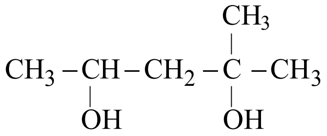
26. The IUPAC name of



$CH_3-\underset{OH}{\underset{|}{\overset{\overset{H}{|}}{C}}}-CH_2-CH_2-CH_2-\underset{Br}{\underset{|}{\overset{\overset{Br}{|}}{C}}}-CH_3$ is

(a) 6, 6- dibromoheptan -2- ol
(b) 2, 2- dibromoheptan -6- ol
(c) 6, 6- dibromoheptan -2- al
(d) None of these

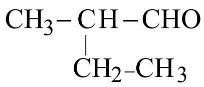
27. The IUPAC name of the compound



$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{\overset{\overset{CH_3}{|}}{C}}}-CH_3$ is

(a) 1, 1- dimethylbutane -1, 3-diol
(b) 1, 3. 3- trimethylpropane -1, 3-diol
(c) 2- methylpentane -2, 4- diol
(d) 1, 3, 3- trimethyl -1, 3- propanediol

28. Choose the correct IUPAC name for

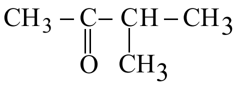


$CH_3-\underset{CH_2-CH_3}{\underset{|}{CH}}-CHO$

(a) Butan - 2- aldehyde
(b) 2- methylbutanal
(c) 3- methylisobutyraldehyde
(d) 2- ethylpropanal

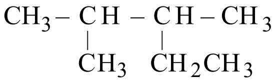
29. The IUPAC name of the compound having the molecular formula Cl_3C-CH_2CHO is
(a) 3, 3, 3- trichloropropanal
(b) 1, 1, 1- trichloropropanal
(c) 2, 2, 2- trichloropropanal
(d) Chloral

30. The incorrect IUPAC name is

(a) 

$CH_3-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{CH_3}}{CH}-CH_3$

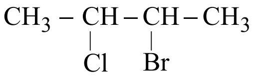
2-methyl-3-butanone

(b) 

$CH_3-\underset{\overset{|}{CH_3}}{CH}-\underset{\overset{|}{CH_2CH_3}}{CH}-CH_3$

2, 3 -dimethylpentane

(c) $CH_3-C\equiv CCH(CH_3)_2$
4-methyl-2-pentyne

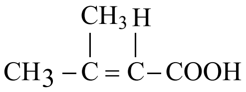
(d) 

$CH_3-\underset{\overset{|}{Cl}}{CH}-\underset{\overset{|}{Br}}{CH}-CH_3$

3-chloro-2-bromobutane

31. The systematic name of $(CH_3)_2\,CH-COOH$ is
(a) 2- propanoic acid
(b) isobutanoic acid
(c) 2- methylpropanoic acid
(d) 2- methylbutanoic acid

32. The IUPAC name of the formula,



$CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{H}{|}}{C}-COOH$ is

(a) 2-methyl-2-butenoic acid
(b) 3-methyl-3-butenoic acid
(c) 3-methyl-2-butenoic acid
(d) 2-methyl-3-butenoic acid

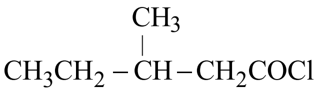
33. IUPAC name of $CH_2 = CHCN$ is
(a) Ethenenitrile (b) Vinyl cyanide
(c) Cyanoethene (d) 2-propenenitrile

34. The compound

 is

known by which of the following names ?
(a) Bicyclo [2.2.2] octane
(b) Bicyclo [2.2.1] octane
(c) Bicyclo [1.2.1] octane
(d) Bicyclo [1.1.1] octane

35. The IUPAC name of the compound,

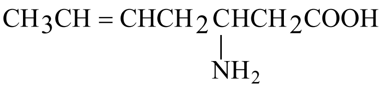


$CH_3CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2COCl$ is

(a) 3-Methylpentanoyl chloride
(b) 3- Methylbutanoyl chloride
(c) 1- Chloro - 3- ethylbutanone
(d) 1- Chloro - 3- methylpentanone

36. The IUPAC name of $CH_3CH{=}CHCOOC_2H_5$ is
(a) Ethyl but-1-enoate (b) Ethyl but-2-enoate
(c) Ethyl prop-2-enoate (d) None of these

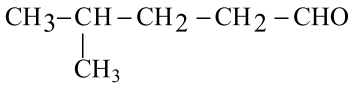
37. The IUPAC name of the compound



$CH_3CH = CHCH_2\underset{\overset{|}{NH_2}}{CH}CH_2COOH$ is

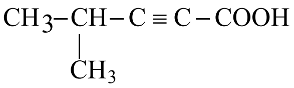
(a) 5- amino - 2 - heptenoic acid
(b) β - amino- δ - heptanoic acid
(c) 5- amino hex - 2- enecarboxylic acid
(d) 3- amino -5- heptenoic acid

38. Indicate the wrongly named compound

(a) 

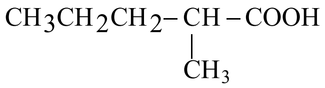
$CH_3-\underset{\overset{|}{CH_3}}{CH}-CH_2-CH_2-CHO$

(4-methyl -1- pentanal)

(b) 

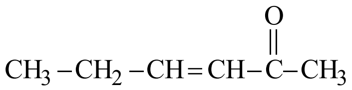
$CH_3-\underset{\overset{|}{CH_3}}{CH}-C\equiv C-COOH$

(4- methyl -2- pentyne -1- oic acid)

(c) 

$CH_3CH_2CH_2-\underset{\overset{|}{CH_3}}{CH}-COOH$

(2- methyl -1- pentanoic acid)

(d) 

$CH_3-CH_2-CH{=}CH-\overset{\overset{O}{\|}}{C}-CH_3$

(3- hexen -5- one)

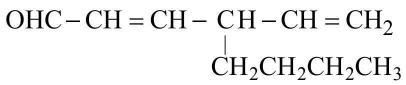
39. The IUPAC name of tert–butylchloride is
(a) 4-chlorobutane
(b) 2-chlorobutane
(c) 1-chloro-3-methylpropane
(d) 2-chloro-2-methylpropane

40. The IUPAC name of acraldehyde is
(a) Prop-2-en-1-al (b) Propenylaldehyde
(c) But-2-en-1-al (d) Propenal

41. Vinylcarbinol is
(a) $HO{-}CH_2{-}CH{=}CH_2$
(b) $CH_3C(OH){=}CH_2$
(c) $CH_3{-}CH{=}CH{-}OH$
(d) $CH_3{-}C(CH_2OH){=}CH_2$

42. IUPAC name of 4- isopropyl-m-xylene is
(a) 1-isopropyl-2-, 4 -dimethylbenzene
(b) 4-isopropyl-m-xylene
(c) 1-isopropyl -3, 5- dimethylbenzene
(d) 4- isopropyl-3, 5- dimethylbenzene

43. The IUPAC name of



$\mathrm{OHC-CH=CH-\underset{\underset{CH_2CH_2CH_2CH_3}{|}}{C}H-CH=CH_2}$ is

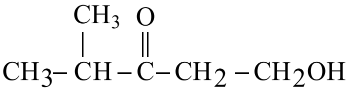
(a) 5- vinyloct -3- en -1 -al

(b) 4- butyl- 2,5 - hexadien -1-al

(c) 5- vinyloct - 5- en - 8- al

(d) 3- butyl -1, 4 - hexandien - 8 -al

44. The IUPAC name of



$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{O}{\|}}{C}-CH_2-CH_2OH}$ is

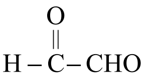
(a) 1- hydroxy -4- methyl -3- pentanone

(b) 2- methyl -5- hydroxy -3- pentanone

(c) 4- methyl -3- oxo -1- pentanol

(d) Hexanol -1 - one -3

45. The correct IUPAC name of

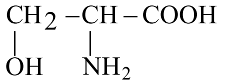


$\mathrm{H-\overset{\overset{O}{\|}}{C}-CHO}$ is

(a) Formylmethanal (b) 1, 2-ethanedione

(c) 2-oxoethanal (d) 1, 2-ethanedial

46. The IUPAC name of the compound



$\mathrm{\underset{\underset{OH}{|}}{CH_2}-\underset{\underset{NH_2}{|}}{CH}-COOH}$ is

(a) 2- amino-3- hydroxypropanoic acid

(b) 1- hydroxy -2- aminopropan -3- oic acid

(c) 1- amino -2- hydroxypropanoic acid

(d) 3- hydroxy -2- aminopropanoic acid

47. The IUPAC name of the compound

$\mathrm{CH_3-\underset{\underset{OH}{|}}{C}=CH-CH_2-COOH}$

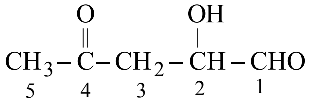
(a) Hydroxypentenoic acid

(b) 4- hydroxy -3- pentenoic acid

(c) 4- hydroxy -4- pentenoic acid

(d) 3- hydroxy -4- methyl-3-ene pentenoic acid

48. The IUPAC name of



$\mathrm{\underset{5}{CH_3}-\underset{4}{\overset{\overset{O}{\|}}{C}}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{OH}{|}}{CH}}-\underset{1}{CHO}}$ is

(a) 5- Oxo-4-hydroxy -2- pentanone

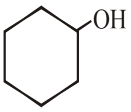
(b) 4- hydroxy -5-al-2- pentanone

(c) 2-hydroxy -4-oxopentanal

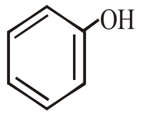
(d) 1-al-4-oxo-2- pentanol

49. The structural formula of cyclohexylalcohol is

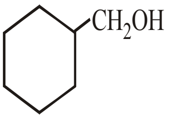
(a)



(b)



(c)



(d) None of these

50. The structural formula of 2-methyl-2-butene is

(a) $CH_3-CH(CH_3)-CH=CH_2$

(b) $CH_3-CH_2-C(CH_3)=CH_2$

(c) $CH_3-CH=CH-CH_3$

(d) $CH_3-CH=C(CH_3)-CH_3$

51. An organic compound X (molecular formula $C_6H_7O_2N$) has six carbon atoms in a ring system, two double bonds and a nitro group as substituent , X is

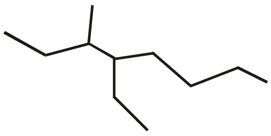
(a) Homocyclic but not aromatic

(b) Aromatic but not homocyclic

(c) Homocyclic and aromatic

(d) Heterocyclic and aromatic

52. Name of the compound given below is



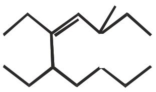
(a) 3- methyl -4- ethyloctane

(b) 2, 3- diethylheptane

(c) 5- ethyl - 6- methyloctane

(d) 4- ethyl- 3- methyloctane

53. The correct IUPAC name of the compound,



is

(a) 5, 6 diethyl - 8- methyldec - 6 - ene

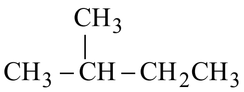
(b) 6- Butyl - 5 - ethyl - 3- methyloct - 4- ene

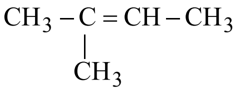
(c) 5, 6- diethyl - 3 - methyldec - 4- ene

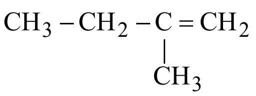
(d) 2, 4, 5- triethylnon - 3- ene.

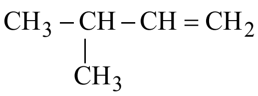
Exercise-3 | PAST COMPETITION MCQs

1. 2-Methyl 2-butene will be represented as **[CBSE-PMT 1992]**

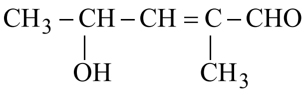
(a) 
$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2CH_3$

(b) 
$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$

(c) 
$CH_3-CH_2-\underset{\underset{CH_3}{|}}{C}=CH_2$

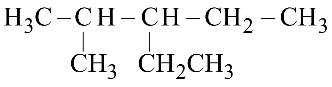
(d) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$

2. The IUPAC name of **[CBSE-PMT 1992]**


$CH_3-\underset{\underset{OH}{|}}{CH}-CH=\underset{\underset{CH_3}{|}}{C}-CHO$

(a) 4-Hydroxy-1-methylpentanal
(b) 4-Hydroxy-2-methylpent-2-en-1-al
(c) 2-Hydroxy-4-methylpent-3-en-5-al
(d) 2-Hydroxy-3-methylpent-2-en-5-al

3. Which of the following IUPAC names is correct for the compound? **[CBSE-PMT 1994]**

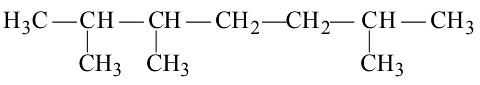

$H_3C-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-CH_3$

(a) 2-Methyl-3-ethylpentane
(b) 3-Ethyl-2-methylpentane
(c) 2-Ethyl-3-methylpentane
(d) 3-Methyl-2-ethylpentane

4. The first organic compound, synthesized in the laboratory, was **[CBSE-PMT 1995]**

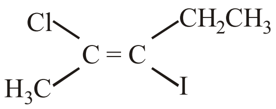
(a) alcohol (b) acetic acid
(c) urea (d) none of these

5. The IUPAC name of **[CBSE-PMT 1996]**


$H_3C-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$ is

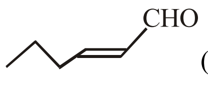
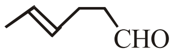
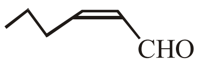
(a) 1, 3-isopropyl-3-methylpropane
(b) 2, 3, 6-trimethylheptane
(c) 2, 5, 6-trimethylheptane
(d) 2, 6, 3-trimethylheptane

6. IUPAC name for the compound **[CBSE-PMT 1998]**

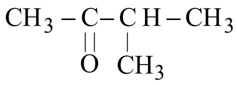

is

(a) trans-3-iodo-4-chloro-3-pentene
(b) cis-2-chloro-3-iodo-2-pentene
(c) trans-2-chloro-3-iodo-2-pentene
(d) cis-3-iodo-4-chloro-3-pentene

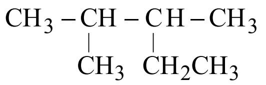
7. The correct structure of trans-2 hexenal is **[CBSE-PMT 1999]**

(a) 
(b) 
(c) 
(d) 

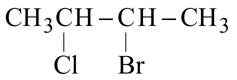
8. The incorrect IUPAC name is **[CBSE-PMT 2001]**

(a) 
$CH_3-\underset{\underset{O}{||}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

2-Methyl-3-butanone

(b) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_3$

2,3-Dimethylpentane

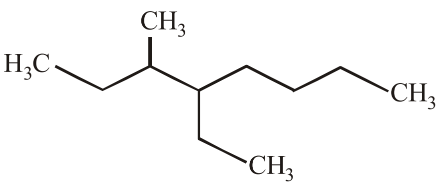
(c) 
$CH_3\underset{\underset{Cl}{|}}{CH}-\underset{\underset{Br}{|}}{CH}-CH_3$

2-Bromo-3-chlorobutane

(d) $CH_3-C\equiv CCH(CH_3)_2$

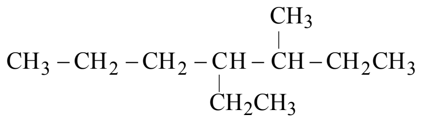
4-Methyl-2-pentyne

9. Name of the compound given below is **[CBSE-PMT 2003]**



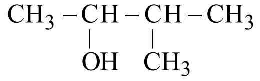
(a) 5-ethyl-6-methyloctane
(b) 4-ethyl-3-methyloctane
(c) 3-methyl-4-ethyloctane
(d) 2, 3-diethylheptane

10. Names of some compounds are given. Which one is not correct in IUPAC system? **[CBSE-PMT 2005]**

(a) 

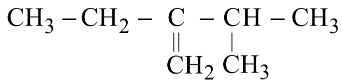
$CH_3-CH_2-CH_2-\underset{CH_2CH_3}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_2CH_3$

3-Methyl-4-ethyl heptane

(b) 

$CH_3-\underset{OH}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$

3-Methyl-2-butanol

(c) 

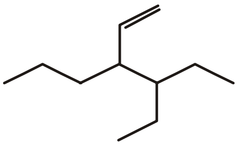
$CH_3-CH_2-\underset{CH_2}{\underset{||}{C}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$

2-Ethyl-3-methyl-but-1-ene

(d) $CH_3-C\equiv C-CH-(CH_3)_2$

4-Methyl-2-pentyne

11. The correct IUPAC name of the compound



is **[CBSE-PMT 2011]**

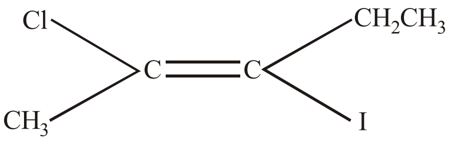
(a) 4-Ethyl-3-propyl hex-1-ene

(b) 3-Ethyl-4-ethenyl heptane

(c) 3-Ethyl-4-propyl hex-1-ene

(d) 3-(1-ethylpropyl) hex-1-ene

12. The IUPAC name of the following compound is



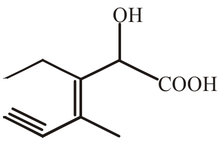
(a) trans-2-chloro-3-iodo-2-pentene **[CBSE-PMT 2011 M]**

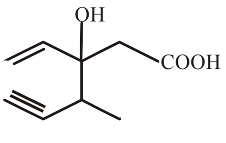
(b) cis-3-iodo-4-chloro-3-pentene

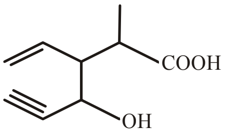
(c) trans-3-iodo-4-chloro-3-pentene

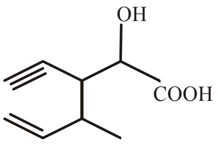
(d) cis-2-chloro-3-iodo-2-pentene

13. Structure of the compound whose IUPAC name is 3-ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid is : **[NEET 2013]**

(a) 

(b) 

(c) 

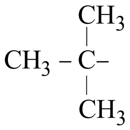
(d) 

14. The structure of isobutyl group in an organic compound is

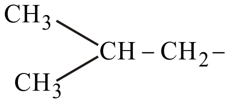
(a) 

$CH_3-\underset{|}{CH}-CH_2-CH_3$ **[NEET 2013]**

(b) $CH_3-CH_2-CH_2-CH_2-$

(c) 

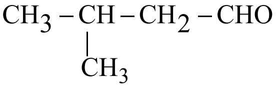
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-$

(d) 

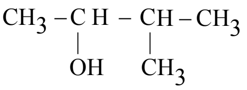
$(CH_3)_2CH-CH_2-$

15. Which of the following compounds has wrong IUPAC name? **[AIEEE 2002]**

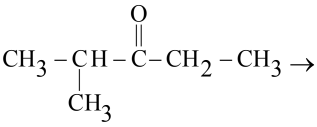
(a) $CH_3-CH_2-CH_2-COO-CH_2CH_3$ → ethyl butanoate

(b) 

$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CHO$ → 3-methyl-butanal

(c) 

$CH_3-\underset{OH}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$ → 2-methyl-3-butanol

(d) 

$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-CH_2-CH_3$ → 2-methyl-3-pentanone

16. The IUPAC name of $CH_3COCH(CH_3)_2$ is **[AIEEE 2003]**

(a) 2-methyl-3-butanone

(b) 4-methylisopropyl ketone

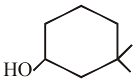
(c) 3-methyl-2-butanone

(d) Isopropylmethyl ketone

17. The general formula $C_nH_{2n}O_2$ could be for open chain **[AIEEE 2003]**

(a) carboxylic acids (b) diols

(c) dialdehydes (d) diketones

18. The IUPAC name of the compound is 

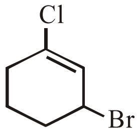
[AIEEE 2004]

(a) 3, 3-dimethyl - 1- cyclohexanol
(b) 1, 1-dimethyl-3-hydroxy cyclohexane
(c) 3, 3-dimethyl-1-hydroxy cyclohexane
(d) 1, 1-dimethyl-3-cyclohexanol

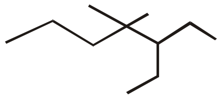
19. Which of the following will have a mesoisomer also? **[AIEEE 2004]**

(a) 2, 3- Dichloropentane
(b) 2, 3-Dichlorobutane
(c) 2-Chlorobutane
(d) 2-Hydroxypropanoic acid

20. The IUPAC name of the compound shown below is : **[AIEEE 2006]**



(a) 3-bromo-1-chlorocyclohexene
(b) 1-bromo-3-chlorocyclohexene
(c) 2-bromo-6-chlorocyclohex-1-ene
(d) 6-bromo-2-chlorocyclohexene

21. The IUPAC name of  is

(a) 3-ethyl-4, 4-dimethylheptane **[AIEEE 2007]**
(b) 1, 1-diethyl-2,2-dimethylpentane
(c) 4, 4-dimethyl-5,5-diethylpentane
(d) 5, 5-diethyl-4,4-dimethylpentane.

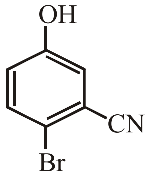
22. The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is **[AIEEE 2008]**

(a) $-COOH, -SO_3H, -CONH_2, -CHO$
(b) $-SO_3H, -COOH, -CONH_2, -CHO$
(c) $-CHO, -COOH, -SO_3H, -CONH_2$
(d) $-CONH_2, -CHO, -SO_3H, -COOH$

23. The IUPAC name of neopentane is **[AIEEE 2009]**

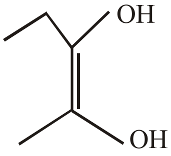
(a) 2, 2-dimethylpropane (b) 2-methylpropane
(c) 2, 2-dimethylbutane (d) 2- methylbutane

24. The IUPAC name of the following compound is **[IIT-JEE 2009]**



(a) 4-Bromo-3-cyanophenol
(b) 2-Bromo-5-hydroxybenzonitrile
(c) 2- Cyano-4-hydroxybromobenzene
(d) 6-Bromo-3-hydroxybenzonitrile

Exercise-4 | Applied MCQs

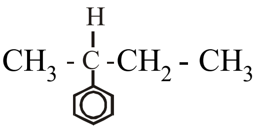
1. IUPAC name of  is :

(a) But – 2 ene – 2, 3– diol
(b) Pent – 2 –ene – 2, 3 – diol
(c) 2 – methylbut – 2 – ene – 2, 3 – diol
(d) Hex – 2 – ene – 2, 3 – diol

2. IUPAC name of  is :

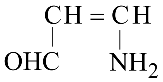
(a) 5 - methylhexanol (b) 2 - methylhexanol
(c) 2 - methylhex - 3 - enol (d) 4 - methylpent - 2 - enol

3. IUPAC name of following compound is :



$CH_3-\overset{H}{C}H-CH_2-CH_3$

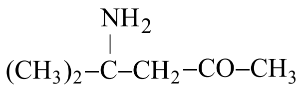
(a) 2 - cyclohexylbutane (b) 2 - phenylbutane
(c) 3 - cyclohexylbutane (d) 3 - phenylbutane

4. The IUPAC name of  is

$\underset{OHC}{CH}=\underset{NH_2}{CH}$

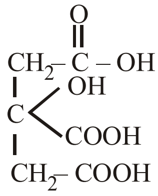
(a) 1 - amino prop - 2 - enal
(b) 3 - amino prop - 2 - enal
(c) 1 - amino - 2 - formylethene
(d) 3 - amino - 1 - oxoprop - 2 - ene

5. The given compound in IUPAC may be called,



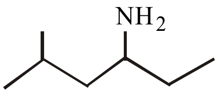
$(CH_3)_2-\overset{NH_2}{C}-CH_2-CO-CH_3$

(a) Diacetone
(b) Acetoneamine
(c) Diacetoneamine
(d) 4 - amino - 4 - methylpentane - 2 - one

6. The IUPAC name of compound  is:

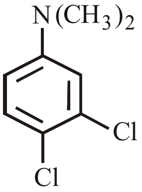
(a) 1, 2, 3 - tricarboxy - 2, 1 - propane
(b) 3 - carboxy - 3 hydroxy - 1 , 5 - pentanedioic acid
(c) 3 - hydroxy - 3 - carboxy - 1, 5 - pentanedioic acid
(d) 2 - hydroxy propane -1, 2, 3 - tricarboxylic acid.

7. What is the IUPAC name of the following compound ?



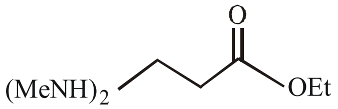
(a) 2-methyl-4-hexanamine
(b) 5-methyl-3-hexanamine
(c) 2-methyl-4-amino hexane
(d) 5-methyl-3-amino hexane

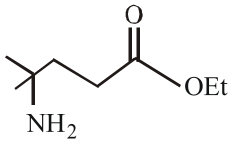
8. Which of the following is the correct IUPAC name of the compound ?

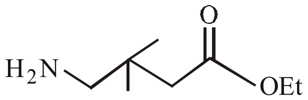


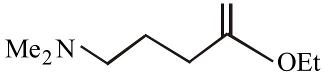
(a) 1, 2-dichloro-4-(N, N-dimethyl) aniline
(b) Dimethyl – (3, 4-dichlorophenyl) amine
(c) 3, 4-dichloro - N, N-dimethyl aniline
(d) N, N-dimethylamino - 3, 4-dichlorobenzene

9. Which one of the following is ethyl-4-(dimethyl amino) butanoate ?

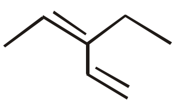
(a) 

(b) 

(c) 

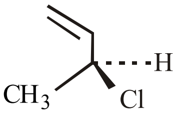
(d) 

10. The acceptable IUPAC name for the molecule including E – Z designation



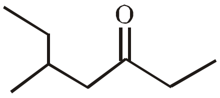
(a) Z – 3 – Propyl – 1, 3 – pentadiene
(b) E – 3 – Propyl – 1, 3 – pentadiene
(c) Z – 3 – Ethenyl – 1, 3 – hexadiene
(d) E – 3 – Ethenyl – 1, 3 – hexadiene

11. What is the IUPAC name of the compound ?



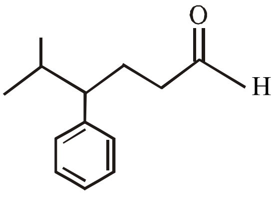
(a) 2 – chloro – 2 – butene
(b) 3 – chloro – 1 – butene
(c) 3 – methyl – 3 – chloropropene – 1
(d) 3 – chloro – 3 – methyl – 1 – propene

12. What is the IUPAC name of the following compound ?



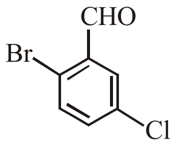
(a) 3 – methyl – 5 – heptanone
(b) 5 – methyl – 3 – heptanone
(c) 5 – ethyl – 3 – hexanone
(d) 2 – ethyl – 4 – hexanone

13. Identify the correct IUPAC name of the compound given below



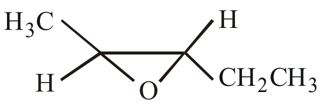
(a) 4 – benzyl – 5 – methyl hexanal
(b) 2 – methyl – 3 – phenyl hexanal
(c) 5 – isopropyl – 5 – phenyl butanal
(d) 5 – methyl – 4 – phenyl hexanal

14. Which of the following is the IUPAC name of the compound



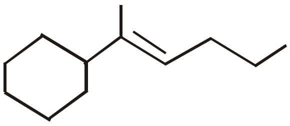
(a) o – bromo – m – Chlorobenzaldehyde
(b) 2 – bromo – 5 – Chlorobenzaldehyde
(c) 6 – bromo – 3 – Chlorobenzaldehyde
(d) 1 – bromo – 4 – Chlorobenzaldehyde

15. The IUPAC name of the following epoxide is



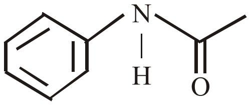
(a) cis – 2 – ethyl – 3 – methyloxirane
(b) trans – 1 – ethyl – 2 – methyl oxycyclopropane
(c) trans – 2 – ethyl – 3 – methyloxirane
(d) trans – 1 – ethyl – 2 – methyl ethane epoxide

16. The IUPAC name of the following compound



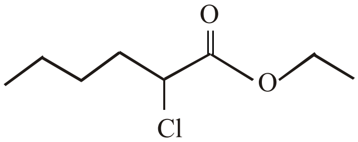
(a) E – 1 – cyclopentyl – 2 – hexene
(b) E – 2 – cyclohexyl – 2 – hexene
(c) Z – 1 – cyclopentyl – 1 – hexene
(d) Z – 2 – cyclopentyl – 2 – hexene

17. The IUPAC name of the following compounds is



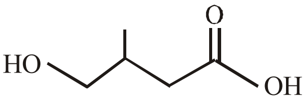
(a) N – phenyl ethanamide (b) N – phenyl ethanone
(c) N – phenyl methanamide (d) None of these

18. What is the name of the following compound ?



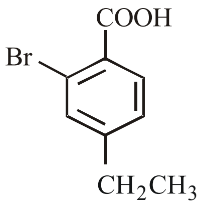
(a) 2 – chlorohexyl ethanoate
(b) ethyl – 2 chloro hexanoate
(c) 1 – chlorohexyl ethanoate
(d) ethyl – 1 chloro hexanoate

19. The IUPAC name of the following compound.



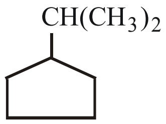
(a) 4 – hydroxy – 3 – methyl butanoic acid
(b) 1 – hydroxy – 2 – methyl butanoic acid
(c) 3 – hydroxy – 2 – methyl butanoic acid
(d) 3 – (hydroxymethyl) butanoic acid

20. What is the IUPAC name of the following compound ?



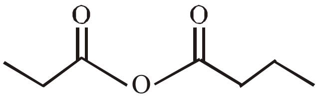
(a) 6 – bromo – 4 – ethylbenzene carboxylic acid
(b) 2 – bromo – 4 – ethylbenzene carboxylic acid
(c) Ortho – bromo – paraethyl benzoic acid
(d) 4 – bromo – 3 – ethyl benzoic acid

21. What is the IUPAC name of the compound ?



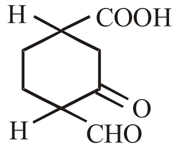
(a) 1, 1 – dimethyl – 1 – cyclopentyl methane
(b) 2 – cyclopentyl propane
(c) 1 – (1 – methyl) ethyl cyclopentane
(d) Cumene.

22. The accepted IUPAC name of the following compound.



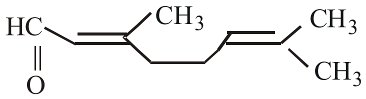
(a) Propanoic anhydride
(b) Butanoic propanoic anhydride
(c) Ethyl butanoate
(d) 4, 6 – dioxo heptane

23. The IUPAC name of the compound



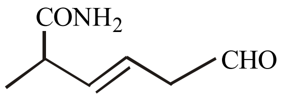
(a) 4-formyl-3-oxo cyclohexane-1-carboxylic acid
(b) 2, 4-dioxo cyclohexanoic acid
(c) 2, 4-dioxo heptanoic acid
(d) None of these

24. The correct IUPAC name of the compound



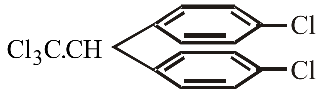
(a) 2, 6 – dimethyl octa – 2, 6 – dien – 1 – al
(b) 3, 7 – dimethyl hepta – 2, 6 – dien – 1 – al
(c) 3, 7 – dimethyl octa – 2, 6 – dien – 1 – al
(d) 2, 6 – dimethyl – 2, 6 – dien – 8 – al

25. The IUPAC name of the compound



(a) 5 – formyl – 2 – methyl pent – 3 – en – 1 – amide
(b) 2 – carbamoyl hexanal
(c) 2 – carbamoyl hex – 3 – en – 1 – al
(d) 6 – Keto – 2 – methyl hexanamide

26. The correct name of the compound (IUPAC)

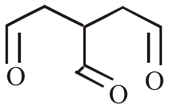


(a) D. D. T.
(b) Gammexane
(c) p, p’-dichloro diphenyl trichloroethane
(d) 1, 1, 1-trichloro-2, 2-bis (4-Chlorophenyl) ethane

27. The IUPAC name of the compound

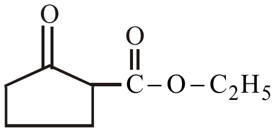
(a) 3 – methyl spiro [4, 5] dec – 2 – ene
(b) 2 – Methyl spiro [4, 5] dec – 1 – ene
(c) 2 – Methyl [5, 4] dec – 1 – ene
(d) 3 – Methyl spiro [5, 4] dec – 2 – ene

28. The IUPAC name of the compound



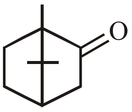
(a) 1, 2, 3 – triformyl propane
(b) Propane – 1, 2, 3 – tricarbaldehyde
(c) 3 – formyl – 1, 5 – pentane dial
(d) Propane – 1, 2, 3 – trial

29. The correct name (IUPAC) of the compound



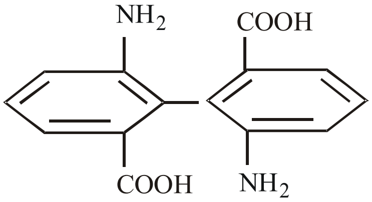
(a) 2 – carbethoxy cyclopentan – 1 – one
(b) ethyl – 2 – oxo cyclopentanoate
(c) carbethoxy cyclopentanone
(d) None of these

30. The accepted IUPAC name of the camphor is



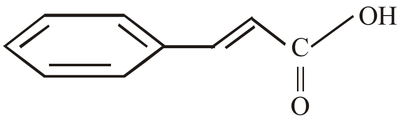
(a) 1, 7, 7 – trimethyl bicyclo [2. 2. 1] heptan – 2 – one
(b) 1, 7, 7, – trimethyl bicyclo [2. 1. 2] heptan – 2 – one
(c) 1, 2, 2 – trimethyl bicyclo [2. 2. 1] heptan – 6 – one
(d) None of these

31. The IUPAC name of



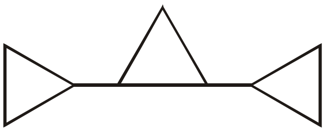
(a) o, o’ – diamino – o, o’ – dicarboxy biphenyl
(b) 6, 6’ – diamino diphenyl – 2, 2’ – dicarboxylic acid
(c) diamino dicarboxy biphenyl
(d) None of these

32. The IUPAC name of



(a) 3 – phenyl prop – 2 – enoic acid
(b) Cinnamic acid
(c) 1 – Styrene acid
(d) 3 – Cyclohexyl – 2 – propenoic acid

33. The correct IUPAC name of

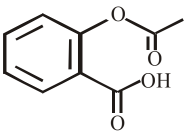


(a) tri cyclopropane
(b) 1, 1’, 2’, 1” – tercyclopropane
(c) tricyclopropyl propane
(d) 1, 1’, 2, 2’ – tercyclo butane

34. IUPAC name of

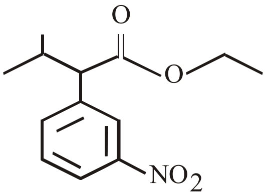
(a) spiro [4, 5] decane	(b) spiro [3, 5] nonone
(c) bicyclopentyl hexane	(d) bicyclo [5, 4, 0] decane

35. Aspirin has the structure . It IUPAC name is



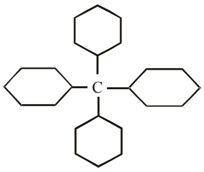
(a) Carbomethoxy benzoic acid
(b) Methyl – 2 – carboxy benzoate
(c) 2 – carboxy phenyl ethanoate
(d) O – carboxy phenyl acetate

36. IUPAC name of the compound



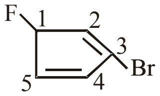
(a) ethyl-3-methyl-2-(3-nitro) phenyl butanoate
(b) ethyl-2-methyl-2-(m-nitro) phenyl propanoate
(c) ethyl-2-methyl-2-(3-nitro) phenyl propanoic acid
(d) None of these

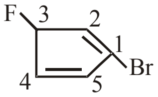
37. The IUPAC name of the compound

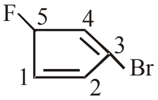


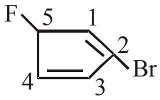
(a) Tetraphenyl methane
(b) 1, 1, 1, 1 – tetra phenyl methane
(c) 1, 1, 1, 1 – tetra cyclohexyl methane
(d) Neophenyl

38. Which of the following numberings is correct ?

A


B


C


D


(a) A (b) B (c) C (d) D

Hints & Solutions

EXERCISE 1

1. 1-Methoxypropane, $CH_3OCH_2CH_2CH_3$ or 2-methoxypropane, $CH_3\text{-}OCH(CH_3)_2$.

2. (i) –CHO (II) $-NO_2$

3. The primary suffix indicates whether the carbon chain is saturated or unsaturated while the secondary suffix indicates the functional group present in the molecule.

4. 3–Methylbut–l–ene.

5. 2-Bromo-4-methylpentan-3-one.

6. 2, 4-dimethyl-5-oxopentanoic acid.

10. (i) 3-Ethyl-4-methylheptan-5-en-2-one

(ii) 3-Nitrocyclohex-1-ene.

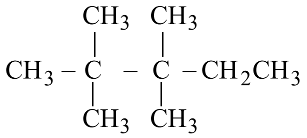
13. (b) **14.** (b) **15.** (d) **16.** (b) **17.** **(c)**

18. **(a)** **19.** **(a)** **20.** **(c)** **21.** **(a)** **22.** **(c)**

EXERCISE 2

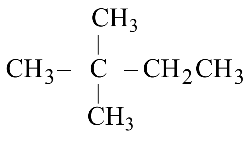
1. **(a)** CaH_2 is formed by the donation of two electrons from Ca atom (having two electrons in the outermost shell) to two H atoms (each having one electron in the outermost shell).

2. **(d)**



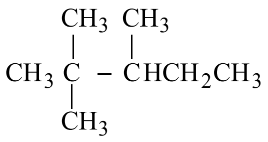
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_2CH_3$

(a)



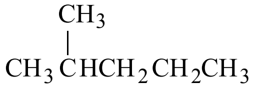
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2CH_3$

(b)



$CH_3\underset{CH_3}{\overset{CH_3}{C}}-\overset{CH_3}{C}HCH_2CH_3$

(c)



$CH_3\overset{CH_3}{C}HCH_2CH_2CH_3$

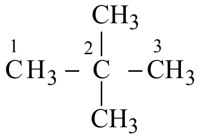
(d)

3. **(d)** In isopentane, $(CH_3)_2CH\,CH_2\,CH_3$, every carbon is having hydrogen atom(s).

4. **(b)** When the sum of locants is same, viz. 2 + 3 = 5, lower alkyl group should be given lower numeral number, i.e., here it should be 2-methyl and 3-ethyl and not the reverse.

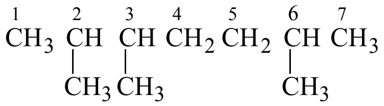
Further, in writing the IUPAC name, prefix should be arranged in the alphabetic order, i.e., 3-ethyl should be written first followed by 2-methyl.

5. **(c)** In such questions, first draw the structure of the molecule and then name the molecule observing the required rules for IUPAC nomenclature.



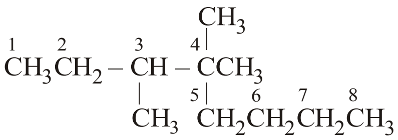
$\overset{1}{C}H_3-\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{3}{C}H_3$

6. **(b)**



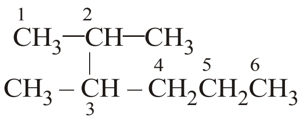
$\overset{1}{C}H_3\,\underset{CH_3}{\overset{2}{C}H}\,\underset{CH_3}{\overset{3}{C}H}\,\overset{4}{C}H_2\,\overset{5}{C}H_2\,\underset{CH_3}{\overset{6}{C}H}\,\overset{7}{C}H_3$

7. **(b)**



$\overset{1}{C}H_3\overset{2}{C}H_2-\underset{CH_3}{\overset{3}{C}H}-\underset{\overset{5}{C}H_2\overset{6}{C}H_2\overset{7}{C}H_2\overset{8}{C}H_3}{\overset{CH_3}{\overset{4}{C}}}CH_3$

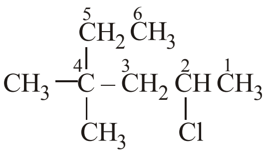
8. **(b)**



$\begin{array}{l}\overset{1}{C}H_3-\overset{2}{C}H-CH_3\\ \quad\;\;|\\ CH_3-\underset{3}{C}H-\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3\end{array}$

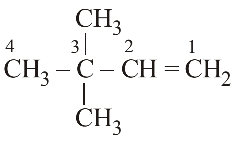
9. **(a)**

10. **(d)**



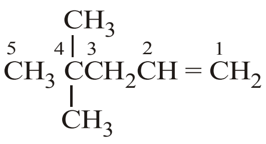
$CH_3-\underset{CH_3}{\overset{\overset{5}{C}H_2\overset{6}{C}H_3}{\overset{4}{C}}}-\overset{3}{C}H_2\,\underset{Cl}{\overset{2}{C}H}\,\overset{1}{C}H_3$

11. **(c)**



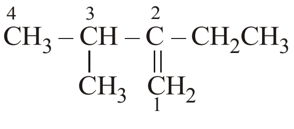
$\overset{4}{C}H_3-\underset{CH_3}{\overset{CH_3}{\overset{3}{C}}}-\overset{2}{C}H=\overset{1}{C}H_2$

12. **(b)**



$\overset{5}{C}H_3\,\underset{CH_3}{\overset{CH_3}{\overset{4}{C}}}\overset{3}{C}H_2\overset{2}{C}H=\overset{1}{C}H_2$

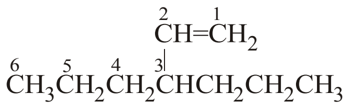
13. **(a)**



$\overset{4}{C}H_3-\underset{CH_3}{\overset{3}{C}H}-\underset{\underset{1}{C}H_2}{\overset{2}{C}}-CH_2CH_3$

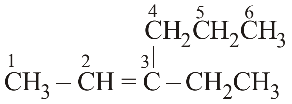
Here numbering should be done in a way that simpler alkyl group(s) is (are) present on the main chain

14. (b)



$$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{\overset{2}{C}H=\overset{1}{C}H_2}{\overset{3}{C}H}CH_2CH_2CH_3$$

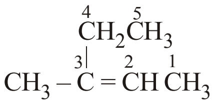
15. (c)



$$\overset{1}{C}H_3-\overset{2}{C}H=\overset{\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3}{\overset{3}{C}}-CH_2CH_3$$

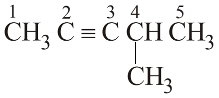
Double bond should be present on the minimum possible number in the lengthiest possible carbon chain.

16. (c)



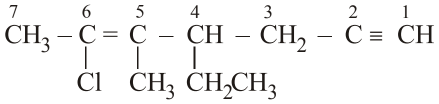
$$CH_3-\overset{\overset{4}{C}H_2\overset{5}{C}H_3}{\overset{3}{C}}=\overset{2}{C}H\overset{1}{C}H_3$$

17. (a)



$$\overset{1}{C}H_3\overset{2}{C}\equiv\overset{3}{C}\underset{CH_3}{\overset{4}{C}H}\overset{5}{C}H_3$$

18. (a)



$$\overset{7}{C}H_3-\underset{Cl}{\overset{6}{C}}=\underset{CH_3}{\overset{5}{C}}-\underset{CH_2CH_3}{\overset{4}{C}H}-\overset{3}{C}H_2-\overset{2}{C}\equiv\overset{1}{C}H$$

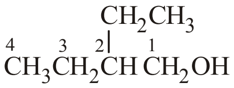
Remember a triple bond gets priority over the double bond, hence it is principal functional group here, thus suffix should be **–yne** and not **–ene**

19. (c)

20. (c) $\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H_2Cl$

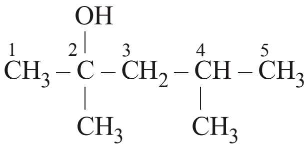
21. (a) Since **b** (from bromo) comes earlier in alphabetical order than **c** (from chloro), the correct name should be 2, 3-dibromo-1, 4-dichlorobutene-2 and not 1,4-dichloro-2, 3-dibromobutene-2.

22. (a)



$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{CH_2CH_3}{\overset{2}{C}H}\overset{1}{C}H_2OH$$

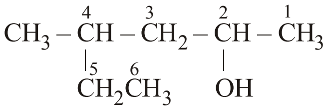
23. (a)



$$\overset{1}{C}H_3-\underset{CH_3}{\overset{OH}{\overset{2}{C}}}-\overset{3}{C}H_2-\underset{CH_3}{\overset{4}{C}H}-\overset{5}{C}H_3$$

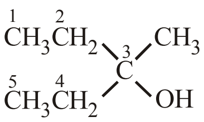
Select the lengthiest possible chain having functional (–OH) group.

24. (c)



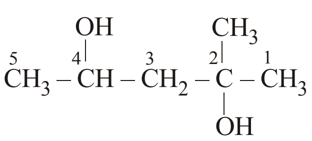
$$CH_3-\underset{\overset{5}{C}H_2\overset{6}{C}H_3}{\overset{4}{C}H}-\overset{3}{C}H_2-\underset{OH}{\overset{2}{C}H}-\overset{1}{C}H_3$$

25. (b)



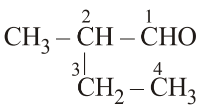
26. (a)

27. (c)



$$\overset{5}{C}H_3-\overset{OH}{\overset{4}{C}H}-\overset{3}{C}H_2-\underset{OH}{\overset{CH_3}{\overset{2}{C}}}-\overset{1}{C}H_3$$

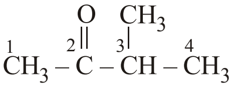
28. (b)



$$CH_3-\underset{\overset{3}{C}H_2-\overset{4}{C}H_3}{\overset{2}{C}H}-\overset{1}{C}HO$$

29. (a)

30. (a)



$$\overset{1}{C}H_3-\overset{\overset{O}{\|}}{\overset{2}{C}}-\overset{CH_3}{\overset{3}{C}H}-\overset{4}{C}H_3$$

3-Methyl-2-butanone

31. (c) **32. (c)**

33. (d) $\overset{3}{C}H_2=\overset{2}{C}H-\overset{1}{C}N$

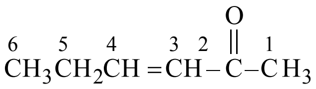
Nitrile carbon is also counted in the carbon chain

34. (a) **35. (a)**

36. (b) $\overset{4}{C}H_3-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}OOC_2H_5$

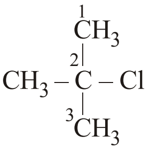
37. (d)

38. (d)



$$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H=\overset{3}{C}H-\overset{\overset{O}{\|}}{\overset{2}{C}}-\overset{1}{C}H_3$$

39. (d) *tert* - Butyl chloride is

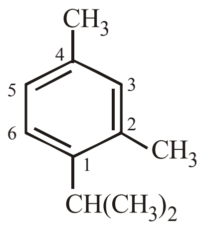


$$CH_3-\underset{\overset{3}{C}H_3}{\overset{\overset{1}{C}H_3}{\overset{2}{C}}}-Cl$$

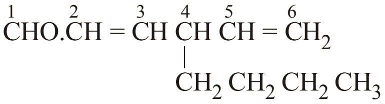
40. (a) $\overset{3}{C}H_2=\overset{2}{C}H-\overset{1}{C}HO$ (acraldehyde)

41. (a) Carbinol is methyl alcohol (CH_3OH), hence vinylcarbinol should be $\overset{3}{C}H_2=\overset{2}{C}H\overset{1}{C}H_2OH$ (prop-2-enol)

42. (a) 4 - Isopropyl -*m*-xylene



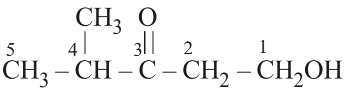
43. (b)



$$\overset{1}{C}HO.\overset{2}{C}H=\overset{3}{C}H\underset{CH_2CH_2CH_2CH_3}{\overset{4}{C}H}\overset{5}{C}H=\overset{6}{C}H_2$$

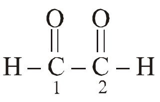
Carbon chain should include all functional groups, although it may be smaller in length, –CHO should be given lowest number.

44. (a)



$$\overset{5}{C}H_3-\overset{CH_3}{\overset{4}{C}H}-\overset{\overset{O}{\|}}{\overset{3}{C}}-\overset{2}{C}H_2-\overset{1}{C}H_2OH$$

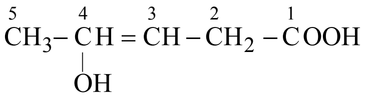
45. (d)



$$H-\underset{1}{\overset{\overset{O}{\|}}{C}}-\underset{2}{\overset{\overset{O}{\|}}{C}}-H$$

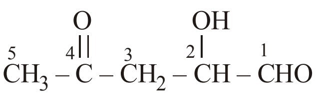
46. (a)

47. (b)



$$\overset{5}{C}H_3-\underset{OH}{\overset{4}{C}H}=\overset{3}{C}H-\overset{2}{C}H_2-\overset{1}{C}OOH$$

48. (c)

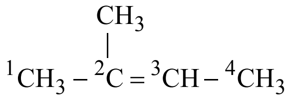


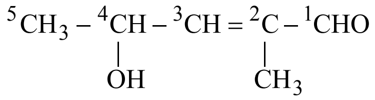
$$\overset{5}{C}H_3-\overset{\overset{O}{\|}}{\overset{4}{C}}-\overset{3}{C}H_2-\overset{OH}{\overset{2}{C}H}-\overset{1}{C}HO$$

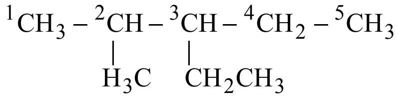
– CHO gets priority over – CO

49. (a) **50. (d)** **51. (a)** **52. (d)** **53. (c)**

EXERCISE 3

1. **(b)** 
$$^{1}CH_3-{}^{2}\overset{\overset{CH_3}{|}}{C}={}^{3}CH-{}^{4}CH_3$$
2-Methyl-2-butene

2. **(b)** 
$$^{5}CH_3-{}^{4}\underset{\underset{OH}{|}}{CH}-{}^{3}CH={}^{2}\underset{\underset{CH_3}{|}}{C}-{}^{1}CHO$$
4-Hydroxy-2-methylpent-2-en-1-al

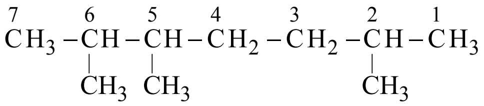
3. **(b)** 
$$^{1}CH_3-{}^{2}\underset{\underset{H_3C}{|}}{CH}-{}^{3}\underset{\underset{CH_2CH_3}{|}}{CH}-{}^{4}CH_2-{}^{5}CH_3$$
3-Ethyl-2-methylpentane

4. **(c)** The vital force theory suffered first death blow in 1828 when Wohler synthesized the Ist organic compound urea in the laboratory from inorganic compounds reported below :

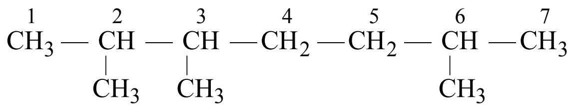
$$NH_4CNO \xrightarrow[\text{rearrangement leading}]{\text{to isomeric charge}} \underset{\text{Urea}}{NH_2CONH_2}$$

Later on a further blow to vital force theory was given by Kolbe (1845) who prepared acetic acid, the first organic compound, in laboratory from its elements.

5. **(b)** When many substituents are present, the numbering is done from the end where the sum of locants is the lowest (lowest sum rule)

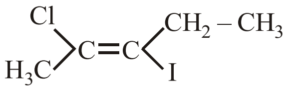

$$\overset{7}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{6}{CH}}-\underset{\underset{CH_3}{|}}{\overset{5}{CH}}-\overset{4}{CH_2}-\overset{3}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$$

2, 5, 6 trimethyl heptane (wrong)
$2+5+6=13$


$$\overset{1}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\underset{\underset{CH_3}{|}}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{6}{CH}}-\overset{7}{CH_3}$$

$2+3+6=11$

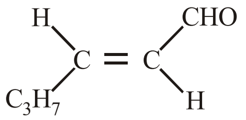
2, 3, 6 TriMethyl Heptane (correct)

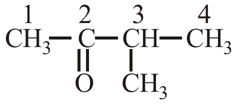
6. **(c)** 

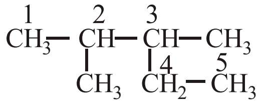
As in this compound the common groups i.e highly electronegative halogen atoms are on opposite side, hence it is a trans isomer.

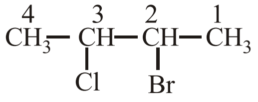
Thus its name is trans-2-chloro-3-iodo-2-pentene.

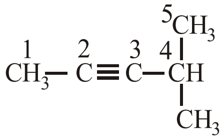
7. **(a)** When similar atoms are on opposite side the compound is in *trans*-form

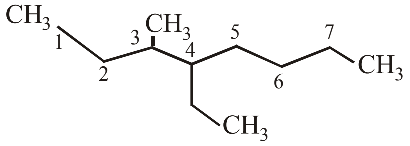


8. **(a)** 
$$\overset{1}{CH_3}-\underset{\underset{O}{\|}}{\overset{2}{C}}-\underset{\underset{CH_3}{|}}{\overset{3}{CH}}-\overset{4}{CH_3}$$
3 Methyl-2- butanone


$$\overset{1}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\underset{\underset{\overset{4}{C}H_2-\overset{5}{C}H_3}{|}}{\overset{3}{CH}}-CH_3$$
2,3dimethyl pentane

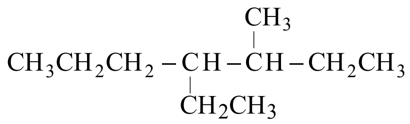

$$\overset{4}{CH_3}-\underset{\underset{Cl}{|}}{\overset{3}{CH}}-\underset{\underset{Br}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$$
2 Bromo 3 chlorobutane


$$\overset{1}{CH_3}-\overset{2}{C}\equiv\overset{3}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{^{5}CH_3}{|}}{\overset{4}{CH}}}$$
4 - Methyl-2-pentyne

9. **(b)** 

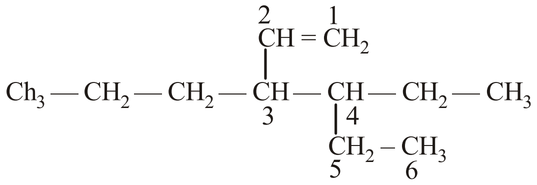
4 ethyl - 3 methyl octane

10. **(a)** Correct IUPAC name of

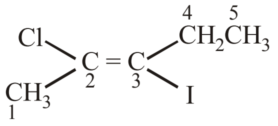

$$CH_3CH_2CH_2-\underset{\underset{CH_2CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_2CH_3$$

is 4-Ethyl-3–methyl heptane

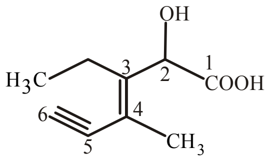
11. **(a)** The given compound is


$$Ch_3-CH_2-CH_2-\underset{3}{\overset{\overset{\overset{2}{C}H=\overset{1}{C}H_2}{|}}{CH}}-\underset{\underset{\underset{5\ \ 6}{CH_2-CH_3}}{|4}}{CH}-CH_2-CH_3$$

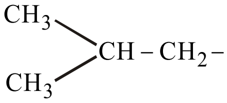
4 ethyl- 3-propyl hex – 1 – ene

12. **(a)** 

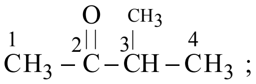
Correct IUPAC name of above compound is trans-2-chloro-3-iodo-2-pentene

13. **(a)** 

IUPAC name of the structure is 3-ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid

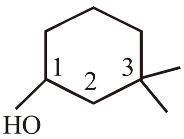
14. (d)  (iso-butyl group)

15. (c) The correct name is 3 - methylbutan 2-ol

16. (c)  ; 3- methyl-2-butanone

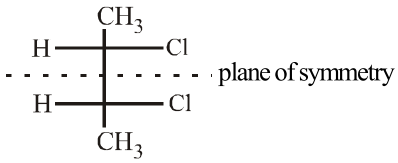
$\overset{1}{CH_3}-\overset{\overset{O}{||}}{\overset{2}{C}}-\overset{\overset{CH_3}{|}}{\overset{3}{CH}}-\overset{4}{CH_3}$

17. (a) $C_nH_{2n}O_2$ is general formula for carboxylic acid

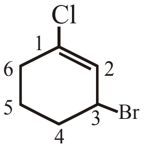
18. (a) 

IUPAC name – 3, 3-Dimethyl -1 cyclohexanol

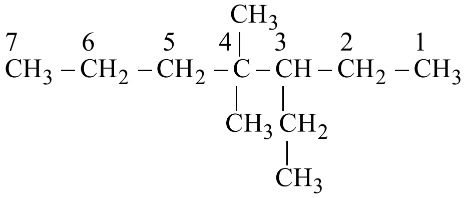
19. (b) The compounds containing two similar assymmetric C-atoms have plane of symmetry and exist in meso from



meso 2, 3 dichlorobutane

20. (a) 

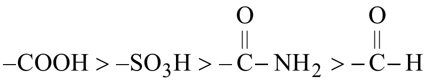
3-bromo-1chlorocyclohexene

21. (a) 

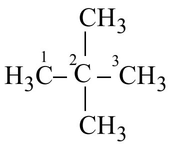
$\overset{7}{CH_3}-\overset{6}{CH_2}-\overset{5}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{4}{C}}}-\underset{\underset{\underset{CH_3}{|}}{CH_2}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$

3–ethyl –4,4–dimethylheptane

22. (a) The correct order of priority for the given functional group is



$-COOH > -SO_3H > -\overset{\overset{O}{||}}{C}-NH_2 > -\overset{\overset{O}{||}}{C}-H$

23. (a) 

$H_3\overset{1}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}-\overset{3}{C}H_3$

Neopentane
or 2,2- Dimethylpropane

24. (b) – CN has highest priority. Further the sum of locants is 7 in (b) and 9 in (d).

EXERCISE 4

1. (b) The compound contains longest chain of 5C - atoms and e of ene is retained as the suffix name starts with constant

2. (d) The compound is an enol containing chain of 5C atoms.

3. (b) The compound is a derivative of butane

4. (b) It contains longest chain of three C atoms having CHO and double bond

5. (d) The compound contains longest chain of 5 C - atoms having $> C = O$ and - NH_2 groups

6. (d) The compound contains longest chain of 3 C - atoms and three -COOH groups and one -OH group attached to it (latest convention).

7. (b) The compound contains longest chain of 6C atoms and amino group. Hence it is an alkanamine.

8. (c) The compound is derivative of aniline. The positions of groups are shown by numbering the nuclear C-atoms.

9. (d) The compound is an ester. Its IUPAC name is derived from alkyl alkanoate.

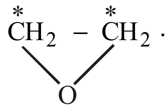
10. (a) Select the longest chain of C-atoms which includes both the double bonds. Further ethenyl and methyl groups at C_3 and C_4 are on the same side. Hence it is Z-isomer.

11. (a) It contains chain of 4C atoms. Double bond is given preference over Cl-atom.

12. (b) The compound is a ketone containing longest chain of 7C-atoms and side chains.

13. (d) The compound is an aldehyde containing longest chain of 6 C-atoms and side chains.

14. (b) The compound is a derivative of benzaldehyde. Start numbering C-atoms of benzene nucleus from C-atom bearing – CHO group.

15. (c) The compound is derivative of oxyrane 

The hydrogen atoms attached to $\overset{*}{C}$–atom are on the opposite side hence it is trans isomer.

16. (b) When acyclic portion contains a multiple bond or functional group, the cyclic portion is treated as substituent.

17. (a) It is derivative of ethanamide having N-phenyl group.

18. (b) The compound is an ethyl ester of hexanoic acid.

19. (a) The compound is a derivative of butanoic acid.

20. (b) The compound is a derivative of benzoic acid. The positions of substituents attached to benzene nucleus are represented by number of C-atoms and not by ortho, meta and para.

21. (c) The cyclic portion contains more C-atoms than acyclic portion. Hence it is derivative of cyclopentane.

22. (b) The compound is anhydride of butanoic and propanoic acid.

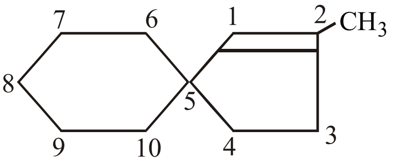
23. (a) It is derivative of cyclohexane. The C-atom bearing – COOH group is to be assigned the number 1.

24. (c) The compound is an aldehyde containing longest chain of 8 C-atoms.

25. (a) The compound is an amide containing longest chain of 5 C-atoms – CHO is substituent group.

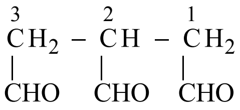
26. (d) The compound is derivative of ethane.

27. (b) It is spiro compound. The numbering begins with the ring atom next to the spiro atom around the smaller ring and then to the spiro atom and finally around the large ring. The total number of C-atoms decides the parent hydrocarbon.



Hence it is 2-methyl spiro[4.5] deca-1-ene.

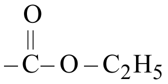
28. (b) When – CHO is treated as side chain, its name is carbaldehyde.



$$\underset{CHO}{\overset{3}{C}H_2} - \underset{CHO}{\overset{2}{C}H} - \underset{CHO}{\overset{1}{C}H_2}$$

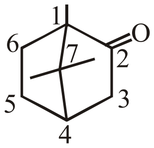
Hence the above is propane – 1, 2, 3 tri carbaldehyde.

29. (a) It is derivative of cyclopentanone having



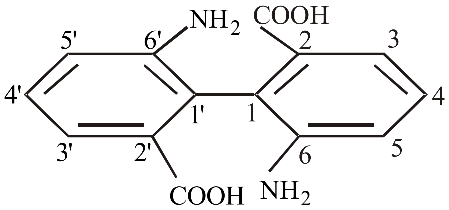
$-\overset{O}{\overset{\|}{C}}-O-C_2H_5$ carbethoxy group at 2C.

30. (a) It is a bridge compound

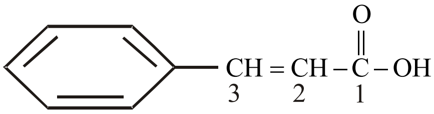


1, 7, 7-trimethyl bicyclo [2. 2. 1] heptan-2-one

31. (b) It is biphenyl derivative

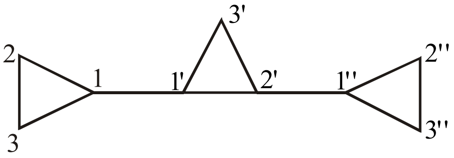


32. (a) It is derivative of propanoic acid



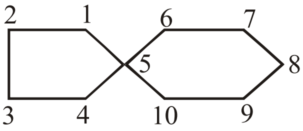
3-phenyl prop-2-enoic acid

33. (b) In such compounds the numbering is done as follows



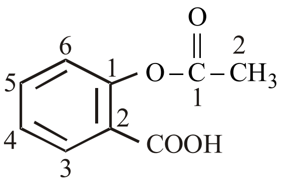
1, 1', 2', 1'' tercyclopropane

34. (a)



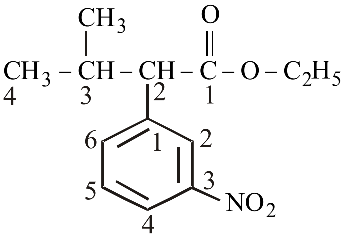
spiro [4.5] decane

35. (c) It is an ester of ethanoic acid



2-carboxy phenyl ethanoate

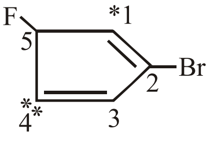
36. (a) It is an ethyl ester of butanoic acid



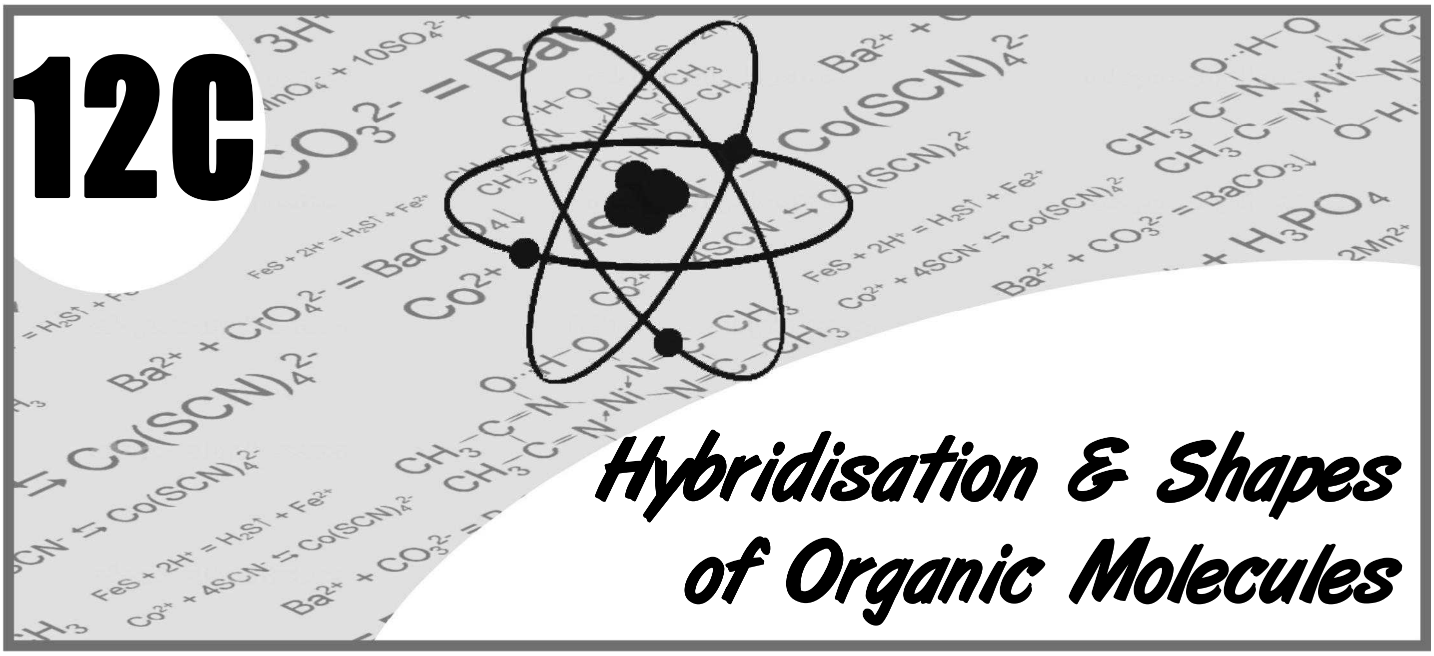
ethyl-3-methyl-2-(3-nitro) phenyl butanoate

37. (c) It is derivative of methane 1, 1, 1, 1-tetracyclohexyl methane.

38. (d)



The numbering of C-atom starts from $\overset{*}{C}$ or $\overset{**}{C}$. But numbering from $\overset{*}{C}$ give minimum locant (2) to Br which is correct.



12C

Hybridisation & Shapes of Organic Molecules

HYBRIDISATION

Sigma bonds are the most common bonds in organic chemistry. All single bonds are sigma (σ) bonds and formed by the overlapping between s-s, s-p and p-p (head on) atomic orbitals present on different atoms. A pi (π) bond results from the overlap of two p-orbitals that are oriented perpendicular to the axis of the nuclei. A π bond is not cylindrically symmetrical. A σ bond is stronger than π bond due to better overlap. All multiple bonds contain one σ bond and others π bond(s).

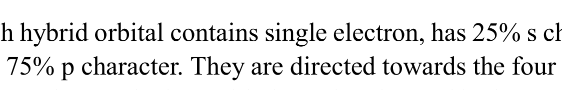
To have more efficient overlapping and to provide more symmetrical structure to the molecule the atomic orbitals on the same atom interact to provide **hybrid** atomic orbitals and the interaction is known as **hybridisation**. The hybrid atomic orbitals have enhanced electron density.

HYBRIDISATION OF CARBON

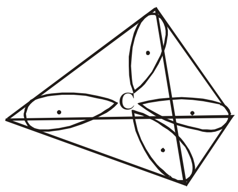
The ground state electronic configuration of carbon is $1s^2, 2s^2 2p_x^1 2p_y^1 2p_z^0$. The electronic configuration of carbon in excited state is $1s^2, 2s^1 2p_x^1 2p_y^1 2p_z^1$.

sp^3 hybridisation:

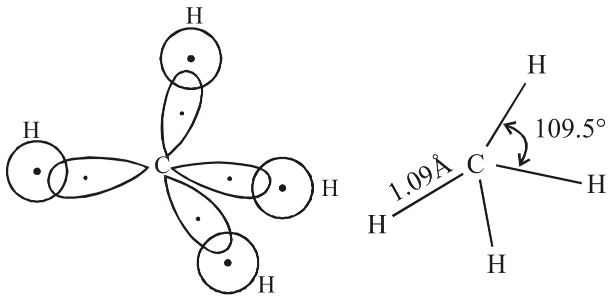
If we superimpose one s and three p atomic orbitals we get 4sp^3 hybrid orbitals.



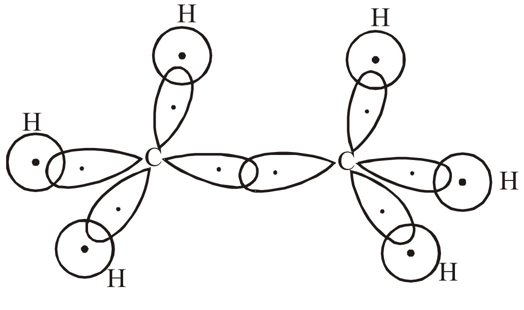
Each hybrid orbital contains single electron, has 25% s character and 75% p character. They are directed towards the four corners of a regular tetrahedron with the carbon located in the centre. The angle between any two *sp*^{3} hybrid orbitals is 109º 28' (109.5º).



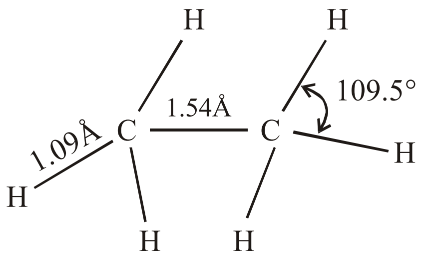
These hybrid orbitals can overlap with four s atomic orbitals provided by four hydrogen atoms to form methane molecule.



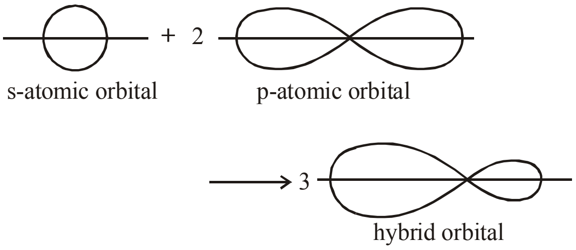
Bonding in Methane



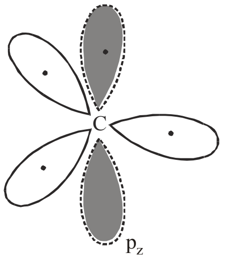
Bonding in Ethane



sp^2 hybridisation: If we superimpose one *s* and two *p* atomic orbitals we get $3sp^2$ hybrid orbitals

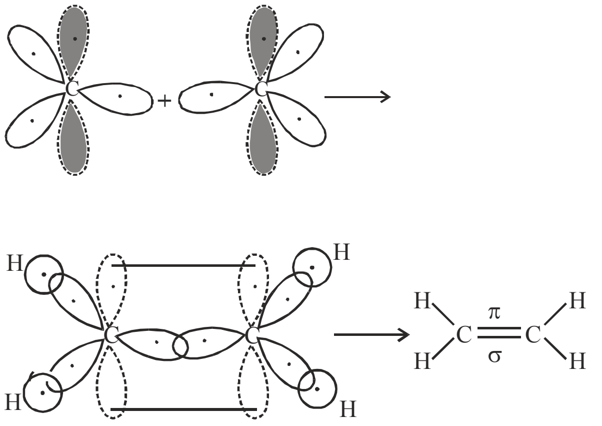


Each sp^2 hybrid orbital has 33% s character and 67% p character. They lie in the same plane with their axis directed towards the corner of an equilateral triangle and are 120º apart from each other. The unhybridised p_z atomic orbital is perpendicular to the plane of sp^2 hybrid orbitals.



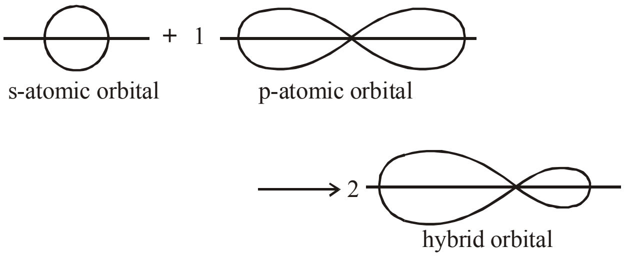
BONDING IN ETHYLENE

Consider two sp^2 hybridised carbon atoms approaching to each other and four hydrogen atoms which provide four *s* atomic orbitals

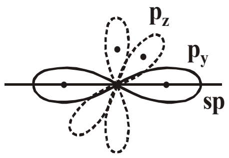


***sp* hybridisation:**

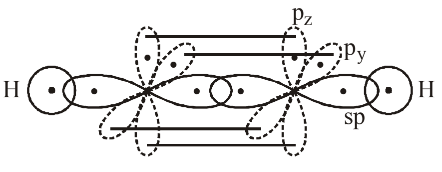
If we superimpose one s and one p atomic orbitals we get 2sp hybrid orbitals.



Each sp hybrid orbital has 50% s character and 50% p character. They are diagonally present with their axis forming an angle of 180º. The unhybridised $2p_y$ and $2p_z$ atomic orbitals are perpendicular to each other and perpendicular to hybrid orbitals also.



BONDING IN ACETYLENE



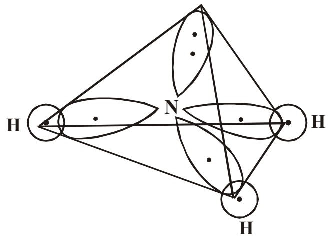
$H—C \equiv C—H$

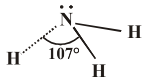
HYBRIDISATION OF NITROGEN

The ground state electronic configuration of nitrogen is

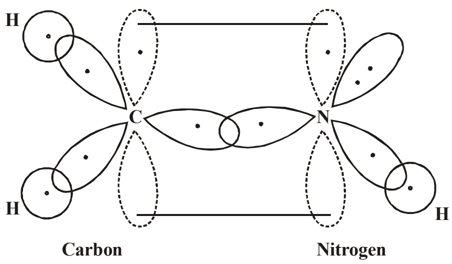
$$_7N = 1s^2, 2s^2 2p_x^1\ 2p_y^1\ p_z^1$$

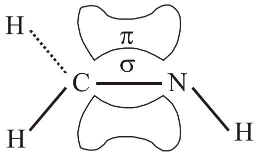
One s and three p atomic orbitals superimpose and give 4 sp^3 hybrid orbitals. These are tetrahedrally present.



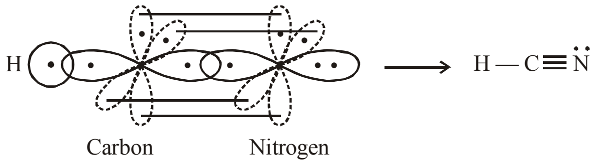


***sp^2* hybridisation:** when nitrogen attaches itself to two other atoms it is present in the sp^2 hybridised form. Consider the formation of methylimine $CH_2 = NH$ in which carbon and nitrogen both are in sp^2 hybrid state





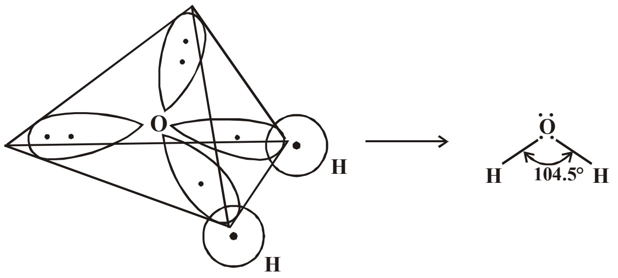
***sp* hybridisation:** when nitrogen is attached to only one atom its hybridisation is sp. In $H-C\equiv N$ both carbon and nitrogen are in sp hybridised form



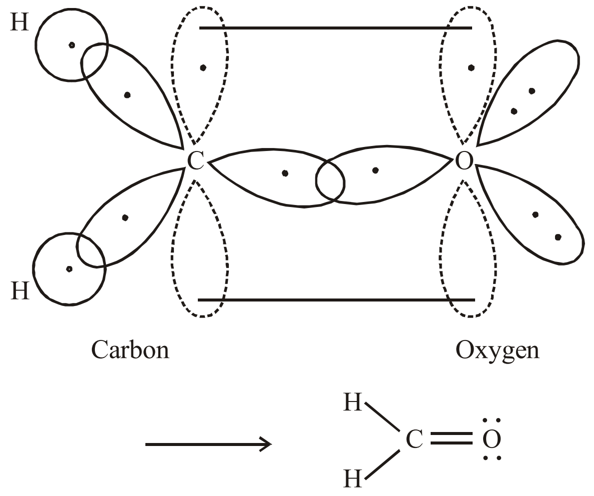
HYBRIDISATION OF OXYGEN

The electronic configuration of oxygen is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$.

sp^3 hybridisation : When oxygen is attached to two atoms the hybridisation is sp^3.



sp^2 hybridisation: When oxygen is attached to one atom as in case of aldehydes and ketones e.g. in Formaldehyde carbon and oxygen, both are in sp^2 hybrid form.

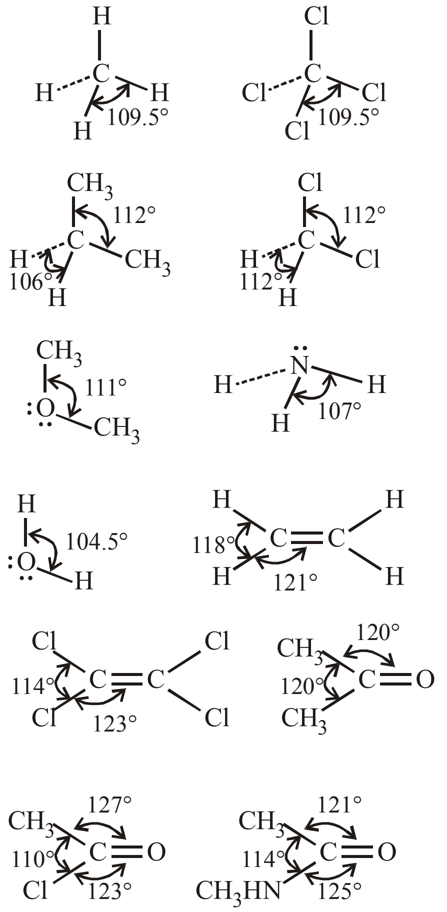


BOND LENGTHS

Some importants bond lengths are as follows

C–C	sp^3-sp^3	1.54 Å	C–O	sp^3-O	1.41 Å
	sp^3-sp^2	1.50 Å		sp^2-O	1.34 Å
	sp^3-sp	1.46 Å	C=O	sp^2-O	1.20 Å
	sp^2-sp^2	1.48 Å		$sp-O$	1.16 Å
	sp^2-sp	1.43 Å	C–N	sp^3-N	1.47 Å
	$sp-sp$	1.38 Å		sp^2-N	1.36 Å
C=C	sp^2-sp^2	1.34 Å	C=N	sp^2-N	1.28 Å
	sp^2-sp	1.31 Å	C≡N	$sp-N$	1.16 Å
	$sp-sp$	1.28 Å			
C≡C	$sp-sp$	1.21 Å			
C–H	sp^3-H	1.11 Å			
	sp^2-H	1.10 Å			
	$sp-H$	1.08 Å			

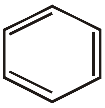
BOND ANGLES IN SELECTED MOLECULES

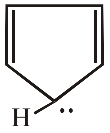


AROMATICITY AND AROMATIC COMPOUNDS

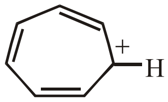
Aromatic indicates a stable system which undergoes substition rather than addition, retaining the closed π-electron system. Many such systems contain only six π electrons, but generally they contain (4n+2) π electrons, where n is an integer.

n = 1


Benzene

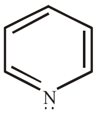


Cyclopentadienyl anion

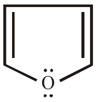


Cycloheptatrienyl cation
(Tropylium cation)

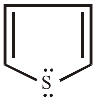
Nonbenzenoid heterocyclic compounds with 6π electrons are aromatics



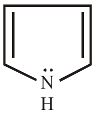
Pyridine



Furan



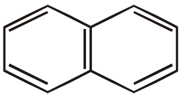
Thiophene

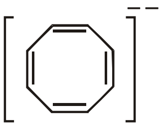


Pyrrole

The hetero atom contributes to non bonded electrons, to complete the sextet.

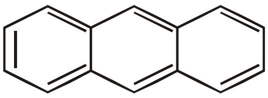
n = 2

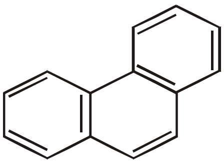

Naphthalene



Cyclo octatetraenyl dianion

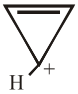
n = 3


Anthracene


Phenanthrene

In general, higher polyclic aromatic compounds are somewhat less stable than benzene.

n = 0 cyclopropenyl cation contains 2π - electrons and is aromatic

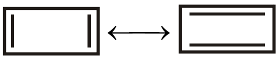


ANTIAROMATICITY

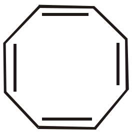
The less stability of monocyclic compounds containing (4n)π electrons than their acyclic analogues is called anti aromaticity. For example

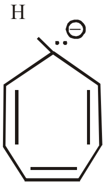
Cyclobutadiene  is less stable than 1,3-Butadiene

Here Resonance is the cause of destabilisation (hence the concept of antiaromaticity)

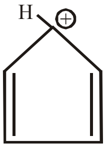


More examples of antiaromatic compounds

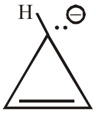

Cyclooctatetraene
(8π electrons)



Cycloheptatrienyl anion
(8π electrons)



Cyclopentadienyl cation
(4π electrons)



Cyclopropenyl anion
(4π electrons)

Exercise-1 | NCERT Based Questions

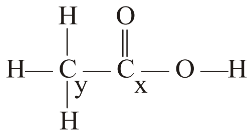
Very Short/ Short Answer Questions

1. Out of ethylene and acetylene which is more acidic and why?

2. Write the type of hybridisation involve in CH_4, C_2H_4 and C_2H_2.

3. What types of hybridisation are involved with the central atom of a molecule having following shapes:
(i) planar, (ii) a regular tetrahedral, (iii) an equilateral triangle.

4. State the hybridisation of the carbon labelled (x) and (*y*) in acetic acid.



$$H-\underset{H}{\overset{H}{\underset{y}{C}}}-\overset{O}{\overset{\|}{\underset{x}{C}}}-O-H$$

5. How hybridization of 'C' atom changes when ethene is hydrogenated?

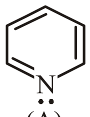
6. Ethane is stable while ethene is quite reactive, explain why?

7. Give hybridisation state of each carbon atom in the following compounds.
(i) $CH_2=C=O$
(ii) $CH_3CH=CH_2$
(iii) $(CH_3)_2CO$
(iv) $CH_3CH_2^-$

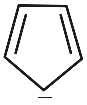
Long Answer Questions

8. The ring systems having following characteristics are aromatic.
(i) Planar ring containing conjugated π bonds.
(ii) Complete delocalisation of the π-electrons in ring system i.e, each atom in the ring has unhybridised p-orbital, and
(iii) Presence of $(4n + 2)$ π-electrons in the ring where *n* is an integer ($n = 0, 1, 2$ ....) [Huckel rule]

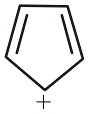
Using this information classify the following compounds as aromatic/non-aromatic.



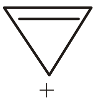
(A)



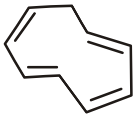
(B)



(C)

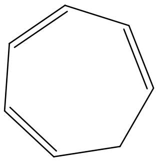


(D)



(E)

9. Will the following compound be aromatic. Explain.



Multiple Choice Questions

10. Butyne-2 contains :
(a) *sp* hybridised carbon atoms only
(b) sp^3 hybridised carbon atoms only
(c) both *sp* and sp^2 hybridised carbon atoms
(d) both *sp* and sp^3 hybridised carbon atoms

11. The correct order towards bond length is
(a) $C-C < C=C < C\equiv C$ (b) $C\equiv C < C=C < C-C$
(c) $C=C < C\equiv C < C-C$ (d) $C=C < C-C < C\equiv C$

12. The C–H bond length is minimum in the bond formed by
(a) *sp-s* overlapping (as in alkynes)
(b) sp^2-*s* overlapping (as in alkenes)
(c) sp^3-*s* overlapping (as in alkanes)
(d) None of these

13. Triple bond of ethyne is made of or Cylindrical shape of an alkyne is due to
(a) Three σ – bonds
(b) Three π – bonds
(c) Two σ and one π – bond
(d) Two π and one σ – bond

14. The hybridization of carbon atom in benzene is:
(a) *sp* (b) sp^2 (c) sp^3 (d) dsp^2

15. The conditions for aromaticity is :
(a) molecule must have cyclic clouds of delocalised π electrons
(b) molecule must contain $(4n + 2)\ \pi$ electrons
(c) Both (a) and (b)
(d) None of the above

16. Which one of the following has the shortest carbon carbon bond length ?
(a) Benzene (b) Ethene (c) Ethyne (d) Ethane

17. Shape of methane molecule is
(a) tetrahedral (b) pyramidal
(c) octahedral (d) square planar

18. Which of the following has the shortest C – C bond length?
(a) C_2H_5OH (b) C_2H_6
(c) C_2H_2 (d) C_2H_4

19. The compound 1, 2 - butadiene has
(a) only *sp* hybridized carbon atoms
(b) only sp^2 hybridized carbon atoms
(c) both *sp* and sp^2 hybridized carbon atoms
(d) *sp*, sp^2 and sp^3 hybridized carbon atoms

20. In the following molecule, the two carbon atoms marked by asterisk (*) possess the following type of hybridized orbitals

$H_3C-C^*\equiv C^*-CH_3$

(a) sp^3 orbital (b) sp^2 orbital
(c) *sp* orbital (d) sp^3 and *sp* respectively

21. In ethene, the bond angle(s) is/ are
(a) 109°28 (b) 120°
(c) 180° (d) Both (a) and (c)

22. Electronegativity of carbon atoms depends upon their state of hybridisation. In which of the following compounds, the carbon marked with asterisk is most electronegative?
(a) $CH_3-CH_2-{}^*CH_2-CH_3$
(b) $CH_3-{}^*CH=CH-CH_3$
(c) $CH_3-CH_2-C\equiv{}^*CH$
(d) $CH_3-CH_2-CH={}^*CH_2$

Exercise-2 | CONCEPTUAL MCQs

1. How many primary carbon atoms are there in $CH_3CH_2CH(CH_3)C(CH_3)_2CH_2CH_2CH_3$?
(a) 3 (b) 4
(c) 5 (d) 6

2. The compound which contains all the four 1°, 2°, 3° and 4° carbon atoms is
(a) 2, 3-dimethylpentane
(b) 3-chloro-2, 3-dimethylpentane
(c) 2, 3, 4-trimethylpentane
(d) 3, 3- dimethylpentane

3. Which of the following statements is not correct?
(a) Double bond is shorter than a single bond
(b) Sigma bond is weaker than a π (pi) bond
(c) Double bond is stronger than a single bond
(d) Covalent bond is stronger than hydrogen bond

4. Which of the following statements is not correct for sigma- and pi- bonds formed between two carbon atoms ?
(a) Bond energies of sigma-and pi-bonds are of the order of 264 kJ/mol and 347 kJ/mol, respectively
(b) Free rotation of atoms about a sigma-bond is allowed but not in case of pi-bonds
(c) Sigma-bond determines the direction between carbon atoms but a pi-bond has no primary effect in this regard
(d) Sigma-bond is stronger than a pi-bond

5. The percentage of s- character of the hybrid orbitals in ethane, ethene and ethyne are respectively.
(a) 50, 75, 100 (b) 10, 20. 40
(c) 25, 33, 50 (d) 25, 50, 75

6. Select the molecule which has only one π-bond
(a) $CH\equiv CH$ (b) $CH_2=CHCHO$
(c) $CH_3CH=CH_2$ (d) $CH_3CH=CHCOOH$

7. 2- Pentene contains
(a) 15 σ- and one π- bond (b) 14 σ-and one π- bond
(c) 15 σ- and two π- bonds (d) 14 σ- and two π- bonds

8. The number of pi-bonds in $CH_2=CH-CH=CH-C\equiv CH$ is
(a) 2 (b) 5
(c) 4 (d) 3

9. Which of the following is not aromatic ?
(a) Benzene (b) Pyridine
(c) Pyrimidine (d) 1, 4- Dioxane

10. Toluene has
(a) 6 σ-and 3 π-bonds (b) 9 σ-and 3 π-bonds
(c) 9 σ-and 6 π-bonds (d) 15 σ-and 3 π-bonds

11. The ratio of π- to σ- bonds in benzene is
(a) 1 : 4 (b) 1 : 2
(c) 3 : 1 (d) 1 : 6

12. Which one is false in the following statements?
(a) Each carbon in ethylene is in sp^2- hybridization
(b) Each carbon in acetylene is in sp-hybridization
(c) Each carbon in benzene is in sp^2-hybridization
(d) Each carbon in ethane is in sp^2 -hybridization

13. The hybridization involved in six carbon atoms of benzene is
(a) three sp^3 and three sp^2 (b) three sp^2 and three sp
(c) all six sp (d) all six sp^2

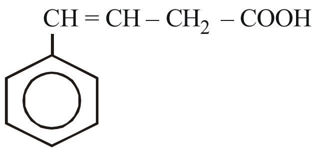
14. In which of the compounds given below there is more than one kind of hybridization (sp, sp^2, sp^3) for carbon ?
(i) $CH_3CH_2CH_2CH_3$ (ii) $CH_3CH=CHCH_3$
(iii) $CH_2=CH-CH=CH_2$ (iv) $H-C\equiv C-H$
(a) (ii) (b) (iii) and (iv)
(c) (i) and (iv) (d) (ii) and (iii)

15. In compound $CH_2 = CH– CH_2– CH_2 – C \equiv CH$, the $C_2 – C_3$ bond is of the type

(a) $sp –sp^2$ (b) $sp^3–sp^3$

(c) $sp –sp^3$ (d) $sp^2–sp^3$

16. The type of hybridizations exhibited by carbons in



are

(a) sp^3 and sp (b) sp^2 only

(c) sp^3 and sp^2 (d) sp^3, sp^2 and sp

17. The hybrid orbitals of carbon atoms numbered 1 and 2 in the compound.

$H_2\overset{1}{C} = \overset{2}{C} = CH_2$ are

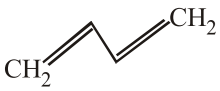
(a) sp only (b) sp and sp^3 respectively

(c) sp^2 and sp^2 respectively (d) sp^2 and sp respectively

18. Which of the following represents the given mode of hybridisation $sp^2–sp^2$ – sp – sp from left to right?

(a) $H_2C = CH – C \equiv N$ (b) $CH \equiv C – C \equiv CH$

(c) $H_2C=C=C=CH_2$ (d)



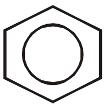
19. In which of the following species, all types of hybrid carbons are present ?

(a) $CH_2 = C = CH_2$ (b) $CH_3–CH=CH–CH_2^+$

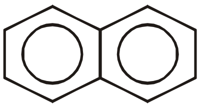
(c) $CH_3–C\equiv C–CH_2^+$ (d) $CH_3–CH=CH–CH_2^-$

20. The chemical system that is non-aromatic is

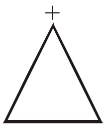
(a)



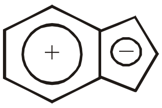
(b)



(c)



(d)



21. The change in the state of hybridization of the asterisked carbon in the following reaction.

$CH_3\overset{*}{C}N \xrightarrow{H_2O} CH_3\overset{*}{C}ONH_2$ is

(a) sp^3 to sp^2 (b) sp^3 to sp

(c) sp to sp^2 (d) sp^2 to sp^3

22. Which of the following carbon atoms is most electronegative?

$\overset{III}{C}H_3 – \overset{II}{C}H_2 – C \equiv \overset{I}{C}H$

(a) I

(b) II

(c) III

(d) All are equally electronegative

23. In benzene, all the six C –C bonds have the same length because of

(a) tautomerism (b) sp^2-hybridization

(c) isomerism (d) inductive effect

24. Bond length between C–C in ethane (I), ethene (II), acetylene (III) and benzene (IV) follows the order:

(a) I > IV > II > III (b) I > II > IV > III

(c) I > II > III > IV (d) III > IV > II > I

25. The bond length between sp^2-hybridized carbon atoms is

(a) 1.20 Å (b) 1.34 Å

(c) 1.54 Å (d) 1.40 Å

26. In which of the following, the bond length between two carbons is equal

(a) 2- Butene (b) Benzene

(c) 1- Butene (d) Propyne

27. The bond length between sp^3 - hybridized carbon and other carbon atom is minimum in

(a) propane (b) propyne

(c) propene (d) butane

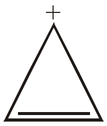
28. Carbon atoms in benzene molecule are inclined at an angle of

(a) 120º (b) 180º

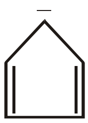
(c) 109º–28 (d) 60º

29. Which of the following compounds is not aromatic?

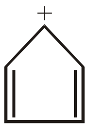
(a)



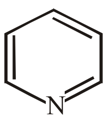
(b)



(c)



(d)



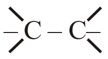
30. As the s - character of hybrid orbital increases, the bond angle

(a) increases (b) decreases

(c) does not change (d) becomes zero

31. Which of the following bonds is strongest ?

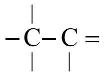
(a)



$>C-C<$

(b) $> C = C <$

(c)



$-\overset{|}{\underset{|}{C}}-\underset{|}{C}=$

(d) $– C \equiv C –$

32. sp^3-hybridization leads to which shape of the molecule ?
(a) Tetrahedral (b) Octahedral
(c) Linear (d) Trigonal planar

33. The cylindrical shape of alkynes is due to
(a) three sigma C – C bonds
(b) three π C – C bonds
(c) two σ C – C and π C – C bonds
(d) one sigma C – C and two π C – C bonds

34. The maximum number of carbon atoms arranged linearly in the molecule,
$CH_3-C\equiv C-CH=CH_2$ is
(a) 5 (b) 4
(c) 3 (d) 2

35. Which of the following is planar in shape ?
(a) Methane (b) Acetylene
(c) Benzene (d) Isobutane

Exercise-3 | PAST COMPETITION MCQs

1. The Cl – C – Cl angle in 1,1,2,2- tetrachloroethene and tetrachloromethane respectively will be about **[CBSE PMT 1988]**
(a) 120° (b) 90° and 109.5°
(c) 109.5° and 90° (d) 120° and 109.5°

2. Which of the following possesses a sp-carbon in its structure? **[CBSE PMT 1989]**
(a) $CH_2=CCl-CH=CH_2$
(b) $CCl_2=CCl_2$
(c) $CH_2=C=CH_2$
(d) $CH_2=CH-CH=CH_2$.

3. Cyclic hydrocarbon 'A' has all the carbon and hydrogen atoms in a single plane. All the carbon carbon bonds have the same length, less than 1.54 Å, but more than 1.34 Å. The C – C – C bond angle will be **[CBSE PMT 1989]**
(a) 109°28' (b) 100°
(c) 180° (d) 120°

4. An organic compound X (molecular formula $C_6H_7O_2N$) has six carbon atoms in a ring system, two double bonds and a nitro group as substituent, X is **[CBSE PMT 1990]**
(a) Homocyclic but not aromatic
(b) Aromatic but not homocyclic
(c) Homocyclic and aromatic
(d) Heterocyclic and aromatic

5. The shortest C – C bond distance is found in
(a) Diamond (b) Ethane **[CBSE PMT 1991]**
(c) Benzene (d) Acetylene

6. An sp^3 hybrid orbital contains **[CBSE PMT 1991]**
(a) 1/4 s-character (b) 1/2 s-character
(c) 1/3 s-character (d) 2/3 s-character.

7. A straight chain hydrocarbon has the molecular formula C_8H_{10}. The hybridization of the carbon atoms from one end of the chain to the other are respectively sp^3, sp^2, sp^2, sp^3, sp^2, sp^2, sp and sp. The structural formula of the hydrocarbon would be : **[CBSE PMT 1991]**
(a) $CH_3C\equiv CCH_2-CH=CHCH=CH_2$
(b) $CH_3CH_2-CH=CHCH=CHC\equiv CH$
(c) $CH_3CH=CHCH_2-C\equiv CCH=CH_2$
(d) $CH_3CH=CHCH_2-CH=CH=C\equiv CH$.

8. When the hybridization state of carbon atom changes from sp^3 to sp^2 and finally to sp, the angle between the hybridized orbitals **[CBSE PMT 1993]**
(a) decreases gradually
(b) decreases considerably
(c) is not affected
(d) increases progressively.

9. The restricted rotation about carbon carbon double bond in 2-butene is due to **[CBSE PMT 1993]**
(a) Overlap of one s- and sp^2 - hybridized orbitals
(b) Overlap of two sp^2 - hybridized orbitals
(c) Overlap of one p- and one sp^2 - hybridized orbitals
(d) Sideways overlap of two p- orbitals.

10. Huckel's rule states that a monocyclic conjugated compound will be aromatic if it contains **[CBSE PMT 1996]**
(a) $(4n+2\pi)$ electrons
(b) $(4\pi+2n)$ electrons
(c) 4π electrons
(d) $(4n+2)\pi$ electrons

11. The structural formula of a compound is $CH_3-CH=C=CH_2$. The types of hybridization at the four carbons from left to right are **[CBSE PMT 1999]**
(a) sp^2, sp^2, sp^2, sp^3 (b) sp^2, sp^3, sp^2, sp^2
(c) sp^3, sp^2, sp, sp^2 (b) sp^3, sp^2, sp^2, sp^2

12. The correct order regarding the electronegativity of hybrid orbitals of carbon is **[CBSE PMT 2006]**
(a) $sp > sp^2 > sp^3$ (b) $sp < sp^2 > sp^3$
(c) $sp < sp^2 < sp^3$ (d) $sp > sp^2 < sp^3$

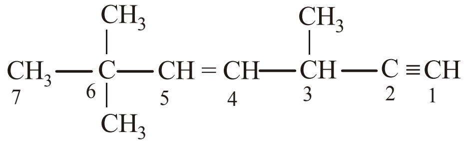
13. In the hydrocarbon

$CH_3 - CH = CH - CH_2 - C \equiv CH$
6 5 4 3 2 1

The state of hybrization of carbons 1, 3 and 5 are in the following sequence : **[CBSE-PMT 2008]**

(a) sp^2, sp, sp^3 (b) sp, sp^3, sp^2
(c) sp, sp^2, sp^3 (d) sp^3, sp^2, sp

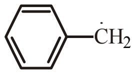
14. The state of hybridization of C_2, C_3, C_5 and C_6 of the hydrocarbon, **[CBSE-PMT 2009]**



$$\underset{7}{CH_3}-\underset{6}{\overset{CH_3}{\underset{CH_3}{C}}}-\underset{5}{CH}=\underset{4}{CH}-\underset{3}{\overset{CH_3}{CH}}-\underset{2}{C}\equiv\underset{1}{CH}$$

is in the following sequence:

(a) sp^3, sp^2, sp^2 and sp (b) sp, sp^2, sp^2 and sp^3
(c) sp, sp^2, sp^3 and sp^2 (d) sp, sp^3, sp^2 and sp^3

15. The radical,  $\dot{C}H_2$ is aromatic because it has : **[NEET 2013]**

(a) 7 p-orbitals and 6 unpaired electrons
(b) 7 p-orbitals and 7 unpaired electrons
(c) 6 p-orbitals and 7 unpaired electrons
(d) 6 p-orbitals and 6 unpaired electrons

16.. In which of the following species is the underlined carbon having sp^3 hybridisation? **[AIEEE 2002]**

(a) $CH_3\underline{C}OOH$ (b) $CH_3\underline{C}H_2OH$
(c) $CH_3\underline{C}OCH_3$ (d) $CH_2=\underline{C}H-CH_3$

17. Which one of the following does not have sp^2 hybridized carbon ? **[AIEEE 2004]**

(a) Acetonitrile (b) Acetic acid
(c) Acetone (d) Acetamide

18. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is (are) : **[IIT-JEE 2012]**

(a) sp and sp^3 (b) sp and sp^2
(c) only sp^3 (d) sp^2 and sp^3

Exercise-4 | Applied MCQs

1. The bond between carbon atom (1) and carbon atom (2) in compound $N \equiv \overset{1}{C} - \overset{2}{C}H = CH_2$ involves the hybridisation

(a) sp^2 and sp^2 respectively (a) sp^3 and sp respectively
(c) sp and sp^2 respectively (d) sp and sp respectively

2. The compound in which $\overset{x}{C}$ uses its sp^3 - hybrid orbitals for bond formation is

(a) $H\overset{X}{C}OOH$ (b) $(H_2N)_2\overset{X}{C}O$
(c) $(CH_3)_3\overset{X}{C}OH$ (d) $CH_3\overset{X}{C}HO$

3. Of the following compounds which will have a zero dipole moment

(a) 1, 1 - dichloroethylene
(b) Trans -1, 2 - dichloroethylene
(c) Cis - 1 , 2 - dichloroethylene
(d) None of these

4. The number of σ - and π - bonds in but- 1 - ene - 3 - yne are

(a) $5\sigma -$ and $5\pi -$ (b) $7\sigma -$ and $3\pi -$
(c) $8\sigma -$ and $2\pi -$ (d) $8\sigma -$ and $4\pi -$

5. The species which use sp^2 - hybrid orbitals in its bonding

(a) PH_3 (b) NH_3
(c) CH_3^+ (d) CH_4

6. Allyl isocyanide has

(a) 9 σ and 4 π - bonds
(b) 8 σ and 5 π - bonds
(c) 9 σ , 3 π and 2 non- bonded electrons
(d) 8 σ , 3 π and 4 non - bonded electrons

7. During elimination reactions, the hybrid state of carbon atoms involved change as shown below:

(a) sp^3 to sp^2 nature
(b) sp^3 to sp nature
(c) No change in hybridised state
(d) Either (a) or (b)

8. In the dehydration reaction,

$CH_3CONH_2 \xrightarrow{P_2O_5} CH_3C \equiv N$,

the hybridisation state of carbon changes from

(a) sp^3 to sp^2 (b) sp to sp
(c) sp^2 to sp (d) sp to sp^3

9. Unpaired electron in $\dot{C}H_3$ occupies

(a) sp - hybrid orbital (b) sp^3 - hybrid orbital
(c) p - orbital (d) sp^2 - hybrid orbital

10. The hybridisation of carbon atom in C - C single bond of $H - C \equiv C - CH = CH_2$ is

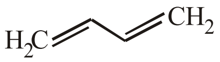
(a) sp^3 - sp^3 (b) sp^2 - sp^2
(c) sp - sp^2 (d) sp^3 - sp

11. Which of the following represents the given mode of hybridisation $sp^2 - sp^2 - sp - sp$ from left to right?

(a) $H_2C = CH - C \equiv CH$

(b) $HC \equiv C - C \equiv CH$

(c) $H_2C = C = C = CH_2$

(d) 

12. The structure of $H_2C = C = CH_2$ is

(a) linear

(b) planar

(c) non-planar

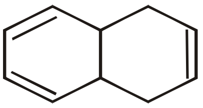
(d) has several resonance structures

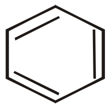
13. Aromatic character of benzene is proved by

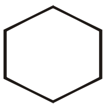
(a) resonance theory (b) aromatic sextet theory

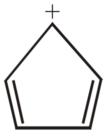
(c) orbital theory (d) All of these

14. Which of the following will show aromatic behaviour ?

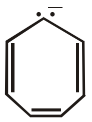
(a) 

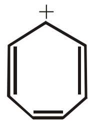
(b) 

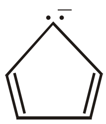
(c) 

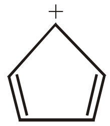
(d) 

15. Which of the following species would be expected to exhibit aromatic character ?

(i) 

(ii) 

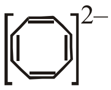
(iii) 

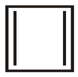
(iv) 

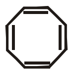
(a) (i) and (iv) (b) (ii) and (iv)

(c) (i) and (iii) (d) (ii) and (iii)

16. Which among the following is aromatic ?


I


II


III


IV


V

(a) I (b) II and V

(c) III (d) IV

17. Which of the following is not aromatic ?

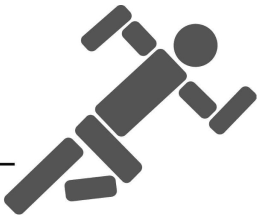
(a) Benzene

(b) Cyclooctatetraenyl dianion

(c) Tropylium ion

(d) Cyclopentadienyl cation

Hints & Solutions



EXERCISE 1

1. Acetylene, due to greater electronegativity of the sp–hybridized carbon.

2. $CH_4 = sp^3$

$C_2H_4 = sp^2$

$C_2H_2 = sp$

3. (i) sp^2, (ii) sp^3, (iii) sp^2.

4. The carbon atom x is sp^2 and carbon atom y is sp^3 hybridised.

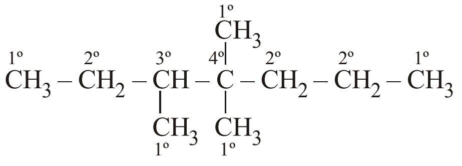
5. Ethene (C_2H_4) has sp^2 hybridized carbon atoms. On hydrogenation, it changes to ethane (C_2H_6) in which carbon atoms are sp^3 hybridized.

10. (d) 11. (b) 12. (a) 13. (d) 14. (b) 15. (c)

16. (c) 17. (a) 18. (c) 19. (d) 20. (c) 21. (b)

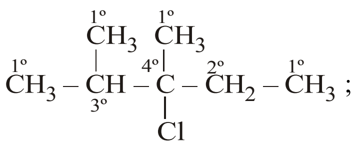
22. (c)

EXERCISE 2

1. (c) 

$$\overset{1^\circ}{CH_3}-\overset{2^\circ}{CH_2}-\underset{\underset{1^\circ}{CH_3}}{\overset{3^\circ}{CH}}-\underset{\underset{1^\circ}{CH_3}}{\overset{\overset{1^\circ}{CH_3}}{\overset{4^\circ}{C}}}-\overset{2^\circ}{CH_2}-\overset{2^\circ}{CH_2}-\overset{1^\circ}{CH_3}\ ;$$

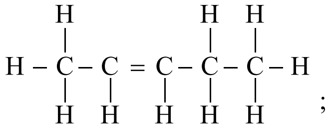
Thus there are five 1° carbon atoms.

2. (b) 

$$\overset{1^\circ}{CH_3}-\underset{3^\circ}{\overset{\overset{1^\circ}{CH_3}}{CH}}-\underset{Cl}{\overset{\overset{1^\circ}{CH_3}}{\overset{4^\circ}{C}}}-\overset{2^\circ}{CH_2}-\overset{1^\circ}{CH_3}\ ;$$

Thus all the four types of carbon atoms are present in this compound.

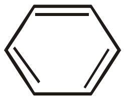
3. (b) 4. (a) 5. (c) 6. (c)

7. (b)  ;

2 – Pentene

No. of σ bonds = 14, No. of π bonds = 1

8. (c) **9. (d)** **10. (d)**

11. (a) 

No. of σ bonds = 12 ; No. of π bonds = 3

∴ Ratio of π : σ bonds = 3 : 12 = 1 : 4

12. (d) **13. (d)**

14. (a) In compounds (i), (iii) and (iv), all carbon atoms are sp^3, sp^2 and sp hybridised, respectivley. However, compound (ii) has sp^2 and sp^3 hybridised carbon atoms;

$$\overset{sp^3}{CH_3}-\overset{sp^2}{CH}=\overset{sp^2}{CH}-\overset{sp^3}{CH_3}$$

15. (d) $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{C}\equiv\overset{6}{CH}$

16. (c) In the compound, all carbon atoms except CH_2 are sp^2 hybridised.

17. (d) $H_2\overset{sp^2}{C}=\overset{sp}{C}=\overset{sp^2}{CH_2}$

18. (a)

19. (c) $\overset{sp^3}{CH_3}-C\equiv\overset{sp}{C}-\overset{sp^2}{CH_2^+}$

Remember that carbocations are sp^2 hybridised.

20. (c) Only species (*c*) is not aromatic.

21. (c) $H_3C-\overset{sp}{C}\equiv N\xrightarrow{H_2O}H_3C-\underset{\underset{O}{\|}}{\overset{sp^2}{C}}-NH_2$

22. (a) Greater the *s* character, more electronegative is the carbon, i.e. *sp* hybridised (having 50% *s* character) carbon having H atom is more electronegative in comparison to C-atom which does not have H atom.

$$_3\overset{sp^3}{C}-\overset{sp^2}{CH_2}-\overset{sp}{C}\equiv\overset{sp}{CH}$$

23. (b)

24. (a) Greater the bond order smaller the bond length.

Molecule	$H_3C–CH_3$ >	C_6H_6 >	$H_2C=CH_2$ >	$HC\equiv CH$
Bond order	1	1.5 (due to resonance)	2	3

25. (b) **26. (b)**

27. (b) (a) $H_3\overset{sp^3}{C}-\overset{sp^3}{CH_2}-\overset{sp^3}{CH_3}$

(b) $\overset{sp^3}{CH_3}-\overset{sp}{C}\equiv\overset{sp}{CH}$

(c) $H_3\overset{sp^3}{C}-\overset{sp^2}{CH}=\overset{sp^2}{CH_2}$

(d) $\overset{sp^3}{CH_3}-\overset{sp^3}{CH_2}-\overset{sp^3}{CH_2}-\overset{sp^3}{CH_3}$

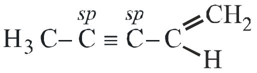
Since *sp* orbital has the smallest size, sp^3 carbon attached to *sp* carbon, i.e., sp^3- *sp* bond should have minimum carbon-carbon single bond length.

28. (a)

29. (c) Species (*a*), (*b*) and (*d*) have 2, 6 and 6 delocalized π electrons in a cyclic structure, hence all these are aromatic. Species (*c*) having 4π electrons is not aromatic

30. (a) **31. (d)** **32. (a)** **33. (d)**

34. (b) The carbon atoms attached to the triple bond lie in a straight line, while the carbon atom of the CH_2 group is inclined at an angle of 120º. Hence, only 4 carbon atoms are arranged in a straight line (linear arrangement).



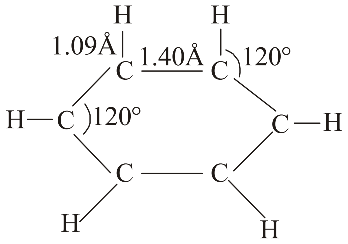
35. (c)

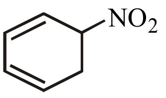
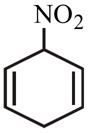
EXERCISE 3

1. (d) Tetrachloroethene being an alkene has sp^2 - hybridized C– atoms and hence the angle Cl – C – Cl is 120° while in tetrachloromethane, carbon is sp^3 hybridized, therefore the angle Cl – C – Cl is 109.5°.

2. (c) $\overset{sp^2}{CH_2}=\overset{sp}{C}=\overset{sp^2}{CH_2}$

3. (d) All the properties mentioned in the question suggest that it is a benzene molecule. Since in benzene all carbons are sp^2–hybridized, therefore, C – C – C angle is 120°



4. (a)  or 

Hence it is homocyclic (as the ring system is made of one type of atoms, i.e. carbon) but not aromatic.As it does not have (4n +2)π electron required for aromaticity.

5. (d) Shortest C – C distance (1.20 Å) is in acetylene.

As acetylene has sp hybridisation, the bond length increases in the order

$$\underset{sp(1.20Å)}{C\equiv C} < \underset{sp^2(1.34Å)}{C=C} < \underset{sp(1.54Å)}{C-C}$$

6. (a) sp^3 orbital has 1/4(25%) s-character. & 75% p character.

7. (d) $\overset{sp^3}{CH_3}\,\overset{sp^2}{CH}=\overset{sp^2}{CH}\,\overset{sp^3}{CH_2}-\overset{sp^2}{CH}-\overset{sp}{C}\equiv\overset{sp}{CH}$

8. (d) Angle increases progressively

sp^3 (109°28'), sp^2 (120°), sp (180°)

9. (d) Rotation around π bond is not possible. If any attempt is made to rotate one of the carbon atoms, the lobes of π-orbital will no longer remain coplanar i.e no parallel overlap will be possible and thus π-bond will break . This is known as concept of restricted rotation. In other words the presence of π-bonds makes the position of two carbon atom.

10. (d) Huckel's rule states that for aromaticity there must be (4n + 2) π electron present in compound where n is an integer

11. (c) $\overset{sp^3}{CH_3}-\overset{sp^2}{CH}=\overset{sp}{C}=\overset{sp^2}{CH_2}$

12. (a) Among the three given hybrid orbitals, sp hybrid orbital is most electronegative. Contribution of s in sp hybrid orbital is maximum (50%) so this orbital is closer to nucleus. Naturally it will have greater tendency to pull electron towards it. Hence it becomes more electronegative and sp^3 becomes least electronegative as it have only 25% S character.

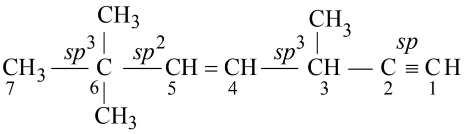
13. (b) C – 1 is *sp* hybridized $(C\equiv C)$

C – 3 is sp^3 hybridized (C– C)

C – 5 is sp^2 hybridized (C = C)

Thus the correct sequence is *sp*, sp^3, sp^2.

14. (d)

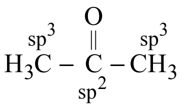


$$\underset{7}{CH_3}\xrightarrow{sp^3}\underset{6}{\overset{CH_3}{\underset{CH_3}{C}}}\xrightarrow{sp^2}\underset{5}{CH}=\underset{4}{CH}\xrightarrow{sp^3}\underset{3}{\overset{CH_3}{CH}}-\underset{2}{\overset{sp}{C}}\equiv\underset{1}{CH}$$

15. (d) Presence of 6*p* orbitals, each containing one unpaired electron, in a six membered cyclic structure is in accordance with Huckel rule of aromaticity.

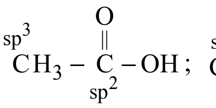
16. (b) In molecules (a), (c) and (d), the carbon atom has a multiple bond, only (b) has sp^3 hybridization.

17. (a)



$$\overset{sp^3}{H_3C}-\underset{sp^2}{\overset{O}{\overset{\|}{C}}}-\overset{sp^3}{CH_3}$$

Acetone

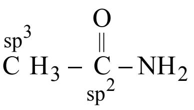


$$;\ \overset{sp^3}{CH_3}-\underset{sp^2}{\overset{O}{\overset{\|}{C}}}-OH;$$

Acetic acid

$\overset{sp^3}{CH_3}-\overset{sp}{C}\equiv N$;

Acetonitrile



$$\overset{sp^3}{C\ H_3}-\underset{sp^2}{\overset{O}{\overset{\|}{C}}}-NH_2$$

Acetamide

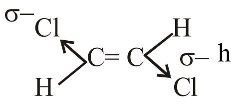
18. (b) Allene (C_3H_4) is $\overset{sp^2}{H_2C}=\overset{sp}{C}=\overset{sp^2}{CH_2}$

EXERCISE 4

1. (c) The C_1 forms 2σ bonds and 2π - bonds (sp-hybridisation) and C_2 forms 3σ bonds and 1π bond (sp^2 hybridisation)

2. (c) See the number of σ bonds formed by $\overset{x}{C}$ in each case. In $H\overset{x}{C}OOH$, $(H_2N)_2\overset{x}{C}O$ and $CH_3\overset{x}{C}HO, \overset{x}{C}$ forms 3σ bonds and 1 π bond, hybridisation is sp^2. In $(CH_3)_3\overset{x}{C}OH$, $\overset{x}{C}$ forms 4σ bonds, hence hybridisation is sp^3

3. (b)



has zero dipole moment

4. (b) $H_2C=CH-C\equiv CH$ has 7σ and 3π

5. (c) $\overset{+}{C}H_3$ is sp^2 hybridised

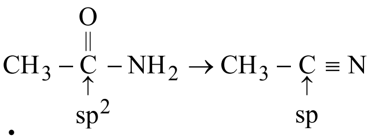
6. (c) Allyl isocyanide has the structure

$H_2C=CH-CH_2-N\overset{\rightarrow}{\equiv}C$

it has 9 σ and 3π bonds along with 2 non- bonded electrons

7. (d) $\underset{sp^3}{CH_3-CHX_2}\rightarrow\underset{sp^2}{CH_2=CHX}\rightarrow\underset{sp}{CH\equiv CH}$

8. (c)



$$CH_3-\underset{\underset{sp^2}{\uparrow}}{\overset{O}{\overset{\|}{C}}}-NH_2\rightarrow CH_3-\underset{\underset{sp}{\uparrow}}{C}\equiv N$$

9. (b) $\dot{C}H_3$ is sp^3 hybridised and unpaired electron is present in sp^3 hybridised orbital

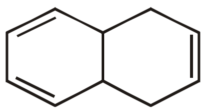
10. (c) Count σ and π bonds to get answer

11. (a) $\xrightarrow[\text{from left to right}]{\overset{sp^2}{H_2C}=\overset{sp^2}{CH}-\overset{sp}{C}\equiv\overset{sp}{CH}}$

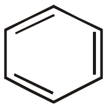
12. (c) The hydrogen atoms on terminal C-atoms lie in perpendicular planes and hence the molecule as a whole is non-planar. $H_2C=C=CH_2$

13. (d)

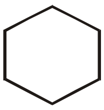
14. (b)



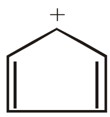
Non-aromatic
(unconjugated 6π electrons)



Aromatic
(conjugated 6π electrons)



Alicyclic

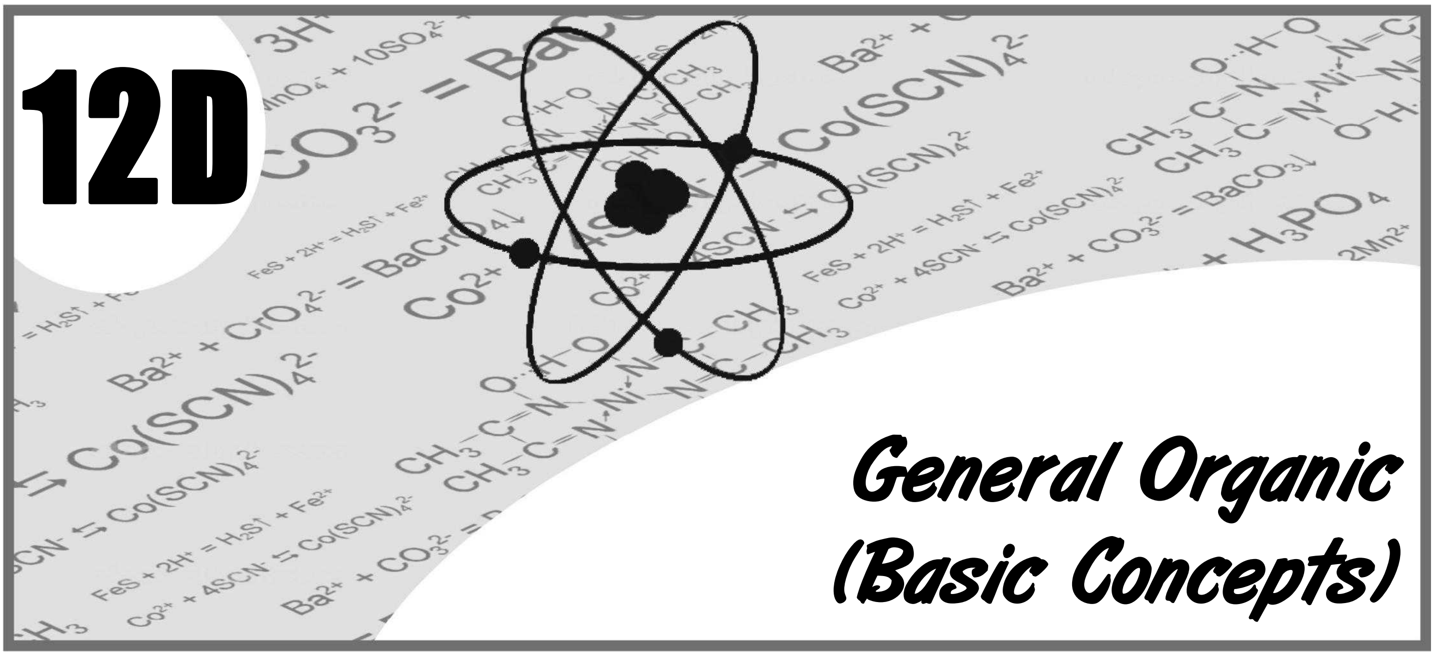


Antiaromatic
(conjugated 4π electrons)

15. (d) (ii) and (iii) have delocalized six π electrons and hence these are aromatic; (i) has 8 conjugated π electrons, while (iv) has 4 conjugated π electrons.

16. (a) Only structure I has 8 + 2 = 10π electrons, hence it is aromatic; II has 4, III has 8, IV has 9 and V has 4 electrons, thus II to V are not aromatic.

17. (d) No. of delocalized π electrons in benzene (*a*), cyclooctatetraenyl dianion (*b*), and tropylium ion (*c*) are 6, 10 and 6 respectively. Further all the three species are cyclic, hence all of these are aromatic. Cyclopentadienyl cation (*d*) has 4 π electrons, hence it is not aromatic but actually it is antiaromatic.



12D

General Organic (Basic Concepts)

ELECTRONEGATIVITY

A covalent bond, where the electrons are shared equally is called a non-polar bond (eg H–H) and an unequal sharing of the pair of bonding electrons results in a polar bond. The unequal sharing of electrons is due to the ability of an atom to attract electrons towards itself which is known as Electronegativity.

Elements with higher electronegativity values have greater attraction for bonding electrons.

H						
2.2						
Li	Be	B	C	N	O	F
1.0	1.6	1.8	2.5	3.0	3.4	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.3	1.6	1.9	2.2	2.6	3.2
						Br
						3.0
						I
						2.7

Electronegativity increases from left to right and decreases from top to bottom.

INDUCTIVE EFFECT (I)

The displacement of shared pair of electrons towards the more electronegative atom in a molecule is called inductive effect. It is a permanent effect e.g.

$$\overset{\delta+}{H} \rightarrow \overset{\delta-}{Cl}$$

- It develops polarity in a bond or molecule.
- It is transmitted along a chain of atoms but the intensity goes on decreasing with the increase in the size of chain. For example,

  $$\overset{\delta+}{C} \rightarrow C \twoheadrightarrow C \twoheadrightarrow\!\!\!\rightarrow X^{\delta-}$$

Hence transmission can be ignored after the second C-atom. An atom or group which attracts electrons more strongly than hydrogen is said to have a negative inductive effect (–I). An atom or group which attracts electrons less strongly than hydrogen is said to have a positive inductive effect (+I).

$$\overset{+}{N}R_3 > \overset{+}{N}H_3 > NO_2 > CN > COOH > F > Cl > Br > I$$

$$> OAr > OR > OH > C \equiv CR > Ar > H$$

$\longleftarrow$ Increasing – I effect (Electrons attracting)

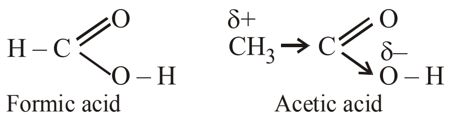
$$O^- > COO^- > CR_3 > CHR_2 > CH_2R > CH_3 > D > H$$

$\longleftarrow$ Increasing + I effect (electrons repelling)

Inductive effect does not change the covalency. The more the inductive effect between a bond, the more is the ionic character of the bond.

Applications :

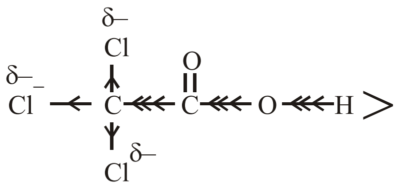
(I) ***Acid character of Acids :*** Formic acid is stronger than acetic acid.



Formic acid Acetic acid

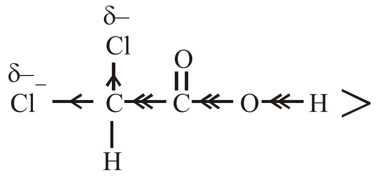
The oxygen atom in acetic acid holds the hydrogen atom more tightly after acquiring negative charge due to +I effect of methyl group. Hence it is less ionised

Acid character of halogens substituted acids. Chloro substituted acetic acids follow the following order for acid character.



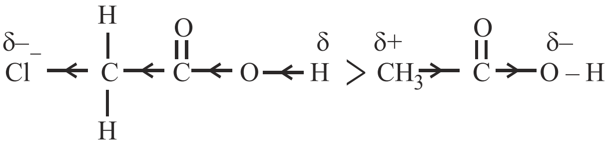
$\overset{\delta-}{Cl^-} \leftarrow \underset{\underset{Cl^{\delta-}}{\downarrow}}{\overset{\overset{\delta-}{Cl}}{\uparrow}}{C} \lll \overset{O}{\overset{\|}{C}} \lll O \lll H >$

Trichloro acetic acid



$\overset{\delta-}{Cl^-} \leftarrow \underset{\underset{H}{|}}{\overset{\overset{\delta-}{Cl}}{\uparrow}}{C} \ll \overset{O}{\overset{\|}{C}} \ll O \ll H >$

Dichloro acetic acid



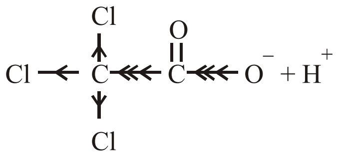
$\overset{\delta-}{Cl^-} \leftarrow \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} \leftarrow \overset{O}{\overset{\|}{C}} \leftarrow \overset{\delta}{O} \leftarrow H > \overset{\delta+}{CH_3} \rightarrow \overset{O}{\overset{\|}{C}} \rightarrow \overset{\delta-}{O} - H$

Monochloro acetic acid Acetic acid

⟵Increasing acid character

The O – H bond is more ionic in nature in trichloro acetic acid and its ionic character decreases from right to left. or

Dispersal of the negative charge after ionisation decreases from left to right which is the cause of decreasing the acid character.



$Cl \leftarrow \underset{\underset{Cl}{\downarrow}}{\overset{\overset{Cl}{\uparrow}}{C}} \lll \overset{O}{\overset{\|}{C}} \lll \overset{-}{O} + \overset{+}{H}$

Dissociation constants ($\times 10^{-5}$) for acids

Acetic acid	*Monochloro acetic acid*	*Dichloro acetic acid*	*Trichloro acetic acid*
1.8	155	500	13,000
Monofluoro acetic acid	*Monochloro acetic acid*	*Monobromo acetic acid*	*Monoiodo acetic acid*
217	155	138	75

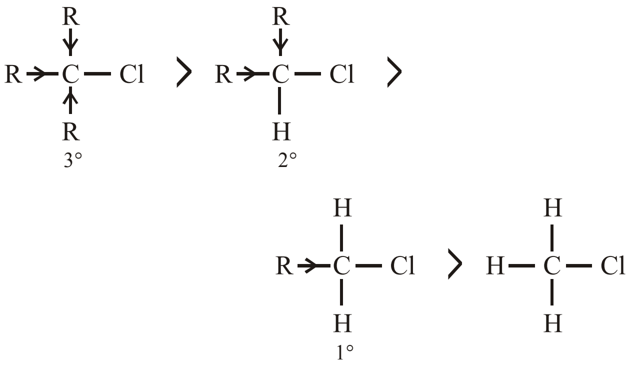
Inductive effect of halogens F > Cl > Br > I

Dissociation constant ($\times 10^{-5}$) of α, β and γ mono chlorobutyric acids

n-Butyric acid	*α-Monochloro butyric acid*
1.5	139
β-Monochloro butyric acid	*γ-Monochloro butyric acid*
8.8	3.0

The transmission of the inductive effect along a chain of carbon atoms weakens as the chain gets longer.

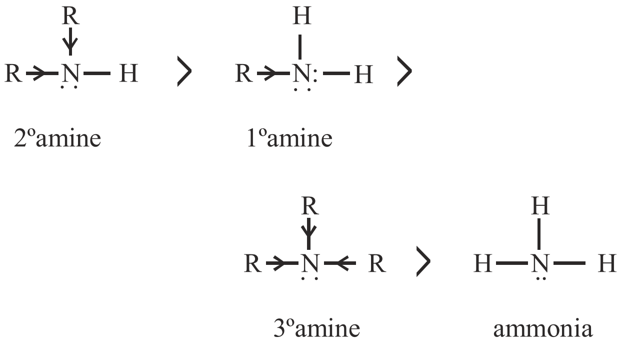
(II) ***Reactivity of Alkyl halides.*** It follows the following order



$R \rightarrow \underset{\underset{R}{\uparrow}}{\overset{\overset{R}{\downarrow}}{C}} - Cl > R \rightarrow \underset{\underset{H}{|}}{\overset{\overset{R}{\downarrow}}{C}} - Cl > R \rightarrow \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - Cl > H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - Cl$

Due to +I effect the intermediate carbonium ions (R_3C^+) are stabilised in the order $t > s > p >$ methyl. Hence the order of reactivity of alkyl halides decreases from right to left.

(III) ***Basic character of Amines.*** It follows the order



$R \rightarrow \overset{\overset{R}{\downarrow}}{\ddot{N}} - H > R \rightarrow \overset{\overset{H}{|}}{\ddot{N}}: - H > R \rightarrow \overset{\overset{R}{\downarrow}}{\ddot{N}} \leftarrow R > H - \overset{\overset{H}{|}}{\ddot{N}} - H$

Although electron density on nitrogen is maximum in $R_3\ddot{N}$ but due to steric hinderance it is less basic.

(IV) ***Inductive effect and dipole moment :***

Inductive effect leads to a dipole moment. The measured dipole moments of some alkyl halides are given below

CH_3Br	C_2H_5Br	$(CH_3)_2CHBr$	$(CH_3)_3CBr$
1.79	1.88	2.04	2.21
CH_3I	C_2H_5I	$(CH_3)_2CHI$	$(CH_3)_3CI$
1.64	1.78	1.84	2.13

+I effect increases from $-CH_3$ to $-C(CH_3)_3$ gp. –I effect of Br is more than I.

(V) ***Estimation of percentage ionic character of bonds :***

% Ionic character of covalent bond

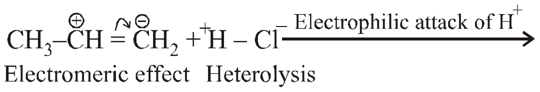
$$= \frac{\text{Observed D.M.}}{\text{Calculated D.M.}} \times 100\%.$$

INDUCTOMETRIC EFFECT

Consider the inductive effect in a bond $\overset{\delta+}{A} \rightarrow\!- \overset{\delta-}{B}$. When some negatively charged ion approaches A, the inductive effect between A – B is temporarily increased which is known as inductometric effect.

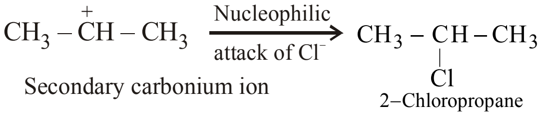
ELECTROMERIC EFFECT (E)

It involves the complete transference of π pair of electrons to one of the atoms joined a multiple bond. It is temporary effect and takes place at the requirement of attacking reagent. Consider the addition of HCl to propene.



$$CH_3-\overset{\oplus}{C}H=\overset{\ominus}{C}H_2+\overset{+}{H}-\overset{-}{Cl}\xrightarrow{\text{Electrophilic attack of }H^+}$$

Electromeric effect Heterolysis



$$CH_3-\overset{+}{C}H-CH_3\xrightarrow[\text{attack of }Cl^-]{\text{Nucleophilic}}CH_3-\underset{\substack{|\\ Cl}}{C}H-CH_3$$

Secondary carbonium ion 2–Chloropropane

Addition takes place according to ***Markownikoff's rule*** which states that the negative portion of attacking reagent goes to carbon atom containing lesser number of hydrogen atoms. The reason for this is that it results in the formation of more stable intermediate secondary carbonium ion.

PEROXIDE EFFECT, KHARASCH EFFECT :

In presence of oxygen or peroxide the addition of HBr to unsymmetrical alkene takes place ***anti to Markownikov's rule*** which is known as peroxide effect or Kharasch effect.

(I) O_2 or peroxide $\longrightarrow R^{\bullet}$ (free radical)
(II) $H-Br+R^{\bullet}\longrightarrow R-H+Br^{\bullet}$
} Chain initiation Steps

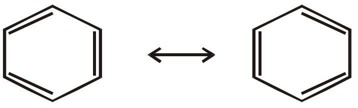
(III) $R-CH=CH_2+Br^{\bullet}\longrightarrow R-\dot{C}H-CH_2Br$
(IV) $R-\dot{C}H-CH_2Br+HBr\longrightarrow R.CH_2.CH_2Br+Br^{\bullet}$
} Chain propagation steps

(V) $Br^{\bullet}+Br^{\bullet}\longrightarrow Br_2$
(VI) $2R\dot{C}H-CH_2Br\longrightarrow R-\underset{\substack{|\\ R-CH-CH_2Br}}{C}H-CH_2Br$
(VII) $R\dot{C}H-CH_2Br+Br^{\bullet}\longrightarrow RCHBrCH_2Br$
} Chain termination steps

The attack of $Br^{\bullet}$ on terminal carbon atom (see step III) results in the formation of more stable secondary free radical. This is the reason that addition takes place anti to markownikoff's rule. HCl and HI do not show peroxide effect. HCl does not give $\dot{C}l$ atoms and HI gives molecular I_2.

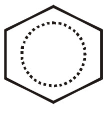
RESONANCE

Representation of certain molecules by various electronic configurations is known as Resonance. Electronic configurations differ only in location of electrons, the atoms must stay in the same conditions. e.g.



(I) Benzene (II)

The real structure is a combination of the resonance forms and is called Resonance hybrid.



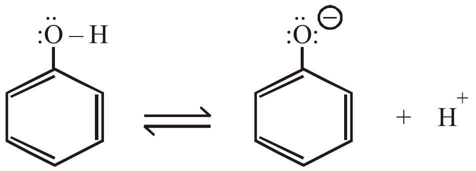
Resonance Hybrid

Feature of resonance

(i) Resonance is a permanent effect.
(ii) It involves the delocalisation of electrons, ***lone pair*** of electrons and ***π pair*** of electrons.
(iii) The number of unpaired (not lone pairs) electrons must stay the same.
(iv) Resonating structure with lowest energy contributes more towards resonance.
(v) Negative charges are most stable on electronegative atoms.
(vi) Resonating structures with maximum bonds and little charge contribute more.
(vii) Real structure resemble the major contributor more than the minor contributor.
(viii) All the atoms participating in resonance must lie in the same plane or must atleast nearly do so.

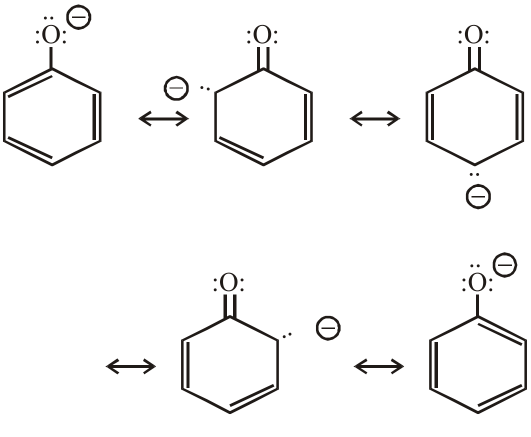
Applications of resonance :

I. Acid character of phenols : Phenols are acidic and Alcohols are neutral.

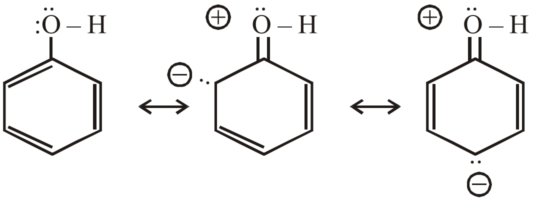


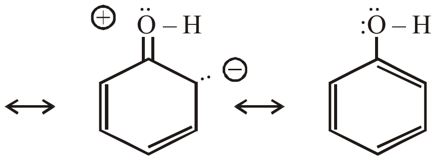
Phenol Phenoxide ion

Resonance stabilisation of Phenoxide ion



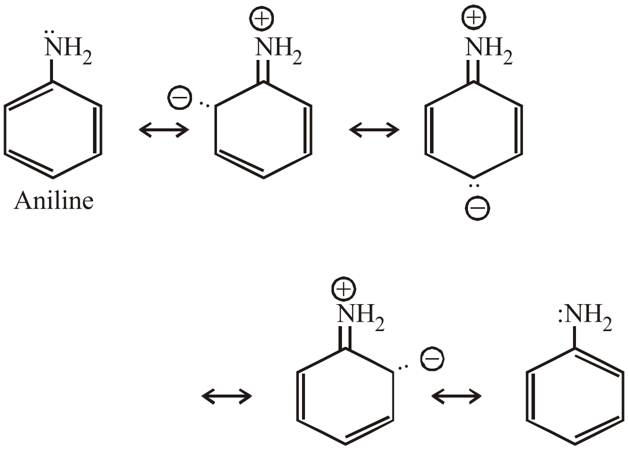
Resonance stabilisation of Phenol molecule :





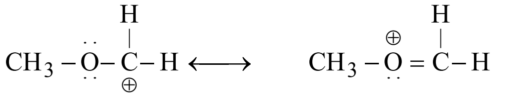
Resonance stabilisation of ***phenoxide*** ion is more than the Resonance stabilisation of ***Phenol*** molecule itself. Hence Phenol will ionise to give phenoxide and H^+ ions.

II. Basic character of amines : Aromatic amines are less basic than aliphatic amines



Due to resonance the unshared pair of electrons present on nitrogen atom is delocalised within benzene nucleus and not available for protonation (to accept H^+). Hence basic character is suppressed.

III. Stability of cations : Methoxy methyl cation is more stable by 76 kcal/mole than methyl Cation.

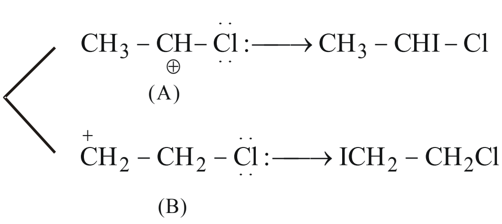


$$CH_3-\ddot{\underset{..}{O}}-\underset{\oplus}{\overset{\overset{H}{|}}{C}}-H \longleftrightarrow CH_3-\overset{\oplus}{\underset{..}{O}}=\overset{\overset{H}{|}}{C}-H$$

More stable (every atom has octet)

IV. Unexpected addition products :

$$CH_2=CH-\ddot{\underset{..}{Cl}}: \xrightarrow{^{+}H/I^{-}}$$



$$CH_3-\underset{\oplus}{CH}-\ddot{\underset{..}{Cl}}: \longrightarrow CH_3-CHI-Cl$$

(A)

$$\overset{+}{C}H_2-CH_2-\ddot{\underset{..}{Cl}}: \longrightarrow ICH_2-CH_2Cl$$

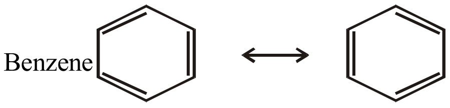
(B)

A is more stable than B

$$CH_3-\overset{\oplus}{CH}-\ddot{\underset{..}{Cl}}: \longleftrightarrow CH_3-CH=\overset{\oplus}{\underset{..}{Cl}}:$$

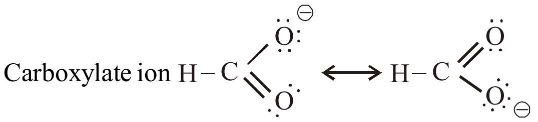
Every atom has octet

V. Resonance and bond lengths :



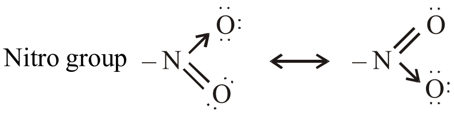
Normal C – C = 1.54 Å, C = C = 1.34 Å,

All C – C bonds in benzene 1.39Å.



Normal C = O = 1.22Å, C – O = 1.4Å,

All C – O bonds in carboxylate ion = 1.28Å



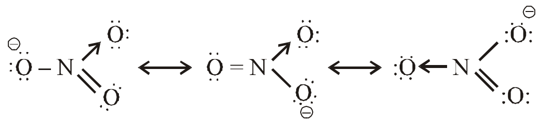
Normal N – O = 1.36Å, N = O = 1.15Å

All N – O bonds in nitro group 1.21 – 1.23 Å

VI. Resonance and bond order : It is obtained by the following relation.

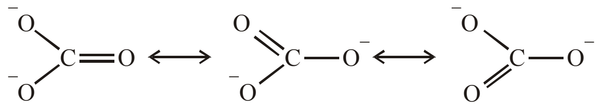
$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms}}{\text{Total number of major resonating forms}}$$

(a) NO_3^- ion



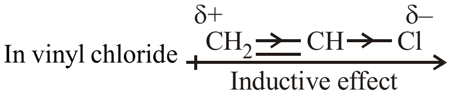
$$\text{B.O.} = \frac{4}{3} = 1.33$$

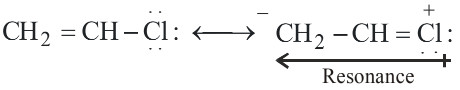
(b) CO_3^{--} ion



$$\text{B.O.} = \frac{4}{3} = 1.33$$

VII. Resonance and Dipole moment : Resonance affects the Dipole moment. D.M. of ethyl chloride is 2.05 Debye.



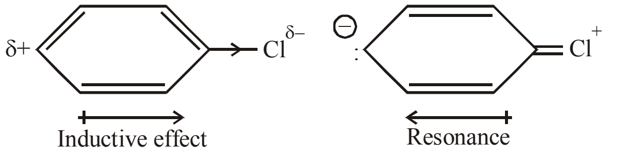


$$CH_2=CH-\ddot{\underset{..}{Cl}}: \longleftrightarrow \overset{-}{C}H_2-CH=\overset{+}{\underset{..}{Cl}}:$$

Resonance

Inductive and resonance induced D.M. operate in opposite direction, hence value is 1.44 Debye.

In chlorobenzene Inductive and Resonance induced D.M. operate in opposite direction.



The value of DM is 1.55 Debye.

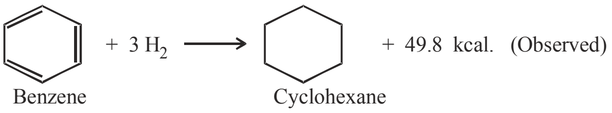
VIII.Resonance Energy (E) : It is given by the equation

$$E_R = E_0 - E_C$$

E_R = Resonance energy, E_0 = Observed heat of formation and E_C = Calculated heat of formation of the most stable of the resonating structures.

In case of unsaturated compunds, Resonance energy is the difference between a measured and calculated heat of hydrogenation e.g.,

$$E_{R(CO_2)} = E_{0(383\ \text{kcal})} = E_{C(346\,\text{kcal})} = 37\ \text{kcal/mol}$$



Calculated value of heat of hydrogenation of benzene

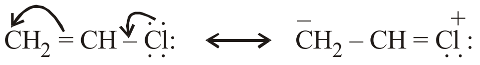
$= 28.6 \times 3 = 85.8$ kcal/mole, RE $= 36.0$ kcal / mole.

The greater the RE, the more is the stability.

MESOMERIC EFFECT (ME) :

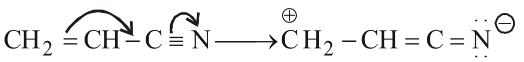
It is a permanent effect and similar to electromeric effect. Like Inductive effect it may be +ME or –ME.

+ME atoms or groups donate electrons to the double bond or conjugated system e.g. –Cl, –Br, –I, NH_2, –NHR, $–NR_2$, –OH, –OR, –SH, –SR etc.



$$CH_2 = CH - \ddot{\underset{..}{C}l}: \longleftrightarrow \overset{-}{C}H_2 - CH = \overset{+}{\underset{..}{C}l}:$$

–ME atoms or groups withdraw electrons eg. $–NO_2$, CN, COOH, CHO, HSO_3.

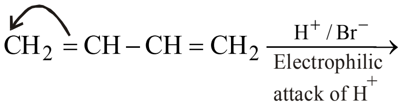


$$CH_2 = CH - C \equiv N \longrightarrow \overset{\oplus}{C}H_2 - CH = C = \ddot{\underset{..}{N}}^{\ominus}$$

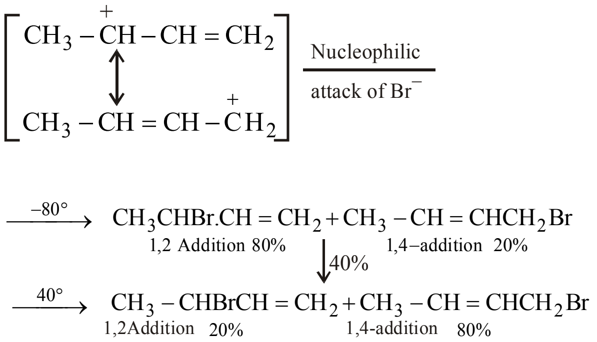
CONJUGATION :

The compounds containing alternate single and double bonds are known as conjugated compounds. Such compounds exhibit certain abnormal properties due to interaction between single and double bonds, known as conjugation

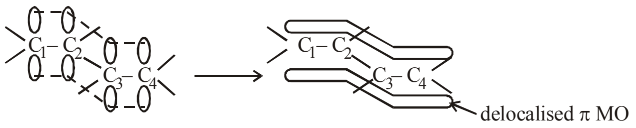
(I) **Abnormal addition reactions *:*** Addition of HBr to 1,3-butadiene.



$$CH_2 = CH - CH = CH_2 \xrightarrow[\text{Electrophilic attack of } H^+]{H^+/Br^-}$$



(II) **Extra stability :** Each C-atom in 1, 3-butadiene is sp^2 hybridised and contains one p_z atomic orbital parallel to each other and perpendicular to the plane of hybrid atomic orbitals. By sidewise overlapping these p_z atomic orbitals form a delocalised π molecular orbital which provides the extra stability to the molecule.



(III) **Bond length *:*** Conjugation affects the bond length. The $C_2 - C_3$ bond length in 1,3-butadiene is 1.47 Å and $C_1 - C_2$ bond length is 1.35Å due to conjugation.

(IV) **Heat of hydrogenation :**

Calculated heat of hydrogenation of 1,3 butadiene

$= 28.6 \times 2 = 57.2$ kcal.

Observed heat of hydrogenation of 1,3-butadiene

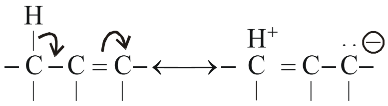
$= 53.7$ kcal.

R.E. $= 57.2 - 53.7 = 3.5$ kcal/mole

Thus due to conjugation 1,3-butadiene is stabilised by 3.5 kcal/mol.

HYPERCONJUGATION :

Introduced by ***Baker*** and ***Nathan*** (1935). The electron release by C–H bond by the effect similar to electromeric effect is known as hyperconjugation. It is a permanent effect.



Hyperconjugated forms

Since there is no apparent bond between C and H^+, the hyperconjugation is also known as ***No bond Resonance***. The magnitude of inductive effect and hyperconjugation follows the order.

$$\text{Increasing Hyperconjugation} \xleftarrow{\quad} {-CH_3,\ -C_2H_5,\ -CH(CH_3)_2,\ -C(CH_3)_3} \xrightarrow{\quad}$$

Increasing Inductive effect

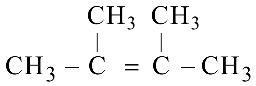
Effects of hyperconjugation :

(I) ***Heat of hydrogenation of Substituted Olefins :***

The greater the number of H.C. forms the more is the stability.

Compound	*Heat of hydrogenation*
$CH_2=CH_2$ Ethylene	32.8 kcal/mol
$CH_3–CH=CH_2$ Propylene	30.1 kcal/mol

(Due to H.C. forms)

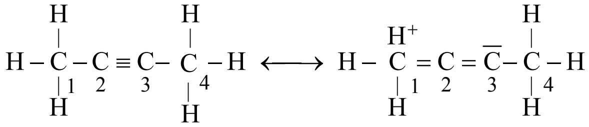


$$CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$$

Tetramethyl ethylene 26.6 kcal mol.

(Due to more H.C. forms)

(II) ***Bond lengths :*** Dimethyl acetylene

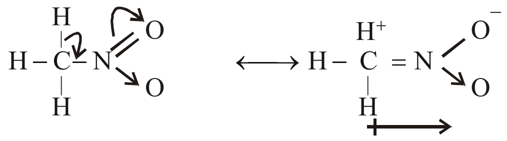


$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-C\equiv C-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \longleftrightarrow H-\underset{\underset{H}{|}}{\overset{H^+}{C}}=C=\bar{C}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H$$

Normal C–C = 1.54Å; $C_1 - C_2$ = 1.46Å

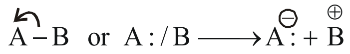
(III) ***Hyperconjugation and dipole moment :***

Calculated dipole moment of nitro methane is 2.59 Debye and the observed value is 3.15 Debye.

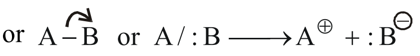


Cleavage of covalent Bond :

(I) ***Heterolytic cleavage / heterolysis :*** shared pair of electrons is retained by one atom



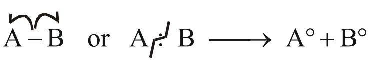
$$A-B \text{ or } A:/B \longrightarrow \overset{\ominus}{A:} + \overset{\oplus}{B}$$



$$\text{or } A-B \text{ or } A/:B \longrightarrow A^{\oplus} + :B^{\ominus}$$

Species carrying negative charge are known as anions; they are rich in electrons hence nucleophilic in nature. In a chemical reaction such species always attack at the point of low electron density. Species carrying positive charge are known as cations, they are electrons deficient hence electrophilic in nature. In a chemical reaction they attack at the point of high electron density.

(II) ***Homolytic cleavage / homolysis :*** The atoms retain one electron each.



$$A-B \text{ or } A/B \longrightarrow A^\circ + B^\circ$$

The resulting species are **neutral**, contain at least one **unpaired** electron hence known as **free radicals**, electron deficient hence **electrophilic** in nature, very reactive, **paramagnetic** in nature, hydrogen abstractor. Homolytic cleavage usually occurs in non polar bonds at high temperature or in presence of UV radiations.

Types of reagents :

(I) ***Electrophilic reagents :*** They have high affinity for electrons

$H^+, H_3O^+, \overset{+}{N}O_2, H\overset{+}{S}O_3, \overset{+}{X}$ (Cl, Br, I), $R^+, R\overset{+}{C}O, \overset{+}{N}O, -\overset{+}{N}\equiv\ddot{N}$

They may be neutral in nature also $AlCl_3$, BF_3, $ZnCl_2$, $FeCl_3$, $SnCl_4$ etc.

(II) ***Nucleophilic reagents :*** Electron rich species and have affinity towards nucleus (which is positively charged).

$-OH^-, RO^-, X^-$ (Cl, Br, I), $RCOO^-, NH_2^-, NO_2^-,$

$SH^-, CN^-, C_6H_5O^-, R-C\equiv C^-$

Neutral nucleophiles are capable of donating a pair of electrons e.g.

$H_2\ddot{O}, R-\ddot{\underset{..}{O}}-H, \ddot{N}H_3, R-\ddot{\underset{..}{S}}-H, R\ddot{N}H_2, R-\ddot{\underset{..}{O}}-R, R-Mg-X$

(III) ***Nucleophilicity is defined by the rate of attack on an electrophilic carbon atom.***

1. Species with negative charge are stronger nucleophiles than analogous species without a negative charge.

   $OH^- > H_2O, \quad SH^- > H_2S, \quad NH_2^- > NH_3$
2. Nucleophilicity decreases from left to right across the periodic table eg.

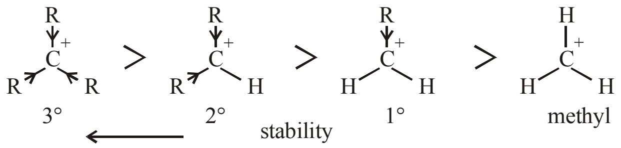
   $OH^- > F^-, \ NH_3 > H_2O$
3. Nucleophilicity increases down the periodic table.

   $I^- > Br^- > Cl^- > F^-, \ HSe^- > HS^- > HO^-$

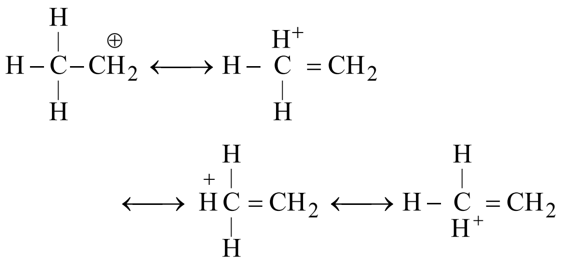
Reaction intermediates :

(I) ***Carbocations (Carbonium ions)*** $>\overset{+}{C}$. These are the species carrying positive charge on the carbon atom, which is sp^2 hybridised, with planar structure. The vacant p-orbital lies perpendicular to the plane of the other atoms. They are strong electrophiles. They are stabilised by alkyl substituents by

(a) ***Inductive effect*** *:*

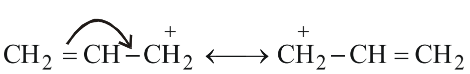


(b) ***Hyperconjugation*** *:* Partial overlapping of filled orbitals with empty ones



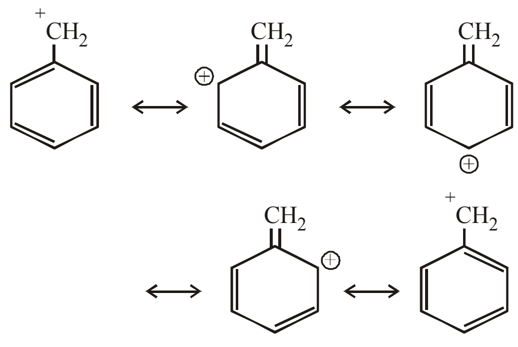
(c) ***Resonance Stabilisation*** *:* Unsaturated carbocations are stabilised by Resonance. e.g.

Allyl Carbonium ion



$$CH_2=CH-\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2-CH=CH_2$$

Benzyl Carbonium ion



The order of stability of different carbonium ions

$$(C_6H_5)_3\overset{+}{C} > (C_6H_5)_2\overset{+}{C}H > (C_6H_5)\overset{+}{C}H_2 >$$

$$CH_2=CH.\overset{+}{C}H_2 > R_3\overset{+}{C} > R_2\overset{+}{C}H > R\overset{+}{C}H_2 > \overset{+}{C}H_3$$

(II) Reactions of carbocations :

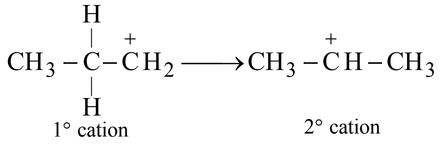
(a) ***Combination with a nucleophile*** :

$$MeCH_2-\overset{+}{C}H_2 \xrightarrow{H_2O} MeCH_2CH_2OH$$

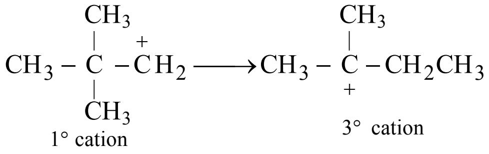
(b) ***Elimination of Proton*** :

$$MeCH_2-\overset{+}{C}H_2 \longrightarrow MeCH=CH_2+H^+$$

(c) ***Rearrangement*** : If 1,2-shift of hydrogen or alkyl can form a more stable carbocation, then such a rearrangement takes place



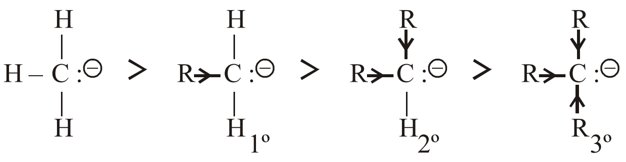
$$CH_3-\underset{H}{\overset{H}{C}}-\overset{+}{C}H_2 \longrightarrow CH_3-\overset{+}{C}H-CH_3$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{+}{C}H_2 \longrightarrow CH_3-\underset{+}{\overset{CH_3}{C}}-CH_2CH_3$$

(III) ***Carbanions (carbo anions)*** $>\overset{\ominus}{C}:$ The species carrying negative charge on the carbon atom which is sp^3 hybridised and tetrahedral. They are nucleophilic in nature and their structure resembles an amine. The stability order is

(a) ***Inductive effect*** :



Methyl ⟵ Stability

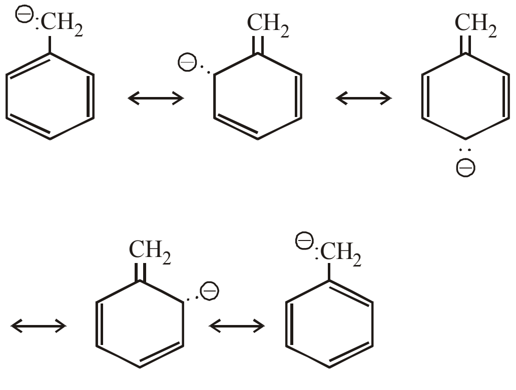
+ I effect of R increases electron density on C making it less stable.

(b) ***Resonance Stabilisation*** :

Allyl Carbanion :

$$CH_2=CH-\ddot{C}H_2^{\ominus} \longleftrightarrow \overset{\ominus}{\ddot{C}}H_2-CH=CH_2$$

Benzyl Carbanion



Resonance stabilisation is more effective than other factors.

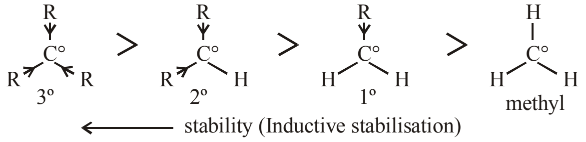
$$(C_6H_5)_3C^- > (C_6H_5)_2\overline{C}H > C_6H_5-\overline{C}H_2 >$$

$$CH_2=CH-\overline{C}H_2 > \overline{C}H_3 > \overline{C}H_2R > \overline{C}HR_2 > \overline{C}R_3$$

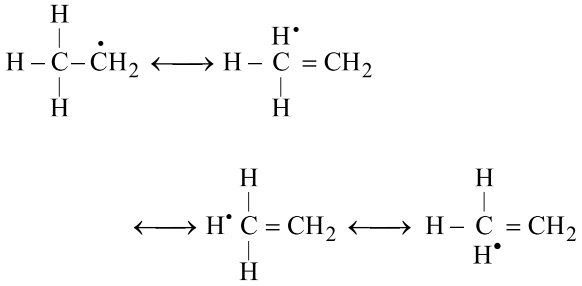
⟵ Stability

(IV) Free radicals $>C^\bullet$ **:** They are sp^2 hybridised and planar. The perpendicular p-orbital contains an odd electron. They lack in octet hence electrophilic in nature. The order of stability is

(a) ***Inductive effect*** :



(b) ***No bond resonance stabilisation / hyperconjugation***:



$$H-\underset{H}{\overset{H}{C}}-\dot{C}H_2 \longleftrightarrow H-\underset{H}{\overset{H^\bullet}{C}}=CH_2$$

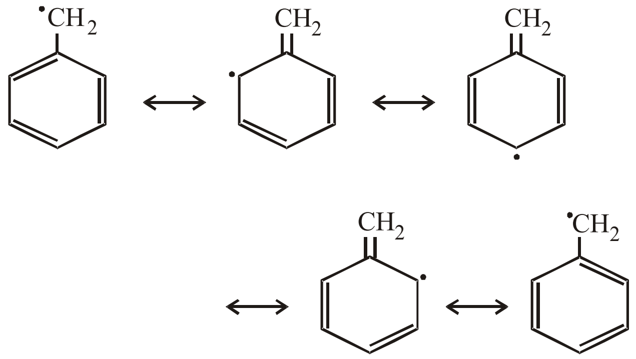
$$\longleftrightarrow H^\bullet\ \underset{H}{\overset{H}{C}}=CH_2 \longleftrightarrow H-\underset{H^\bullet}{\overset{H}{C}}=CH_2$$

(c) ***Resonance stabilisation*** :

Allyl free radical

$$CH_2=CH-\dot{C}H_2 \longleftrightarrow \dot{C}H_2-CH=CH_2$$

Benzyl free radical



Order of stability of various free radicals

$$(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > C_6H_5\dot{C}H_2 > CH_2=CH-\dot{C}H_2$$
$$> (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$$

$\longleftarrow$ Stability

CARBENES $>C$**:** These are uncharged reactive intermediates that contain a divalent carbon atom which is sp^2 hybridised. There is a perpendicular vacant p-orbital.

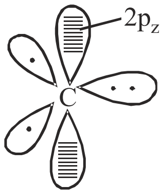
Generation :

(I) $\underset{\text{Diazomethane}}{CH_2N_2} \xrightarrow{\text{U.V.}} \underset{\text{Carbene}}{:CH_2} + N_2$

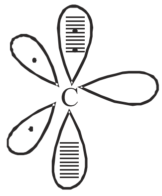
(II) $\underset{\text{Ketene}}{CH_2=C=O} \xrightarrow{\text{U.V.}} :CH_2 + CO$

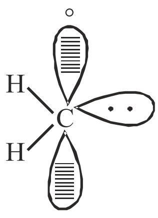
(III) $\underset{\text{Chloroform}}{CHCl_3} \xrightarrow{OH^-} \underset{\text{Dichloro carbene}}{:CCl_2} + HCl$

Singlet carbenes :



Or





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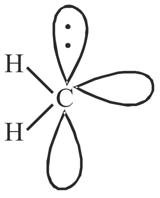
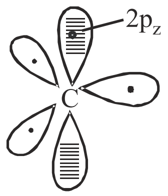
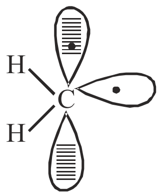


Multiplicity is $A = 2s + 1 = 2 \times 0 + 1 = 1$ $\left(s = +\frac{1}{2} - \frac{1}{2} = 0\right)$

Triplet carbenes :





Multiplicity is $A = 2 \times 1 + 1 = 3$

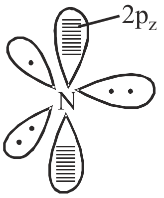
$\left(S = \frac{1}{2} + \frac{1}{2} = 1,\ \text{Two unpaired electrons have parallel spin}\right)$

Triplet is more stable than singlet.

Nitrenes : $R-\overset{..}{\underset{..}{N}}$ Nitrenes are nitrogen analogs of carbenes, nitrogen is sp^2 hybridised.

Generation $\underset{\text{Azide}}{R-\overset{..}{\underset{..}{N}}-N\equiv\overset{..}{\underset{..}{N}}} \xrightarrow{\Delta \text{ or } h\nu} R-\overset{..}{\underset{..}{N}} + N_2$

Structure singlet :



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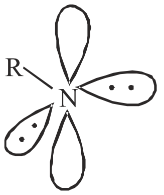
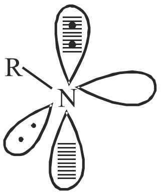
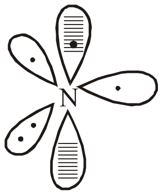




Multiplicity $A = 2s + 1 = 2 \times 0 + 1 = 1$

Triplet :



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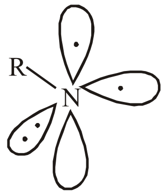
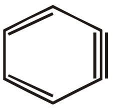
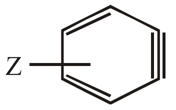


Multiplicity $A = 2s + 1 = 2 \times 1 + 1 = 3$

Arynes : The derivatives of benzyne are called arynes :

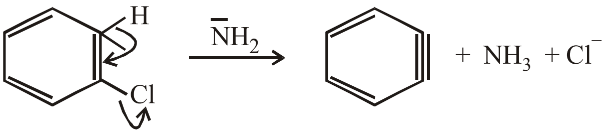


Benzyne



Aryne

Generation :



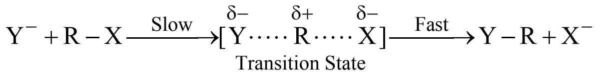
Types of reactions :

(I) Substitution reactions or replacement reactions :

(a) S_N1 : Substitution nucleophilic unimolecular reactions : Such reactions take place in two stages

$$R-X \xrightarrow{\text{Slow}} R^+ + X^-;\ R^+ + Y^- \xrightarrow{\text{Fast}} R-Y$$

(b) S_N2 : Substitution nucleophilic bimolecular reactions :



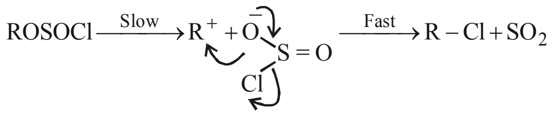
$$Y^- + R-X \xrightarrow{\text{Slow}} \underset{\text{Transition State}}{[\overset{\delta-}{Y}\cdots\cdots\overset{\delta+}{R}\cdots\cdots\overset{\delta-}{X}]} \xrightarrow{\text{Fast}} Y-R+X^-$$

S_N1	S_N2
• 3°>2°>(1° and CH_3X do not go)	CH_3X>1°>2°>3°
• Strength of nucleophile not important	Strong nucleophiles required
• Good ionising solvent required	May go faster in less polar solvent
• Rate = K [RX]	Rate = K [RX] [Nu^-]
• Possible rearrangements	No rearrangements
• Lead to recemisation	Lead to inversion.

(c) S_N1 *:* Substitution nucleophilic internal. Example

$$ROH + SOCl_2 \longrightarrow RCl + SO_2 + HCl$$

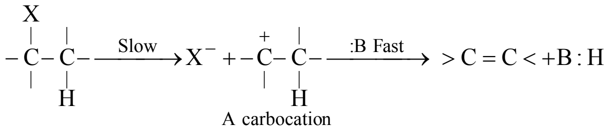
$$ROH + SOCl_2 \longrightarrow RO.SOCl + HCl$$



$$ROSOCl \xrightarrow{\text{Slow}} R^+ + \overset{-}{O}-\underset{Cl}{S}=O \xrightarrow{\text{Fast}} R-Cl+SO_2$$

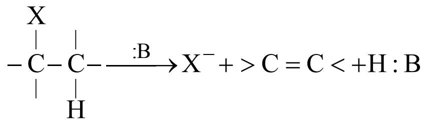
(II) Elimination reactions :

(a) ***E_1*** *:* Elimination unimolecular



$$-\overset{X}{C}-\underset{H}{C}- \xrightarrow{\text{Slow}} X^- + \underset{\text{A carbocation}}{-\overset{+}{C}-\underset{H}{C}-} \xrightarrow{:B\ \text{Fast}} >C=C< + B:H$$

(b) ***E_2*** *:* Bimolecular elimination

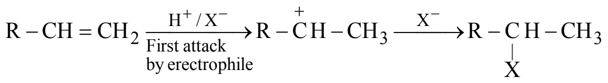


$$-\overset{X}{C}-\underset{H}{C}- \xrightarrow{:B} X^- + >C=C< + H:B$$

E_1 (comparison)	**E_2**
• Good ionising solvent required	Solvent polarity not so important
• Base strength not important	Strong bases are required
• Rate = K [RX]	Rate = K [RX] [B^-]
• Saytzeff orientation	Saytzeff orientation
• Rearrangements are common	No rearrangements

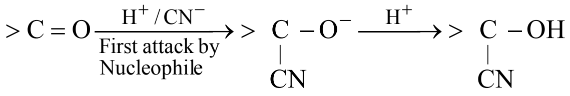
(III) Addition reactions :

(a) Electrophilic Addition reactions, initiation by electrophile e.g.



$$R-CH=CH_2 \xrightarrow[\text{First attack by erectrophile}]{H^+/X^-} R-\overset{+}{C}H-CH_3 \xrightarrow{X^-} R-\underset{X}{C}H-CH_3$$

(b) Nucleophilic addition reactions, initiation by nucleophile e.g.

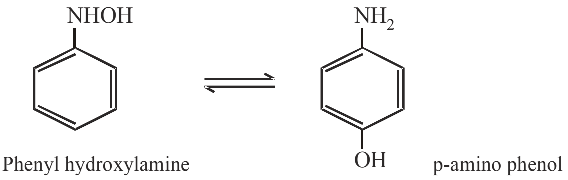


$$>C=O \xrightarrow[\text{First attack by Nucleophile}]{H^+/CN^-} >\underset{CN}{C}-O^- \xrightarrow{H^+} >\underset{CN}{C}-OH$$

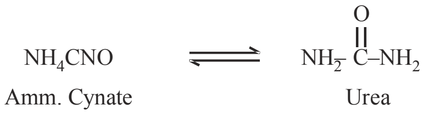
(c) Free radical addition reactions, initiation by free radical

$$R-CH=CH_2 + H\bullet/Br\bullet \xrightarrow{\text{Peroxide}} R-CH_2CH_2Br$$

(IV) Rearrangement reactions :



Phenyl hydroxylamine p-amino phenol



$$\underset{\text{Amm. Cynate}}{NH_4CNO} \rightleftharpoons \underset{\text{Urea}}{NH_2-\overset{O}{\overset{\|}{C}}-NH_2}$$

(V) Polymerisation reactions :

$$\underset{\text{Ethylene}}{nCH_2=CH_2} \longrightarrow \underset{\text{Polythene}}{-(CH_2-CH_2-)_n}$$

DIRECTIVE INFLUENCE OF ATOMS AND GROUPS :

(For electrophilic substitution reactions)

When monosubstitution product of benzene is converted into di-substitution product, the position of second incoming group is decided by the atom or group already present in the benzene nucleus. This is known as directive influence of atoms and groups. Directive influence is governed by three effects :

(I) **Inductive effect** (I) (II) **Electromeric effect** (E)

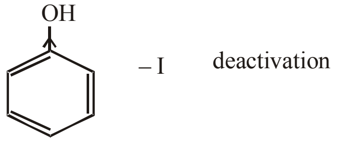
(III) **Resonance** (M)

Any effect that pushes the electrons towards the benzene nucleus is taken as positive and activates the benzene nucleus for further substitution. The effect that pushes the electrons away from benzene nucleus is taken as negative and deactivates the benzene nucleus for further substitution.

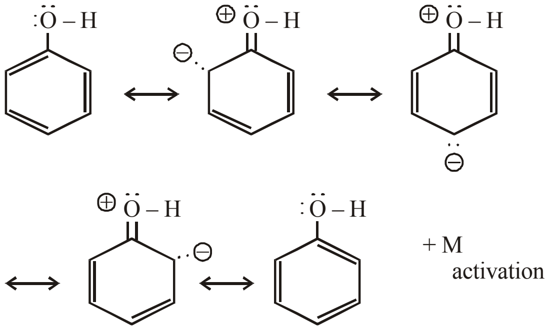
Here we will consider Inductive effect and Mesomeric effect (Resonance) to decide the directive influence of atoms and groups. The electromeric effect is similar to Mesomeric effect and always operate in the same direction, the only difference is the former is temporary and latter is permanent.

(I) Directive influence of OH group :

(a) ***Inductive effect (I)***



(b) ***Mesomeric effect (M)***

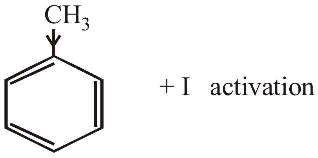


Ortho and para positions become the points of high electron density as + M > > – I. The electrophilic reagent will attack at o- and p- positions. Hence OH gp. is o, p-directing in nature with activation of benzene nucleus.

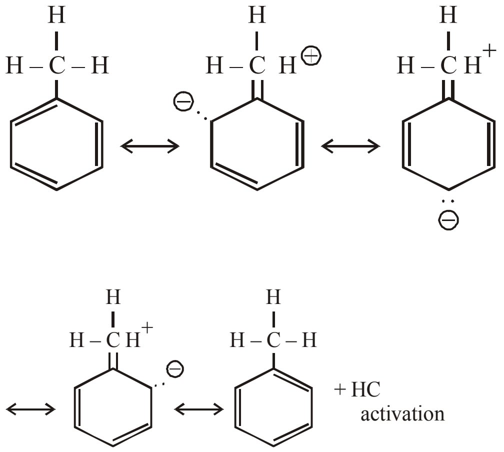
Other examples are $-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$, $-\ddot{\underset{\cdot\cdot}{O}}R$

(II) Directive influence of –CH$_3$ group :

(a) ***Inductive effect (I)***



(b) ***Hyperconjugation (HC)***

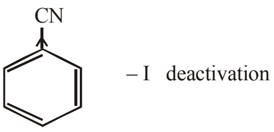


The o, p-positions become the points of high electron density. The electrophilic reagent will attack at o- and p-positions. Hence methyl group is o,p-directing in nature with activation of benzene nucleus.

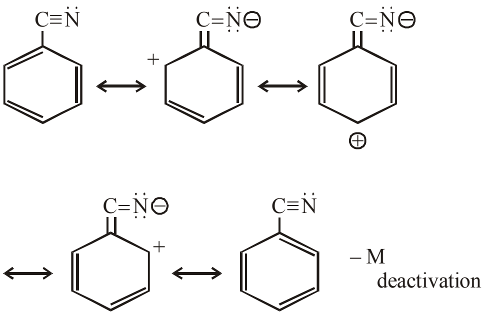
Other examples are : $-C_2H_5$, $-C_3H_7$, $-C_4H_9$ etc.

(III) Directive influence of –CN group :

(a) ***Inductive effect (I)***



(b) ***Mesomeric effect (M)***

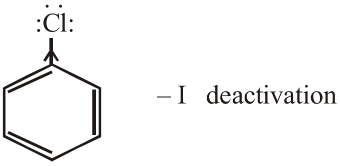


The o,p-positions become the points of low electron density, therefore the electrophilic reagent will attack at the m position. Hence CN is meta directing in nature with deactivation of benzene nucleus.

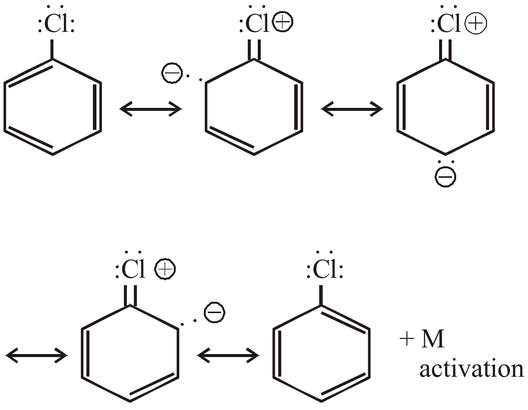
Other examples are : $-NO_2$, COOH, HSO_3, CHO

(IV) Directive influence of –Cl atom :

(a) ***Inductive effect (I)***



(b) ***Mesomeric effect (M)***



By mesomeric effect the o,p positions become the points of high electron density. Further –I > +M, hence Cl is o, p directing in nature with deactivation of benzene nucleus.

Other examples are : –F, Br, I

EASE OF ELECTROPHILIC SUBSTITUTION OF BENZENE AND ITS DERIVATIVES :

1. Strongly activating (o, p directing) :

$$-\ddot{N}H_2,\ -NHR,\ -\ddot{N}R_2,\ -\ddot{\underset{\cdot\cdot}{O}}H$$

2. Moderately activating (o, p directing) :

$$-\ddot{\underset{\cdot\cdot}{O}}CH_3,\ -\ddot{\underset{\cdot\cdot}{O}}C_2H_5,\ -\ddot{N}HCOCH_3$$

3. Weakly activating (o, p-directing) :

$$-CH_3, -C_2H_5, -C_3H_7, C_6H_5$$

4. Benzene itself.
5. Deactivating (o, p - directing) : F, Cl, Br, I
6. Deactivating (m-directing) :

$NO_2, -\overset{+}{N}(CH_3)_3$, CN, COOH, COOR, SO_3H, CHO, – COR

Again

$$NH_2 > OH > OCH_3 > NHCOCH_3 > C_6H_5 > CH_3$$

⟵ activation of benzene nucleus

COMMON ELECTROPHILIC SUBSTITUTION REACTIONS

(I) *Nitration*

$$HNO_3 + 2H_2SO_4 \longrightarrow \overset{+}{N}O_2 + H_3\overset{+}{O} + 2HSO_4^-$$

Electrophile $\overset{+}{N}O_2$

(II) *Sulphonation*

$$2H_2SO_4 \longrightarrow HSO_4^- + H_2O + HS^+O_3$$

Electrophile $H\overset{+}{S}O_3$ or SO_3

(III) *Halogenation*

$$X_2 + FeCl_3 \longrightarrow FeCl_3X^- + X^+ \qquad \text{Electrophile } X^+$$

(IV) *Friedel Craft's alkylation*

$$RX + AlCl_3 \longrightarrow R^+ + AlCl_4^- \qquad \text{Electrophile } R^+$$

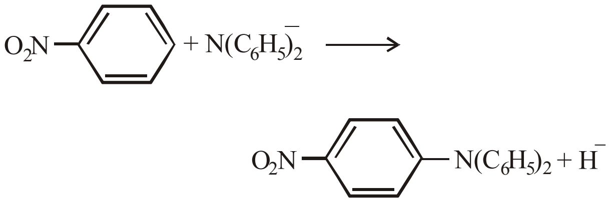
(V) *Friedel crafts acylation*

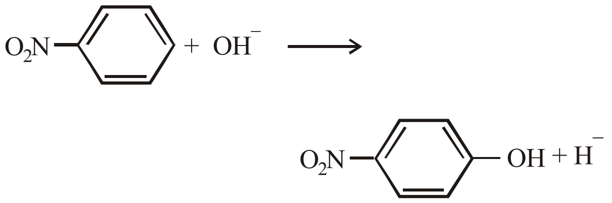
$$RCOCl + AlCl_3 \longrightarrow R\overset{+}{C}O + AlCl_4^-$$

Electrophile $R\overset{+}{C}O$

NUCLEOPHILIC SUBSTITUTION OF BENZENE

It does not occur with benzene itself, but it does occur with some substituted benzenes.





H^- much less stable hence some oxidising reagent with which H^- can react facilitate the nucleophilic substitution.

Exercise-1 | NCERT BASED QUESTIONS

Very Short/ Short Answer Questions

1. Is neopentyl radical, 4°?

2. Arrange the following:

(i) $-NO_2$, –COOH, –F, –CN, –I, in increasing order of–I effect.

(ii) $-CH_3$, –D, $-C(CH_3)_3$, $-CH(CH_3)_2$, $-CH_2CH_3$ in decreasing order of +I effect.

3. What do you mean by (i) Homolytic fission (ii) Heterolytic fission.

4. Arrange the following:

(i) $C_6H_5\dot{C}HCH_3$, $C_6H_5\dot{C}HCH=CH_2$, $C_6H_5CH_2\dot{C}H_2$, $C_6H_5\dot{C}(CH_3)_2$ in order of increasing stability.

(ii) $CH_3CH_2^+$, $C_6H_5CH_2^+$, $(CH_3)_3C^+$, $CH_2=CHCH_2^+$ in order of decreasing stability.

(iii) $HC \equiv C^-$, $CH_2=CH^-$, $CH_3CH_2^-$, CH_3^-, $(CH_3)_2CH^-$, $C_6H_5CH_2^-$ in order of increasing stability.

5. What are carbocations (carbonium ion)? Discuss their types.

6. What are free radicals ? Discuss their types.

7. How does (i) an electron withdrawing group (EWG) and (ii) an electron donating group (EDG) influence the acid strength of carboxylic acid?

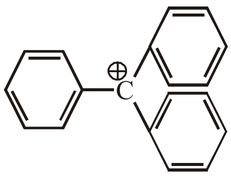
8. Which of the following species behaves as (i) a nucleophile, (ii) an electrophile, (iii) both, or (iv) neither?

$:\ddot{\underset{\cdot\cdot}{I}}:^{-}$, H_3N, $BeCl_2$, NO_2^+, $CH_3C \equiv N:$,

H_2, $H_2C = \ddot{C}:$, CH_4

9. What are carboanions? Discuss their types.

10. The structure of triphenylmethyl cation is given below. This is very stable and some of its salts can be stored for months. Explain the cause of high stability of this cation.



11. Identify the most stable species in the following set of ions giving reasons:

(i) $\overset{+}{C}H_3$, $\overset{+}{C}H_2Br$, $\overset{+}{C}HBr_2$, $\overset{+}{C}Br_3$

(ii) $\overset{\ominus}{C}H_3$, $\overset{\ominus}{C}H_2Cl$, $\overset{\ominus}{C}HCl_2$, $\overset{\ominus}{C}Cl_3$

12. Why does SO_3 act as an electrophile?

Long Answer Questions

13. What are reaction intermediates ? How are they generated by bond fission ?

14. (i) Select electrophiles out of the following:
H^+, Na^+, Cl^-, C_2H_5OH, $AlCl_3$, SO_3, CN^-, $CH_3CH_2^+$,: CCl_2, R–X

(ii) Select nucleophiles from the following:
BF_3, NH_3, ^-OH, R–X, C_2H_5OH.

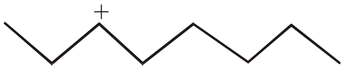
15. Categorise the following species as electrophiles or nucleophiles

HS^-, BF_3, ROH

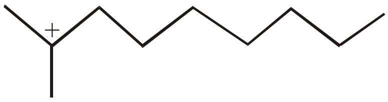
Multiple Choice Questions

16. Select the most stable carbocation from amongst the following

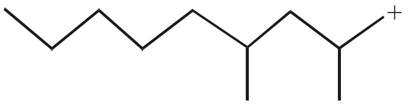
(a)



(b)



(c)



(d)

17. What is the correct order of decreasing stability of the following cations ?

I. $CH_3-\overset{\oplus}{C}H-CH_3$

II. $CH_3-\overset{\oplus}{C}H-OCH_3$

III. $CH_3-\overset{\oplus}{C}H-CH_2-OCH_3$

(a) II > I > III (b) II > III > I
(c) III > I > II (d) I > II > III

18. The order of decreasing stability of the carbanions
$(CH_3)_3C^-$ (I); $(CH_3)_2CH^-$ (II); $CH_3CH_2^-$ (III);
$C_6H_5CH_2^-$ (IV) is

(a) I > II > III > IV (b) IV > III > II > I
(c) IV > I > II > III (d) I > II > IV > III

19. The most stable free radical among the following is

(a) $C_6H_5CH_2\dot{C}H_2$ (b) $C_6H_5\dot{C}HCH_3$

(c) $CH_3\dot{C}H_2$ (d) $CH_3\dot{C}HCH_3$

20. Which of the following is *not* a nucleophile?

(a) CN^- (b) OH^-

(c) NH_3 (d) BF_3

21. The kind of delocalization involving sigma bond orbitals is called

(a) Inductive effect

(b) Hyperconjugation effect

(c) Electromeric effect

(d) Mesomeric effect

22. Which of the following is an electrophile ?

(a) Lewis acid

(b) Lewis base

(c) Negatively charged species

(d) None of the above

23. Which of the following pairs represent electrophiles?

(a) $AlCl_3$, H_2O (b) SO_3, NO_2^+

(c) BF_3, H_2O (d) NH_3, SO_3

24. Electromeric effect is a

(a) permanent effect (b) temporary effect

(c) resonance effect (d) inductive effect

Exercise-2 | CONCEPTUAL MCQs

1. Which of the following is correct regarding the – I effect of the substituents?

(a) $-NR_2 < -OR < -F$ (b) $-NR_2 > -OR < -F$

(c) $-NR_2 < -OR > -F$ (d) $-NR_2 > -OR > -F$

2. Polarization of electrons in acrolein may be written as

(a) $\overset{\delta-}{CH_2} = CH - \overset{\delta+}{CH} = O$ (b) $\overset{\delta-}{CH_2} = CH - CH = \overset{\delta+}{O}$

(c) $\overset{\delta-}{CH_2} = \overset{\delta-}{CH} - CH = O$ (d) $\overset{\delta+}{CH_2} = CH - CH = \overset{\delta-}{O}$

3. Heterolytic fission of a covalent bond in organic molecules gives

(a) free radicals (b) cations and anions

(c) only cations (d) only anions

4. In which of the following homolytic bond fission takes place ?

(a) Alkaline hydrolysis of ethyl chloride

(b) Addition of HBr to double bond

(c) Photochlorination of methane

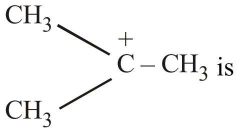
(d) Nitration of benzene

5. Homolytic fission of C–C bond in ethane gives an intermediate in which carbon is

(a) sp^3-hybridised (b) sp^2-hybridised

(c) sp-hybridised (d) sp^2d-hybridised

6. Among the following, the true property about



$(CH_3)_2\overset{+}{C}-CH_3$ is

(a) it is non-planar

(b) its C^+ is sp^2-hybridized

(c) an electrophile can attack on its C^+

(d) it does not undergo hydrolysis

7. Which of the following is the most stable carbocation (carbonium ion)?

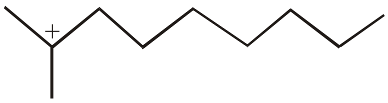
(a) $CH_3CH_2^+$ (b) $(CH_3)_2\overset{+}{C}H$

(c) $(CH_3)_3\overset{+}{C}$ (d) $C_6H_5\overset{+}{C}H_2$

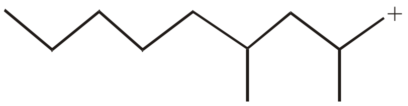
8. Select the most stable carbocation from amongst the following

(a)

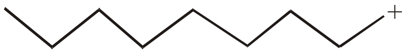
(b)



(c)



(d)



9. The most stable carbonium ion among the following is

(a) $C_6H_5\overset{+}{C}HC_6H_5$ (b) $C_6H_5\overset{+}{C}H_2$

(c) $CH_3\overset{+}{C}H_2$ (d) $C_6H_5CH_2\overset{+}{C}H_2$

10. Which of the following is most stable?

(a) Ph_3C^+ (b) Ph_2CH^+

(c) $PhCH_2^+$ (d) Tropylium cation

11. Consider the following carbocations

I. $C_6H_5\overset{+}{C}H_2$ II. $C_6H_5CH_2\overset{+}{C}H_2$

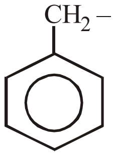
III. $C_6H_5\overset{+}{C}HCH_3$ IV. $C_6H_5\overset{+}{C}(CH_3)_2$

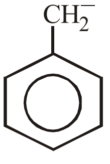
The correct sequence for the stability of these carbocations is

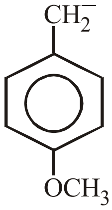
(a) II < I < III < IV (b) II < III < I < IV

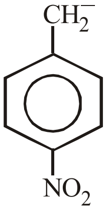
(c) III < I < II < IV (d) IV < III < I < II

12. The most stable carbanion among the following is

(a) 

(b) 

(c) 

(d) 

13. The order of decreasing stability of the carbanions $(CH_3)_3C^-$ (I); $(CH_3)_2CH^-$ (II); $CH_3CH_2^-$ (III); $C_6H_5CH_2^-$ (IV) is

(a) I > II > III > IV
(b) IV > III > II > I
(c) IV > I > II > III
(d) I > II > IV > III

14. The most stable free radical among the following is

(a) $C_6H_5CH_2\dot{C}H_2$
(b) $C_6H_5\dot{C}HCH_3$
(c) $CH_3\dot{C}H_2$
(d) $CH_3\dot{C}HCH_3$

15. Intermediate involved in Reimer-Tiemann reaction is

(a) carbocation
(b) carbanion
(c) carbene
(d) free radical

16. For the reaction of phenol with $CHCl_3$ in presence of KOH, the electrophile is

(a) $^+CHCl_2$
(b) $:CCl_2$
(c) $\dot{C}HCl_2$
(d) CCl_4

17. In the mechanism of Hofmann reaction which intermediate rearranges to alkyl isocyanate?

(a) Bromamide
(b) Nitrene
(c) Nitroso
(d) Amide

18. Which of the following is an electrophile?

(a) H_2O
(b) NH_3
(c) $AlCl_3$
(d) $C_2H_5NH_2$

19. Which of the following is *not* a nucleophile?

(a) CN^-
(b) OH^-
(c) NH_3
(d) BF_3

20. Which of the following is not a nucleophile?

(a) H_2O
(b) CH_3OH
(c) H_2
(d) NH_3

21. Which of the following behaves both as a nucleophile and as an electrophile ?

(a) $CH_3C \equiv N$
(b) CH_3OH
(c) $CH_2 = CHCH_3$
(d) CH_3NH_2

22. Which of the following has the highest nucleophilicity?

(a) F^-
(b) OH^-
(c) CH_3^-
(d) NH_2^-

23. The correct nucleophilicity order is

(a) $CH_3^- < NH_2^- < HO^- < F^-$
(b) $CH_3^- \simeq NH_2^- > HO^- \simeq F^-$
(c) $CH_3^- > NH_2^- > HO^- > F^-$
(d) $NH_2^- > F^- > HO^- > CH_3^-$

24. What is the decreasing order of strength of the bases OH^-, NH_2^-, $HC \equiv C^-$ and $CH_3CH_2^-$?

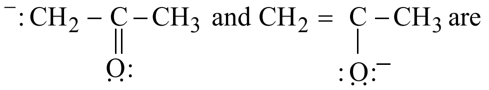
(a) $CH_3CH_2^- > NH_2^- > HC \equiv C^- > OH^-$
(b) $HC \equiv C^- > CH_3CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > HC \equiv C^- > CH_3CH_2^-$
(d) $NH_2^- > HC \equiv C^- > OH^- > CH_3CH_2^-$

25. Which is the correct symbol relating the two Kekule structures of benzene ?

(a) $\rightleftarrows$
(b) $\rightarrow$
(c) $\equiv$
(d) $\leftrightarrow$

26. Point out the incorrect statement about resonance?

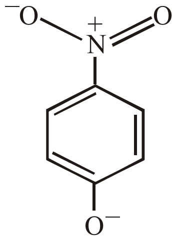
(a) Resonance structures should have equal energy
(b) In resonating structures, the constituent atoms must be in the same position
(c) In resonating structures, there should not be same number of electron pairs
(d) Resonating structures should differ only in the location of electrons around the constituent atoms

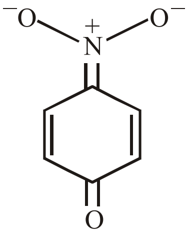
27.  are

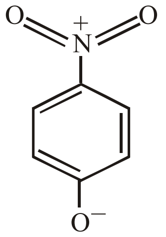
$^-:CH_2 - \underset{\underset{\ddot{O}:}{\|}}{C} - CH_3$ and $CH_2 = \underset{\underset{:\ddot{O}:^-}{|}}{C} - CH_3$ are

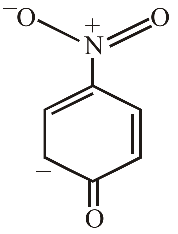
(a) resonating structures
(b) tautomers
(c) geometrical isomers
(d) optical isomers

28. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is

(a) 

(b) 

(c) 

(d) 

29. In which of the following, resonance will be possible?

(a) $CH_3-CH_2-CH_2-CHO$

(b) $CH_2=CH-CH=O$

(c) CH_3COCH_3

(d) $CH_2=CH-CH_2-CH=CH_2$

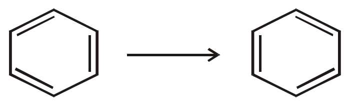
30. Which of the following statements regarding the resonance energy of benzene is *correct*?

(a) Resonance energy is the energy required to break the C–H bond in benzene

(b) Resonance energy is the energy required to break the C–C bond in benzene

(c) Resonance energy is a measure of stability of benzene

(d) Resonance energy is the energy required to convert



31. The heat of hydrogenation of 1-hexene is 126 $kJmol^{-1}$, When a second double bond is introduced in the molecule, the heat of hydrogenation of the resulting compound is 230 kJ mol^{-1}. The resulting compound (diene) is

(a) 1, 3-Hexadiene (b) 1, 4-Hexadiene

(c) 1, 5-Hexadiene (d) Nothing certain

32. Resonance in most of the organic molecules

(a) increases stability (b) decreases stability

(c) increases reactivity (d) None of these

33. The kind of delocalization involving sigma bond orbitals is called

(a) inductive effect

(b) hyperconjugation effect

(c) electromeric effect

(d) mesomeric effect

34. The reaction,

$CH_2=CH-CH_3+HBr \longrightarrow CH_3CHBrCH_3$ is

(a) nucleophilic addition

(b) electrophilic substitution

(c) electrophilic addition

(d) free radical addition

35. The addition of HCN to a carbonyl compound is an example of

(a) nucleophilic substitution

(b) electrophilic addition

(c) nucleophilic addition

(d) electrophilic substitution

36. Acetaldehyde is the rearrangement product of

(a) methyl alcohol (b) allyl alcohol

(c) vinyl alcohol (d) All are correct

Exercise-3 | PAST COMPETITION MCQs

1. For (i) I^-, (ii) Cl^-, (iii) Br^-, the increasing order of nucleophilicity would be **[CBSE-PMT 2007]**

(a) $Cl^- < Br^- < I^-$ (b) $I^- < Cl^- < Br^-$

(c) $Br^- < Cl^- < I^-$ (d) $I^- < Br^- < Cl^-$

2. The order of decreasing reactivity towards an electrophilic reagent, for the following would be **[CBSE-PMT 2007]**

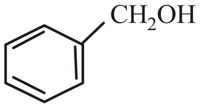
(i) benzene (ii) toluene

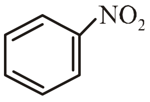
(iii) chlorobenzene (iv) phenol

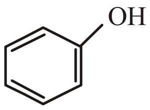
(a) (ii) > (iv) > (i) > (iii) (b) (iv) > (iii) > (ii) > (i)

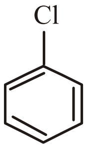
(c) (iv) > (ii) > (i) > (iii) (d) (i) > (ii) > (iii) > (iv)

3. Which one of the following is most reactive towards electrophilic attack ? **[CBSE-PMT 2008]**

(a) 

(b) 

(c) 

(d) 

4. Base strength of : **[CBSE-PMT 2008]**

(A) $H_3C\overset{-}{C}H_2$, (B) $H_2C=CH^-$ and

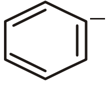
(C) $H-C\equiv C^-$

is in the order of :

(a) (B) > (A) > (C) (b) (C) > (B) > (A)

(c) (A) > (C) > (B) (d) (A) > (B) > (C)

5. The stability of carbanions in the following :

(I) $RC=C^-$ (II) 

(III) $R_2C=CH^-$ (IV) $R_3C-\overset{-}{C}H_2$

is in the order of : **[CBSE-PMT 2008]**

(a) (I) > (II) > (III) > (IV) (b) (II) > (III) > (IV) > (I)

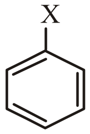
(c) (IV) > (II) > (III) > (I) (d) (I) > (III) > (II) > (IV)

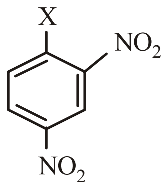
6. Cyclohexanol (I), acetic acid (II), 2, 4, 6-trinitrophenol (III) and phenol (IV) are given. In these the order of decreasing acidic character will be : **[CBSE-PMT 2010]**

(a) III > II > IV > I (b) II > III > I > IV

(c) II > III > IV > I (d) III > IV > II > I

7. The correct order of increasing reactivity of C – X bond towards nucleophile in the following compounds is: **[CBSE-PMT 2010]**


(I)


(II)

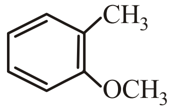
$(CH_3)_3C-X$, (III) $(CH_3)_2CH-X$ (IV)

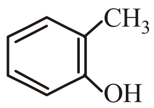
(a) I < II < IV < III (b) II < III < I < IV
(c) IV < III < I < II (d) III < II < I < IV

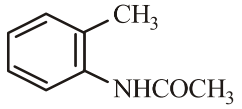
8. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is: **[CBSE-PMT 2010]**

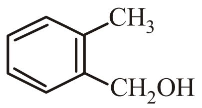
(a) CH_3COOCH_3 (b) CH_3CONH_2
(b) $CH_3COOCOCH_3$ (d) CH_3COCl

9. Which one of the following is most reactive towards electrophilic reagent ? **[CBSE-PMT 2010, 2011]**

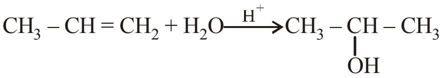
(a)


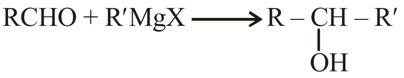
(b)


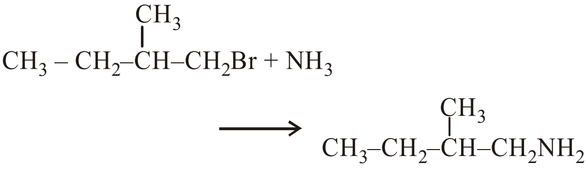
(c)


(d)


10. Which one is a nucleophilic substitution reaction among the following ? **[CBSE-PMT 2011]**

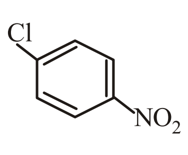
(a)

$CH_3-CH=CH_2+H_2O\xrightarrow{H^+}CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

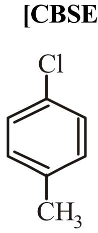
(b)

$RCHO+R'MgX\longrightarrow R-\underset{\underset{OH}{|}}{CH}-R'$

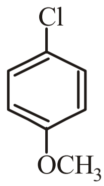
(c)

$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2Br+NH_3 \longrightarrow CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2NH_2$

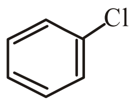
(d) $CH_3CHO+HCN\longrightarrow CH_3CH(OH)CN$

11. Which of the following compounds undergoes nucleophilic substitution reaction most easily ? **[CBSE-PMT 2011 M]**

(a)


(b)


(c)


(d)


12. Some *meta*-directing substituents in aromatic substitution are given. Which one is most deactivating? **[NEET 2013]**

(a) $-SO_3H$ (b) $-COOH$
(c) $-NO_2$ (d) $-C\equiv N$

13. Arrangement of $(CH_3)_3-C-$, $(CH_3)_2-CH-$, CH_3-CH_2- when attached to benzyl or an unsaturated group in increasing order of inductive effect is **[AIEEE 2002]**

(a) $(CH_3)_3-C-<(CH_3)_2-CH-<CH_3-CH_2^-$
(b) $CH_3-CH_2-<(CH_3)_2-CH-<(CH_3)_3-C-$
(c) $(CH_3)_2-CH-<(CH_3)_3-C-<CH_3-CH_2-$
(d) $(CH_3)_3-C-<CH_3-CH_2-<(CH_3)_2-CH-$

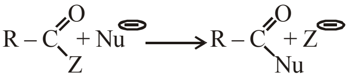
14. The reaction:
$(CH_3)_3C-Br\xrightarrow{H_2O}(CH_3)_3-C-OH$ is a/an **[AIEEE 2002]**

(a) elimination reaction (b) substitution reaction
(c) free radical reaction (d) displacement reaction.

15. In the anion $HCOO^-$ the two carbon-oxygen bonds are found to be of equal length. what is the reason for it ? **[AIEEE 2003]**

(a) The C = O bond is weaker than the C — O bond
(b) The anion $HCOO^-$ has two resonating structures
(c) The anion is obtained by removal of a proton from the acid molecule
(d) Electronic orbitals of carbon atom are hybridised

16. Rate of the reaction **[AIEEE 2004]**



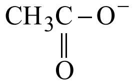
is fastest when Z is

(a) OC_2H_5 (b) NH_2
(c) Cl (d) $OCOCH_3$

17. Due to the presence of an unpaired electron, free radicals are: **[AIEEE 2005]**

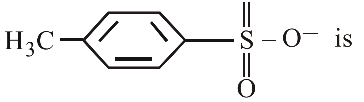
(a) cations (b) anions
(c) chemically inactive (d) chemically reactive

18. The decreasing order of nucleophilicity among the nucleophiles **[AIEEE 2005]**

(a)

$CH_3\underset{\underset{O}{\|}}{C}-O^-$

(b) CH_3O^-

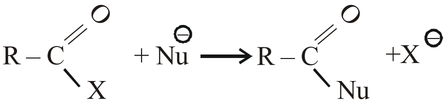
(c) CN^-

(d)


is

(a) (c), (b), (a), (d) (b) (b), (c), (a), (d)
(c) (d), (c), (b), (a) (d) (a), (b), (c), (d)

19. The reaction **[AIEEE2005]**



is fastest when X is

(a) OCOR (b) OC_2H_5
(c) NH_2 (d) Cl

20. The increasing order of stability of the following free radicals is **[AIEEE 2006]**

(a) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

(b) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$

(c) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$

(d) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

21. Presence of a nitro group in a benzene ring **[AIEEE 2007]**

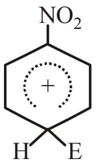
(a) deactivates the ring towards electrophilic substitution

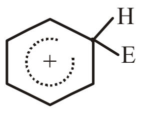
(b) activates the ring towards electrophilic substitution

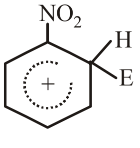
(c) renders the ring basic

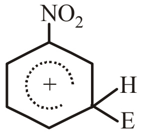
(d) deactivates the ring towards nucleophilic substitution.

22. The electrophile, $E^{\oplus}$ attacks the benzene ring to generate the intermediate σ–complex. Of the following, which σ–complex is lowest energy? **[AIEEE 2008]**

(a)


(b)


(c)


(d)


23. Arrange the carbanions, **[AIEEE 2009]**

$(CH_3)_3\bar{C}, \bar{C}Cl_3, (CH_3)_2\bar{C}H, C_6H_5\bar{C}H_2$

in order of their decreasing stability :

(a) $(CH_3)_2\bar{C}H > \bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_3\bar{C}$

(b) $\bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$

(c) $(CH_3)_3\bar{C} > (CH_3)_2\bar{C}H > C_6H_5\bar{C}H_2 > \bar{C}Cl_3$

(d) $C_6H_5\bar{C}H_2 > \bar{C}Cl_3 > (CH_3)_3\bar{C} > (CH_3)_2\bar{C}H$

24. The correct order of increasing basicity of the given conjugate bases ($R = CH_3$) is **[AIEEE 2010]**

(a) $RCO\bar{O} < HC \equiv \bar{C} < \bar{R} < \bar{N}H_2$

(b) $\bar{R} < HC \equiv \bar{C} < RCO\bar{O} < \bar{N}H_2$

(c) $RCO\bar{O} < \bar{N}H_2 < HC \equiv \bar{C} < \bar{R}$

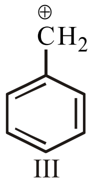
(d) $RCO\bar{O} < HC \equiv \bar{C} < \bar{N}H_2 < \bar{R}$

25. A solution of (–) – 1 – chloro –1– phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of : **[JEE M 2013]**

(a) carbanion (b) carbene

(c) carbocation (d) free radical

26. The order of stability of the following carbocations :

$CH_2 = CH - \overset{\oplus}{C}H_2$; $CH_3 - CH_2 - \overset{\oplus}{C}H_2$;


is :

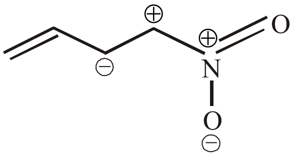
I II III

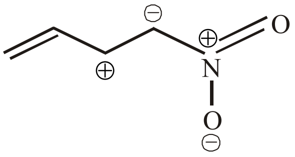
[JEE M 2013]

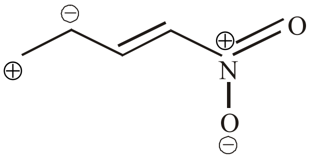
(a) III > II > I (b) II > III > I

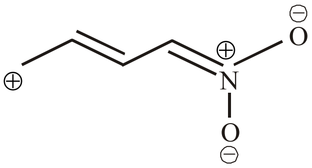
(c) I > II > III (d) III > I > II

27. Among the following, the least stable resonance structure is **[IIT-JEE 2007]**

(a)


(b)


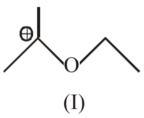
(c)


(d)


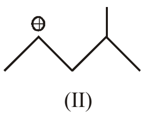
28. Hyperconjugation involves overlap of the following orbitals **[IIT-JEE 2008]**

(a) σ-σ (b) σ - π (c) p- p (d) π-π

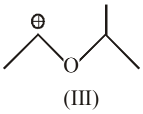
29. The correct stability order for the following species is **[IIT-JEE 2008]**



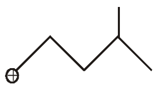
(I)



(II)



(III)

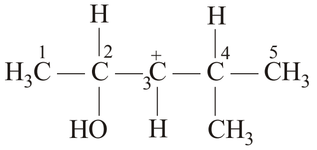


(IV)

(a) (II) > (IV) > (I) > (III) (b) (I) > (II) > (III) > (IV)

(c) (II) > (I) > (IV) > (III) (d) (I) > (III) > (II) > (IV)

30. In the following carbocation, H/CH_3 that is most likely to migrate to the positively charged carbon is **[IIT-JEE 2009]**



$$\overset{1}{H_3C} - \underset{HO}{\overset{H}{C_2}} - \underset{H}{\overset{+}{C_3}} - \underset{CH_3}{\overset{H}{C_4}} - \overset{5}{CH_3}$$

(a) CH_3 at C-4 (b) H at C-4

(c) CH_3 at C-2 (d) H at C-2

31. Among the following compounds, the most acidic is

[IIT-JEE 2011]

(a) *p*-nitrophenol (b) *p*-hydroxybenzoic acid

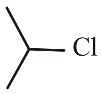
(c) *o*-hydroxybenzoic acid (d) *p*-toluic acid

32. KI in acetone, undergoes S_N2 reaction with each of P, Q, R and S. The rates of the reaction vary as

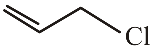
(JEE Advanced 2013)

H_3C-Cl

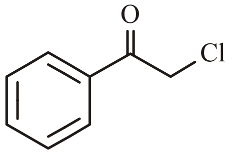
P



Q



R



S

(a) P > Q > R > S (b) S > P > R > Q

(c) P > R > Q > S (d) R > P > S > Q

Exercise-4 | Applied MCQs

1. In E_2 elimination, some compounds follow Hofmann's rule which means

(a) the double bond goes to the most substituted position

(b) the compound is resistant to elimination

(c) no double bond is formed

(d) the double bond goes mainly towards the least substituted carbon

2. S_N1 reaction on optically active substrates mainly gives

(a) retention in configuration

(b) inversion in configuration

(c) racemic product

(d) No product

3. Which of the following contains only three pairs of electrons?

(a) Carbocation (b) Carbanion

(c) Free radical (d) None of these

4. The addition of HBr on butene -2 in presence of peroxide follows the

(a) electrophilic addition (b) free radical addition

(c) nucleophilic addition (d) None of these

5. The stability of 2, 3 - dimethyl-but - 2- ene is more than 2-butene. This can be explained in terms of

(a) resonance (b) hyperconjugation

(c) electromeric effect (d) inductive effect

6. $(CH_3)_4N^+$ is neither an electrophile, nor a nucleophile because it

(a) does not have electron pair for donation as well as cannot attract electron pair

(b) neither has electron pair available for donation nor can accommodate electron since all shells of N are fully occupied

(c) can act as Lewis acid and base

(d) None of these

7. A solution of (+) - 2 - chloro - 2 - phenylethane in toluene racemises slowly in the presence of small amounts of $SbCl_5$ due to the formation of

(a) Carbanion (b) Carbene

(c) Free radical (d) Carbocation

8. Which of the following is singlet carbene ?

(a) $(CH_3)_3C^+$ (b) $C_2H_5\ddot{C}CH_3$

(c) $CH_3\overset{\ominus}{\ddot{C}}HCH_3$ (d) $CH_2=CH-\overset{+}{C}H_2$

9. The reaction,

$C_2H_5I + KOH \rightarrow C_2H_5OH + KI$ is called

(a) hydroxylation substitution

(b) electrophilic substitution

(c) nucleophilic substitution

(d) dehydroiodination

10. An organic compound $C_5H_{11}X$ an dehydrohalogenation gives pentene - 2 only. What is halide

(a) $CH_3CH_2CHXCH_2CH_3$

(b) $(CH_3)_2CHCHXCH_3$

(c) $CH_3CH_2CH_2CHXCH_3$

(d) $CH_3CH_2CH_2CH_2CH_2X$

11. Sulphur trioxide is

(a) an electrophile (b) a nucleophile

(c) a homolytic reagent (d) a base

12. Intermediate product formed in the acid catalysed dehydration of n- propyl alcohol is

(a) $CH_3-CH_2-CH_3$ (b) $CH_3-CH=CH_2$

(c) $CH_3-\overset{+}{C}H-CH_3$ (d) $CH_3-CH_2-\overset{+}{C}H_2$

13. Which of the following is most stable

(a) $CCl_3CH(OH)_2$ (b) $(CH_3)_2.C.(OH)_2$

(c) $CH_3C.Cl(OH)_2$ (d) $CH_3CH(OH)_2$

14. Chlorine in vinyl chloride is less reactive because

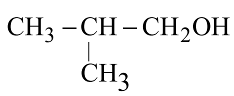
(a) sp^2 - hybridised carbon has more acidic character than sp^3 - hybridised carbon

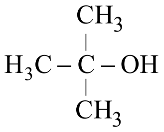
(b) C - Cl bond develops partial double bond character

(c) of resonance

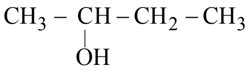
(d) All are correct

15. The compound which gives the most stable carbonium ion on dehydration :

(a)

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

(b)

$H_3C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$

(c) $CH_3-CH_2-CH_2-CH_2OH$

(d)

$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3$

16. Among the following compounds which is most reactive towards nitration

(a) Benzene (b) Nitrobenzene

(c) Toluene (d) Chlorobenzene

17. Example of chlorinolysis is

(a) $CH_2=CH_2 \longrightarrow C_2H_4Cl_2$

(b) $CCl_4+H_2O \longrightarrow COCl_2+2HCl$

(c) $CHCl_3+4NaOH \longrightarrow HCOONa+3NaCl+2H_2O$

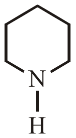
(d) $C_3H_8 \xrightarrow{Cl_2} CCl_4+C_2Cl_6+8HCl$

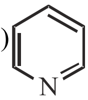
18. During debromination of meso - dibromobutane, the major compound formed is :

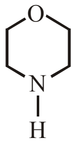
(a) n - butane (b) 1 - butene

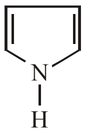
(c) Cis - 2 - butene (d) Trans - 2 - butene

19. In the following compounds

(I)


(II)


(III)


(IV)


the order of basicity is :

(a) IV > I > III > II (b) III > I > IV > II

(c) II > I > III > IV (d) I > III > II > IV

20. In the following groups

–OAc (I)

–OMe (II)

$–OSO_2Me$ (III)

$–OSO_2CF_3$ (IV)

the order of leaving group ability is

(a) I > II > III > IV (b) IV > III > I > II

(c) III > II > I > IV (d) II > III > IV > I

21. The intermediate during the addition of HCl to propene in the presence of peroxide is

(a) $CH_3\dot{C}HCH_2Cl$ (b) $CH_3\overset{+}{C}HCH_3$

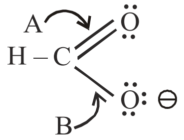
(c) $CH_3CH_2\dot{C}H_2$ (d) $CH_3CH_2\overset{+}{C}H_2$

22. Which of the following acids has the smallest dissociation constant ?

(a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH

(c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$

23. One of the equivalent energy resonance structures for formate anion is shown below



Which C – O bond is longer ?

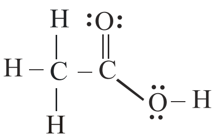
(a) A

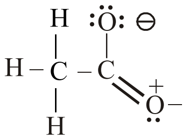
(b) B

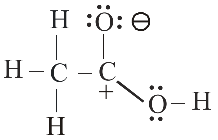
(c) Both are equal

(d) Structure shown is not correct

24. Which of the following resonance structure is lowest in energy?

(A)


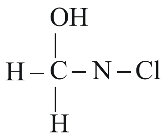
(B)


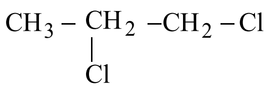
(C)


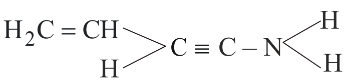
(a) A (b) B

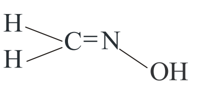
(c) C (d) All have same energy

25. The structure that does not have an error is

(A)

$H-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-N-Cl$

(B)

$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH_2}}-CH_2-Cl$

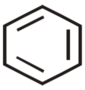
(C)


(D)


(a) A (b) B

(c) C (d) D

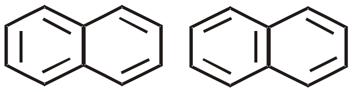
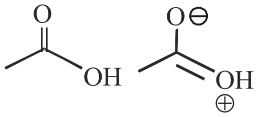
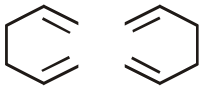
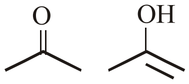
26. How many degrees of unsaturation are there in benzene

 ?

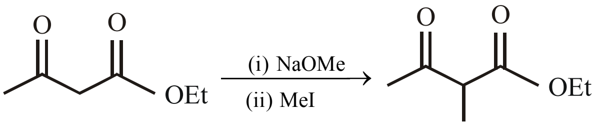
(a) 2　(b) 3

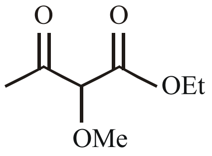
(c) 4　(d) More than 4

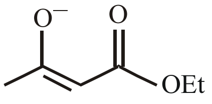
27. Which is incorrect for the following pairs ?

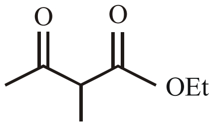
Column I	Column II
(a) 	resonance
(b) 	equilibrium
(c) 	equilibrium
(d) 	equilibrium

28. What is the mechanistic intermediate in the following reaction



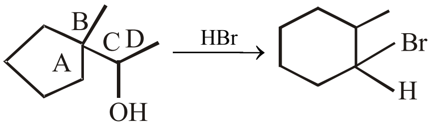
(a) 

(b) 

(c) 

(d) None of these

29. In the reaction shown below the six membered ring is generated by shifting which bond



(a) A　(b) B

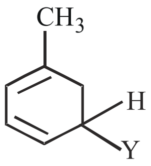
(c) C　(d) D

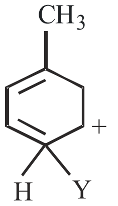
30. When HI is added on to propene in presence of peroxide the intermediate formed is

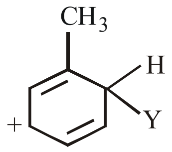
(a) $CH_3\overset{+}{C}HCH_3$　(b) $CH_3CH_2\overset{+}{C}H_2$

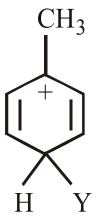
(c) $CH_3\overset{\bullet}{C}HCH_2I$　(d) $CH_3CH_2\overset{\bullet}{C}H_2$

31. Which of the followings is most stable ?

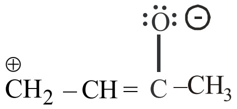
(a) 

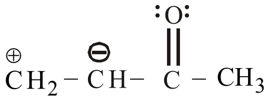
(b) 

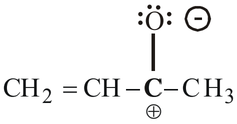
(c) 

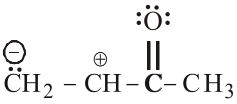
(d) 

32. The stable resonating form of vinyl methyl ketone is

(a) 
$\overset{\oplus}{C}H_2-CH=\overset{\overset{:\ddot{O}:^{\ominus}}{|}}{C}-CH_3$

(b) 
$\overset{\oplus}{C}H_2-\overset{\ominus}{C}H-\overset{\overset{:O:}{\|}}{C}-CH_3$

(c) 
$CH_2=CH-\underset{\oplus}{\overset{\overset{:\ddot{O}:^{\ominus}}{|}}{C}}-CH_3$

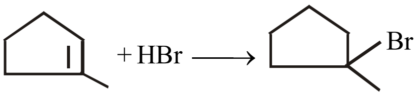
(d) 
$\overset{\ominus}{\ddot{C}}H_2-\overset{\oplus}{C}H-\overset{\overset{:\ddot{O}:}{\|}}{C}-CH_3$

33. Hyperconjugation involves

(a) $\sigma-\pi$ conjugation　(b) $\sigma-\pi$ delocalisation

(c) no bond resonance　(d) All of these

34. The following reaction

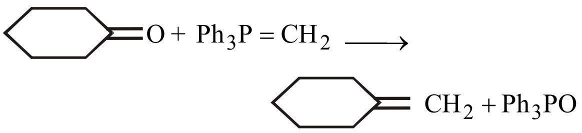


is an example of

(a) elimination reaction　(b) nucleophilic subsitution

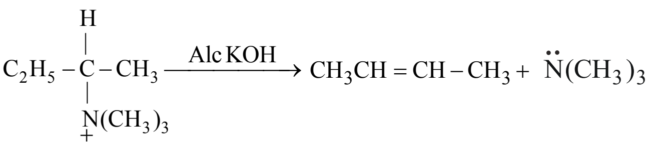
(c) electrophilic addition　(d) nucleophilic addition

35. Which of the following reactions is elimination reaction?

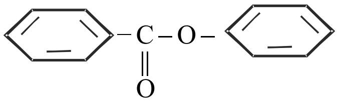
(a) 

(b) $C_2H_5Cl+KOH\rightarrow C_2H_5OH+KCl$

(c)


$C_2H_5-\underset{\underset{\overset{+}{N}(CH_3)_3}{|}}{\overset{\overset{H}{|}}{C}}-CH_3\xrightarrow{\text{Alc KOH}}CH_3CH=CH-CH_3+\ddot{N}(CH_3)_3$

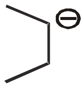
(d) None of them

36.  electrophilic substitution will occur at

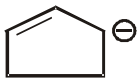
(a) meta in second ring
(b) ortho/para in the first ring
(c) meta in the first ring
(d) ortho/para in the second ring

37. The correct order of the stability of the following carbanions is

(i) $R\overset{\ominus}{C}H_2$

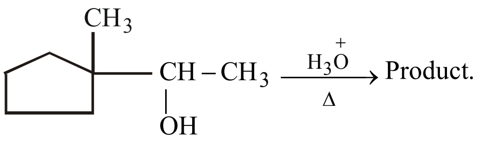
(ii) 

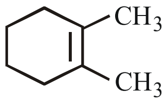
(iii) 

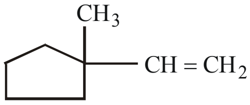
(iv) 

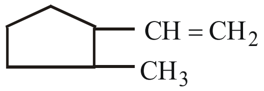
(a) III > IV > I > II
(b) I > II > III > IV
(c) I > III > II > IV
(d) IV > III > II > I

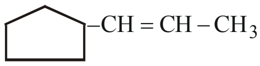
38. The major product of dehydration of the following



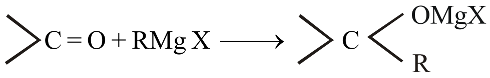
(a) 

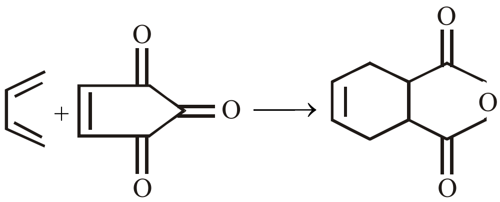
(b) 

(c) 

(d) 

39. Which among the following is substitution reaction ?

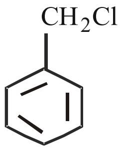
(a) 

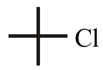
(b) 

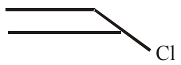
(c) $R_3COH \xrightarrow[\text{Conc.HCl}]{\text{Anhy.ZnCl}_2}$ Turbidity

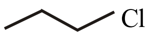
(d) All of these

40. Which of the following reactions cannot proceed by S_N1 mechanism ?

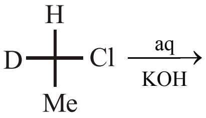
(a) 

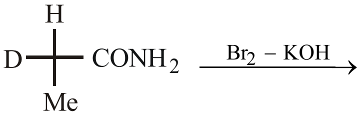
(b) 

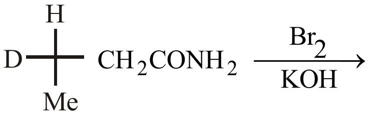
(c) 

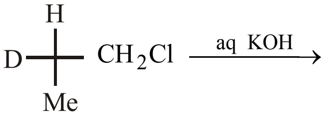
(d) 

41. The change occuring with conversion of configuration

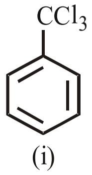
(a) 
$D-\overset{H}{\underset{Me}{C}}-Cl \xrightarrow[\text{KOH}]{\text{aq}}$

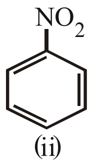
(b) 
$D-\overset{H}{\underset{Me}{C}}-CONH_2 \xrightarrow{Br_2-KOH}$

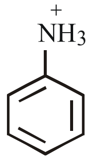
(c) 
$D-\overset{H}{\underset{Me}{C}}-CH_2CONH_2 \xrightarrow[\text{KOH}]{Br_2}$

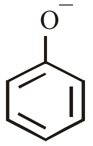
(d) 
$D-\overset{H}{\underset{Me}{C}}-CH_2Cl \xrightarrow{\text{aq KOH}}$

42. In which case the $\overset{+}{NO_2}$ will attack at the meta position


(i)


(ii)


(iii)


(iv)

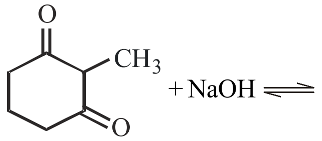
(a) I, II, III
(b) II, IV
(c) II and III only
(d) II only

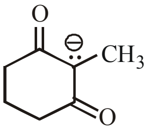
43. Arrange the following in order of decreasing basicity

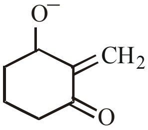
A. CH_3CH_2MgBr
B. $HC\equiv CMgBr$
C. CH_3CH_2OMgBr

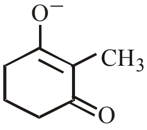
(a) A > C > B
(b) A > B > C
(c) C > B > A
(d) B > A > C

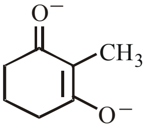
44. Which of the following is not a resonance form of the enolate ion formed in the following acid base equilibrium



(a) 

(b) 

(c) 

(d) 

Hints & Solutions

EXERCISE 1

1. No. It is 1°.

2. (i) $-NO_2 > -CN > -COOH > -F > -I$

   (ii) $-C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3 > -CH_3 > -D$.

4. (i) $C_6H_5CH_2\dot{C}H_2 < C_6H_5\dot{C}HCH_3 < C_6H_5\dot{C}(CH_3)_2 < C_6H_5\dot{C}H{-}CH{=}CH_2$.

   (ii) $(CH_3)_3C^+ > C_6H_5CH_2^+ > CH_2{=}CHCH_2^+ > CH_3CH_2^+$

   (iii) $(CH_3)_2CH^- < CH_3CH_2^- < CH_3^- < CH_2{=}CH^- < C_6H_5CH_2^- < HC \equiv C^-$.

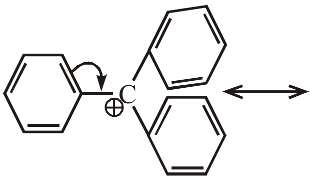
8. (i) *Nucleophiles :* $:\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{I}}:$, $H_3N:$

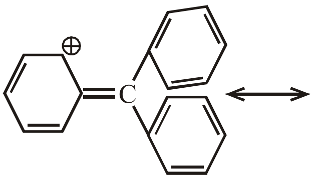
   (ii) *Electrophiles :* $BeCl_2$ and NO_2^+

   (iii) *Both :* $CH_3C \equiv N:$ and $H_2C = \ddot{C}:$

   (iv) Neither : CH_4 and H_2.

10. Stabilised due to nine possible canonical structures.





Other canonical structures

16. (b) 17. (a) 18. (b) 19. (b) 20. (d) 21. (b)

22. (a) 23. (b) 24. (b)

EXERCISE 2

1. **(a)** Greater the electronegativity, higher is the -I effect. Thus $-F > -OR > -NR_2$

2. **(d)** Due to – I effect of the – CHO group, oxygen acquires-δ - charge and the terminal carbon acquires δ + charge.

$$\overset{\delta+}{C}H_2 = CH - \underset{\substack{|\\H}}{C} = \overset{\delta-}{O}$$

3. **(b)** 4. **(c)**

5. **(b)** Homolytic fission of the C – C bond gives free radicals in which carbon is sp²- hybridised.

6. **(b)** In carbocations, carbon bearing positive charge is always sp²-hybridised

7. **(d)** Higher the possibility of delocalisation of the positive charge, greater is stability of the species. Thus

$$C_6H_5\overset{+}{C}H_2 > (CH_3)_3C^+ > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2$$

Benzyl carbocation is more stable than *tert*-butyl due to resonance in the former.

8. **(b)** Structure (*b*) is a 3° carbocation, while (*a*) is 2° and (*c*) and (*d*) are 1° carbocations; thus (*b*) is the most stable.

9. **(a)** Higher the possibility of delocalisation, greater is its stability; in $C_6H_5\overset{+}{C}HC_6H_5$, +ve charge can delocalise over two benzene rings.

10. **(a)** Same as above, in Ph_3C^+, +ve charge can delocalise over three benzene rings.

11. **(a)** I. $C_6H_5\overset{+}{C}H_2$ 1° Benzylic II. $C_6H_5CH_2\overset{+}{C}H_2$ 1°

   III. $C_6H_5\overset{+}{C}HCH_3$ 2° benzylic IV. $C_6H_5\overset{+}{C}(CH_3)_2$ 3° benzylic

   3° Benzylic (IV) > 2° Benzylic (III) > 1° Benzylic (I) > 1° (II)

12. **(d)** $-NO_2$ group, being strong electron-withdrawing, disperses the –ve charge, hence stabilizes the concerned carbanion.

13. (b) $C_6H_5CH_2^- > CH_3CH_2^- > (CH_3)_2CH^- > (CH_3)_3C^-$

Dispersal of –ve charge due to resonance and - I effect

Intensification of –ve charge due to + I effect of CH_3 gps.

14. (b) $C_6H_5\dot{C}HCH_3$ is a 2° benzylic free radical, hence stabilized most due to resonance.

15. (c)

16. (b) Dichlorocarbene, $:CCl_2$ (a carbene) is the electrophile formed as an intermediate in Reimer-Tiemann reaction.

17. (b) **18. (c)**

19. (d) BF_3 has electron deficient B, hence it is an electrophile.

20. (c) H_2 has no lone pair of electrons, hence cannot function as a nucleophile.

21. (a) Due to the presence of a lone pair of electrons on N, $CH_3C \equiv N:$ acts as a nucleophile. Further due to greater electronegativity of N than C, the C atom of $- C \equiv N$ carries a positive charge and hence behaves as an electrophile.

22. (c)

23. (c) Nucleophilicity increases with the decrease in electronegativity of the central atom. Since electronegativity follows the order: F > O > N > C; nucleophilicity of the concerned group will follow the reverse order i.e.,

$$CH_3^- > NH_2^- > OH^- > F^-$$

24. (a) Stronger the acid, weaker the conjugate base. Since acid character follows the order

$$H_2O > NH_3 > HC \equiv CH > CH_3 - CH_3$$

(Acid character),

the basic character of their conjugate bases decreases in the reverse order, i.e.,

$$CH_3CH_2^- > HC \equiv C^- > NH_2^- > OH^- \quad \text{(Basic character)}$$

25. (d)

26. (c) All resonating structures should have same number of electron pairs.

27. (a) The two structures involve only movement of electrons and not of atoms or groups, hence these are resonating structures.

28. (c) In structure (*c*), nitrogen has 10 electrons in the valence shell which is not possible.

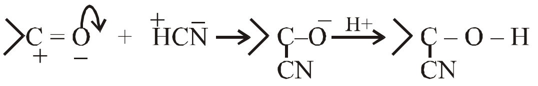
29. (b) Only structure (*b*) has a conjugated system, which is necessary for resonance.

30. (c)

31. (a) Since the given heat of hydrogenation of the diene is less (230 kJ mol^{-1}) than the heat of hydrogenation of two isolated double bonds, i.e. 126 × 2 = 252 kJ mol^{-1}, the diene must be conjugated, i.e., it should be 1,3 - hexadiene, $CH_2 = CH - CH = CH\,CH_2\,CH_3$.

32. (a) **33. (b)** **34. (c)**

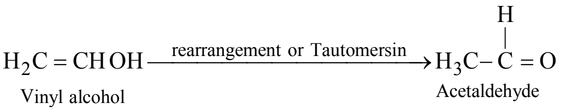
35. (c)



$$>\underset{+}{C} = \underset{-}{O} + \overset{+}{H}C\bar{N} \rightarrow >\underset{CN}{C}-\bar{O} \xrightarrow{H+} >\underset{CN}{C} - O - H$$

Since first attack is nuclephilic in nature (by CN^-) hence the addition is nuclophilic addition.

36. (c)



$$\underset{\text{Vinyl alcohol}}{H_2C = CH\,OH} \xrightarrow{\text{rearrangement or Tautomersin}} \underset{\text{Acetaldehyde}}{H_3C - \overset{H}{C} = O}$$

EXERCISE 3

1. (a) Nucleophilicity increases down the periodic table.

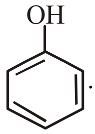
$$I^- > Br^- > Cl^- > F^-$$

2. (c) Electrophiles have high affinity for electrons. They attack at the site where electron-density is highest. Electron donating groups increases the electron density. The electron donating tendency decreases in the order :

$$–OH > –CH_3 > –H > –Cl$$

Therefore, the correct order of reactivity towards electrophile is

$$C_6H_5OH > C_6H_5CH_3 > C_6H_6 > C_6H_5Cl$$

3. (c) Out of the given compounds the most reactive towards electrophilic attack is . Phenol forms phenoxide ion which is stable due to resonance i.e. the correct answer is option (c).

4. (d) The amount of *s*-character in various hybrid orbitals is as follows.

$sp = 50\%$, $sp^2 = 33\%$ and $sp^3 = 25\%$

Therefore s character of the C – H bond in acetylene (*sp*) is greater than that of the C – H bond in alkene (sp^2 hybridized) which in turn has greater *s* character of the C – H bond than in alkanes. Thus owing to a high s character of the C – H bond in alkynes, the electrons constituting this bond are more strongly held by the carbon nucleus with the result the hydrogen present on such a carbon atom can be easily removed as proton. The acidic nature of three types of C – H bonds follows the following order

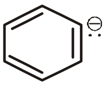
$-C \equiv C - H > - C = C - H > - C - C - H$

Further, as we know that conjugate base of a strong acid is a weak base, hence the correct order of basicity is

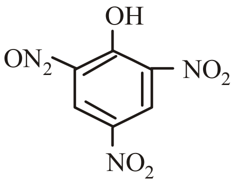
$$H - C \equiv \bar{C} < CH_2 = \bar{C}H < \bar{C}H_2 - CH_3$$

5. **(d)** The stability of carbanions is affected due to resonance, inductive effect and s - character of orbitals. Greater the number of groups having + I group (alkyl group) lesser stable would be the carbanion.

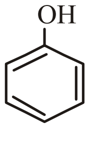
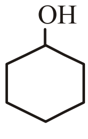
Further stability of carbanion decreases with decrease in s-character. Benzene carbanions are stablized due to resonance, hence the correct order is

$R - C = \bar{C} > R_2C = \overset{\ominus}{C}H >$  $> R_3C - \overset{\ominus}{C}H_2$

The correct order of stability of given carbanion is in the order I > III > II > IV.

6. **(a)**  $> CH_3COOH >$

(III) (II)

 > 

(IV) (I)

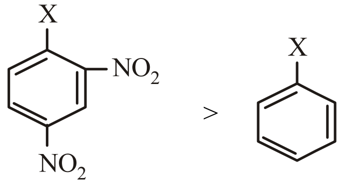
Explanation : Presence of three $-NO_2$ groups in *o*–, *p*– positions to phenolic groups (in III) makes phenol strongly acidic because its corresponding conjugate base is highly stabilised due to resonance. Conjugate base of CH_3COOH, II (*i.e.* CH_3COO^-) is resonance hybrid of two equivalent structures. The conjugate base of phenol, IV is stabilized due to resonance (note that here all resonating structures are not equivalent). The conjugate base of cyclohexanol, I does not exhibit resonance, hence not formed.

7. **(a)** Tertiary alkyl halide is most reactive towards nucleophilic substitution because the corresponding carbocation (3°) is most stable. Aryl halide is least reactive due to partial double bond character of the C – Cl bond.

Presence of $-NO_2$ groups in *ortho* and *para* positions increases the reactivity of the – Cl towards nucleophiles.

$(CH_3)_3 - C - X > (CH_3)_2 - CH_2 - X >$

III IV



II I

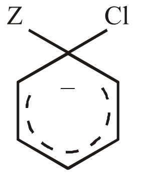
or I < II < IV < III

8. **(d)** Cl^- is the weakest base and hence better leaving group

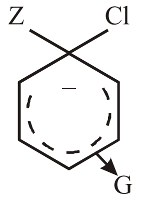
9. **(b)** Due to + M effect of – OH group and hyperconjugation of $-CH_3$ group.

10. **(c)** Because of high electronegativities of the halogen atom, the carbon halogen (C – X) is highly polarised covalent bond. Thus, the carbon atom of the C – X bond becomes a good site for attack by nucleophiles (electron rich species). Nucleophilic substitution reactions are the most common reactions of alkyl halides.

11. **(a)** In S_NAr reactions, a carbanion is formed as an intermediate, so any substituent that increases the stability of carbanion and hence the transition state leading to its formation will enhance the S_NAr reactions. To compare the rates of substitution in chlorobenzene, chlorobenzene having electron-withdrawing group, and chlorobenzene having electron-releasing group, we compare the structures carbanion I (from chlorobenzene), II (from chlorobenzene containing electron-withdrawing group) and III (from chlorobenzene containing electron-releasing group).

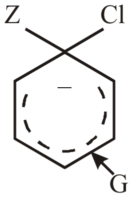


I



II

G withdraws electrons, neutralises (disperses) –ve charge of the ring, stabilises carbanion, facilitates S_N reaction ***(activation effect)***

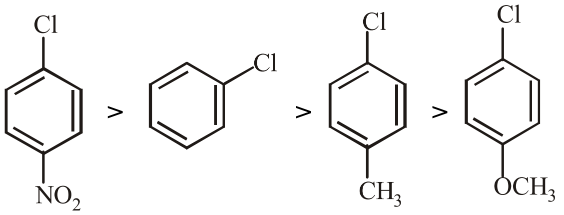


III

G releases electrons, intensifies –ve charge, destabilizes carbanion, retards S_N reaction ***(deactivation)***

NO_2 is activating group and CH_3 and OCH_3 are deactiving group.

Hence, the correct order of nucleophilic substitution reactions



12. **(c)** Decreasing order of deactivating effect of the given *m*-directing group is

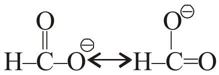
$> NO_2 > -CN > -SO_3H > -COOH$

—NO_2 group is most deactivating group due to strong – E, – I and – M effects.

13. **(b)** –CH_3 group has +I effect, as number of –CH_3 group increases, the inductive effect increases.

14. **(b)** The reaction is nucleophilic sustitution reaction

15. **(b)**



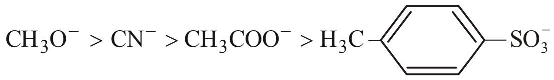
$H-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O} \longleftrightarrow H-\overset{\overset{O^{\ominus}}{|}}{C}=O$

16. **(c)** Cl^- is the best leaving group among the given options.

17. **(d)** Free radicals are electrically neutral, unstable and very reactive on account of the presence of odd electrons.

18. **(b)** The stronger the base the more is the nucleophilic character and vice versa.

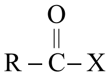
Basic character



$CH_3O^- > CN^- > CH_3COO^- > H_3C-C_6H_4-SO_3^-$

Hence the nucleophilic character.

19. **(d)**



$R-\overset{\overset{O}{\|}}{C}-X$; when X is Cl the C–X bond is more polar and ionic which leaves the compound more reactive for nucleophilic substitution reaction.

20. **(b)** The order of stability of free radicals

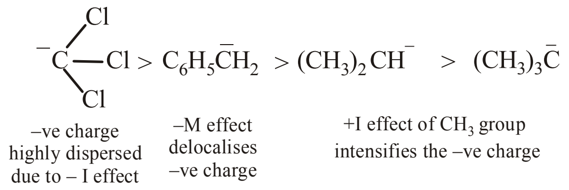
$$(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H$$

The stabilisation of first two is due to resonance and last two is due to inductive effect.

21. **(a)** Nitro group is electron withdrawing group, so it deactivates the ring towards electrophilic substitution.

22. **(b)** In option (b) the complex formed is with benzene whereas in other cases it is formed with nitrobenzene with –NO_2 group in different position (*o*-, *m*-, *p*-). The complex formed with nitrobenzene in any position of –NO_2 group is less stable than the complex formed with benzene so the correct answer is (b). The most stable complex has lowest energy.

23. **(b)**



$^-CCl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2CH^- > (CH_3)_3\bar{C}$

–ve charge highly dispersed due to – I effect

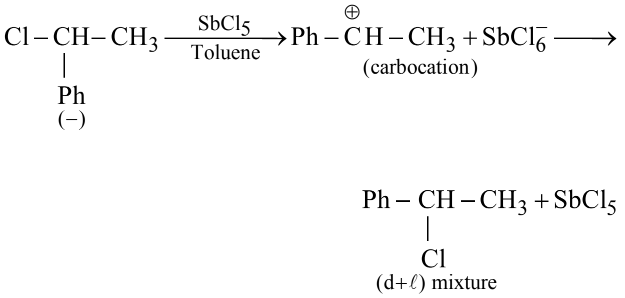
–M effect delocalises –ve charge

+I effect of CH_3 group intensifies the –ve charge

24. **(d)** The correct order of basicity is

$RCOO^- < CH \equiv C^- < -NH_2 < R^-$

25. **(c)** Carbocations are planar hence can be attacked on either side to form racemic mixture.



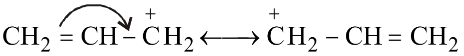
$$\underset{\underset{(-)}{Ph}}{Cl-\underset{|}{C}H-CH_3} \xrightarrow[\text{Toluene}]{SbCl_5} Ph-\overset{\oplus}{C}H-CH_3 + SbCl_6^- \longrightarrow$$

(carbocation)

$$Ph-\underset{\underset{Cl}{|}}{C}H-CH_3 + SbCl_5$$

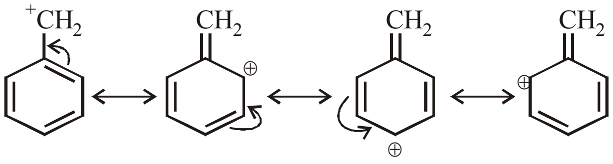
(d+ℓ) mixture

26. **(d)** Higher stability of allyl and aryl substituted methyl carbocation is due to dispersal of positive charge due to resonance



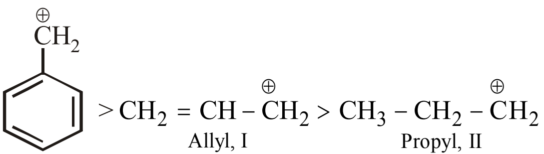
$CH_2 = CH - \overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2 - CH = CH_2$

Resonating structures of allyl carbocation



Resonating structures of benzyl carbocation

whereas in alkyl carbocations dispersal of positive charge on different hydrogen atoms is due to hyperconjugation. Hence the correct order of stability will be



$C_6H_5\overset{\oplus}{C}H_2 > CH_2 = CH - \overset{\oplus}{C}H_2 > CH_3 - CH_2 - \overset{\oplus}{C}H_2$

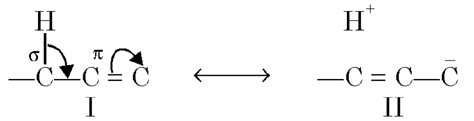
Benzyl, III

Allyl, I

Propyl, II

27. **(a)** Due to similar charges on adjacent atoms, the structure (a) is least stable.

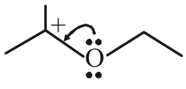
28. **(b)** Alkyl groups with at least one hydrogen atom on the α-carbon atom, attached to an unsaturated carbon atom, are able to release electrons in the following way.



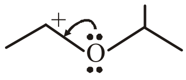
Note that the delocalisation involves σ and π bond orbitals (or *p* orbitals in case of free radicals) ; thus it is also known as σ – π **conjugation.** This type of *electron release due to the presence of the system* H—C—C = C is known as **hyperconjugation**

29. **(d)** The correct stability order is

I > III > II > IV


I

+ M effect, 6 hyper-conjugative H's, 2 CH_3 groups (+ I effect)


III

+ M, 3 hyperconjugative H's, one CH_3 group

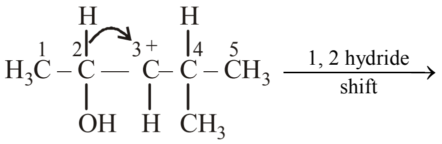

II

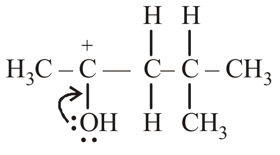
5 hyperconjugative H's 2 R groups


IV

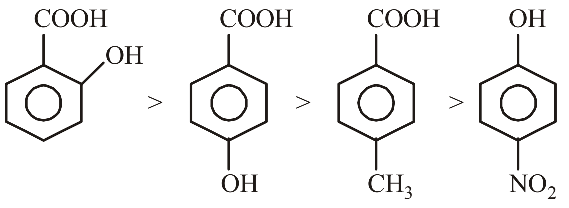
5 hyperconjugative H's one R group

30. **(d)** Migrating tendency of hydride is greater than that of alkyl group. Further migration of hydride from C–2 gives more stable carbocation (stabilized by +R effect of OH group and +I and hyperconjugative effects of methyl group).

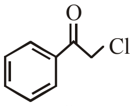
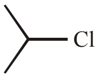



More stable carbocation

31. **(c)** *o*-Hydroxybenzoic acid is strongest acid and the decreasing order of acidity is



32. **(b)**

Compounds		: CH_3-Cl :	 :	
	S	P	R	Q
Relative reactivities towards S_{N^2} reaction	1,00,000 :	200 :	79 :	0.02

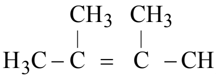
EXERCISE 4

1. **(d)** During E_2 elimination the double bond goes mainly toward the least hindered carbon

2. **(c)** The intermediate planar carbonium ion has equal chances to be attacked from either side leading to racemisation

3. **(a)** $R_3\overset{+}{C}$ has three pairs of electrons in three bonds

4. **(b)** It is free radical addition (See mechanism of peroxide effect)

5. **(b)** 
$H_3C-\underset{}{\overset{CH_3}{\overset{|}{C}}}=\overset{CH_3}{\overset{|}{C}}-CH_3$. The more substituted alkenes have greater number of hyperconjugated forms. Hence they are more stable

6. **(b)** The octet around N is complete, hence it has no electrophilic character. N has no unshared pair of electrons to act as nucleophile

7. **(d)** $SbCl_5$ pulls Cl^- to form $SbCl_6^-$ leaving behind planar $C_6H_5-\overset{+}{C}H-CH_3$ carbonium ion. It can be attacked from either side leading to racemic mixture.

8. **(b)** When in $R_2C:$ (substituted carbene), the two electrons are present in the same orbital with opposite spin it is called singlet state.

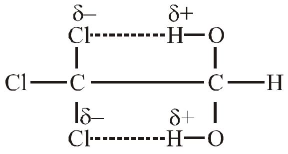
9. **(c)** It is nucleophilic substitution reaction. The nucleophile is OH^- obtained from KOH

10. **(a)** 3 - Halopentane will always give pentene -2 on dehydrohalogenation

11. **(a)** SO_3 is an electrophile since it can accept a lone pair of electrons in α- subshell

12. **(c)** Dehydration of alcohol always leads to the intermediate formation of carbonium ion. In case of n- propyl alcohol, the intermediate $CH_3-CH_2-\overset{+}{C}H_2(1°)$ rearranges to more stable $CH_3-\overset{+}{C}H_2-CH_3(2°)$ ion.

13. (a) Chloral hydrate is stabilised by H - bonding



14. (c) $CH_2=CH-\ddot{\underset{..}{Cl}}: \leftrightarrow \overset{-}{C}H_2-CH=\overset{+}{\underset{..}{Cl}}:$ a double bond is formed between C and Cl. Hence it is less reactive due to resonance

15. (b) $(CH_3)_3COH$ gives tert $(CH_3)_3C^+$. The order of stability of carbonium ions is $3° > 2° > 1° > \overset{+}{C}H_3$

16. (c) Due to hyperconjugation toluene is most reactive for electrophilic substitution reaction (see theory)

17. (d) Chlorinolysis is substitution by chlorine

18. (d) It gives trans - 2 - butene

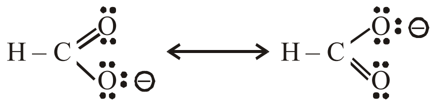
19. (d) In I the unshared pair of electrons on N always available for protonation in III due to presence of electronegative O atom the electron density on N is decreased . In II and IV resonance suppresses the basic character

20. (b) The more the electrons withdrawing groups attached to - O atom, the more is the ease of leaving

21. (b) The addition of HCl to propene proceeds by ionic mechanism and not by free radical mechanism. Hence it forms intermediate carbonium ion

22. (c) $BrCH_2CH_2CO_2H$ is the weakest acid as Br has less -I effect compared to F and is also far from $-CO_2H$ group.

23. (c) Formate ion



Hence A, B bonds are of same length.

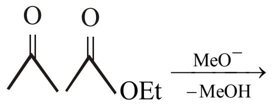
24. (a) The order of stability of resonating structures carrying no charge > carrying minimum charge and each atom having octet complete.

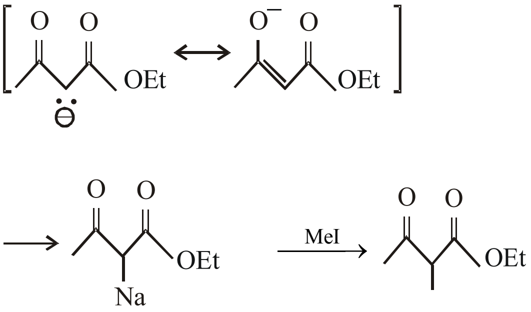
25. (d) In A nitrogen is bivalent, in B and C carbon is pentavalent.

26. (c) The degree of unsaturation is equal to number of hydrogen molecules needed to convert the given compound into an alkane.

27. (b) In (b) the pair has resonance.

28. (b)

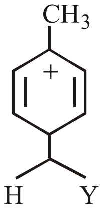




29. (a) Five membered ring is being converted into six membered ring. Hence the sixth bond must come from within the ring.

30. (a) HI does not add on to propene by peroxide effect. Even in presence of peroxide the addition is according to Markownikoff's rule forming intermediate carbonium ion.

31. (d) The structure



carring +ve charge nearest to electrons repelling $-CH_3$ group is most stable.

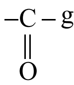
32. (a) In (a) the separation of charges is maximum and electronegative atom oxygen carry –ve charge.

33. (c) correct. (See text.)

34. (c) Addition reactions of alkenes are known as electrophilic addition reactions.

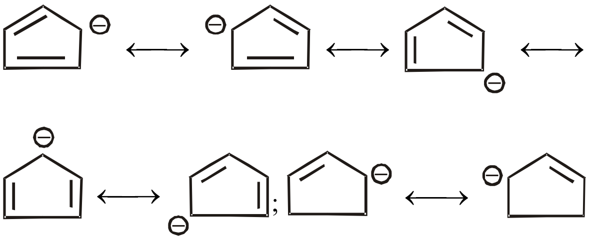
35. (c) The reaction (c) is Hoffmann elimination (see Reaction Mechanisms.)

36. (d) The second ring has o/p directing O-atom and first ring has m-directing

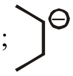


$-\underset{\underset{O}{\|}}{C}-$ group. o/p directing group activate the benzene nucleus.

37. (a)

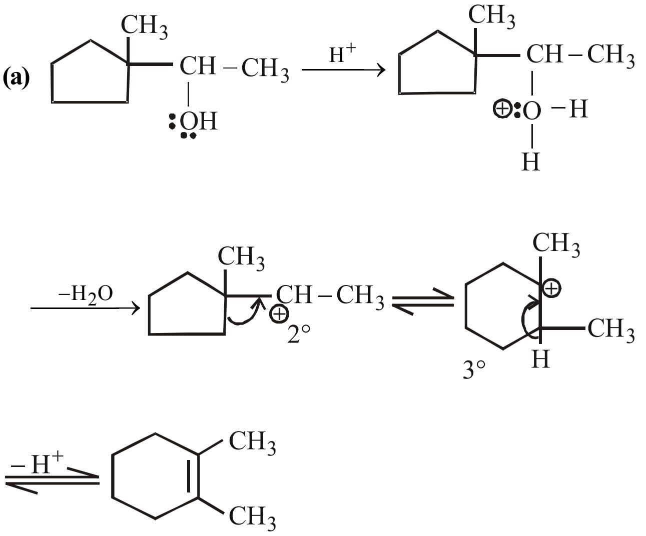


$\overset{\ominus}{R}CH_2$(1°);



(2°)

38. (a)



39. (c) $R_3COH \xrightarrow[\text{Conc. HCl}]{\text{Anhy. ZnCl}_2} R_3C.Cl$

It is substitution reaction. $R_3C.Cl$ being insoluble in H_2O give turbid solution.

40. (d) Aliphatic halides react by S_N2 mechanism.

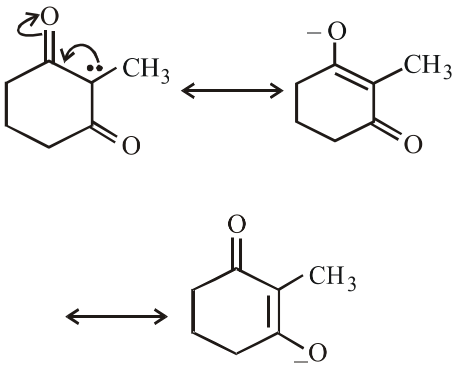
41. (a) CH_3CHDCl is 1° alkyl halide, react with aq. KOH by S_N2 mechanism which always leads to inversion of configuration.

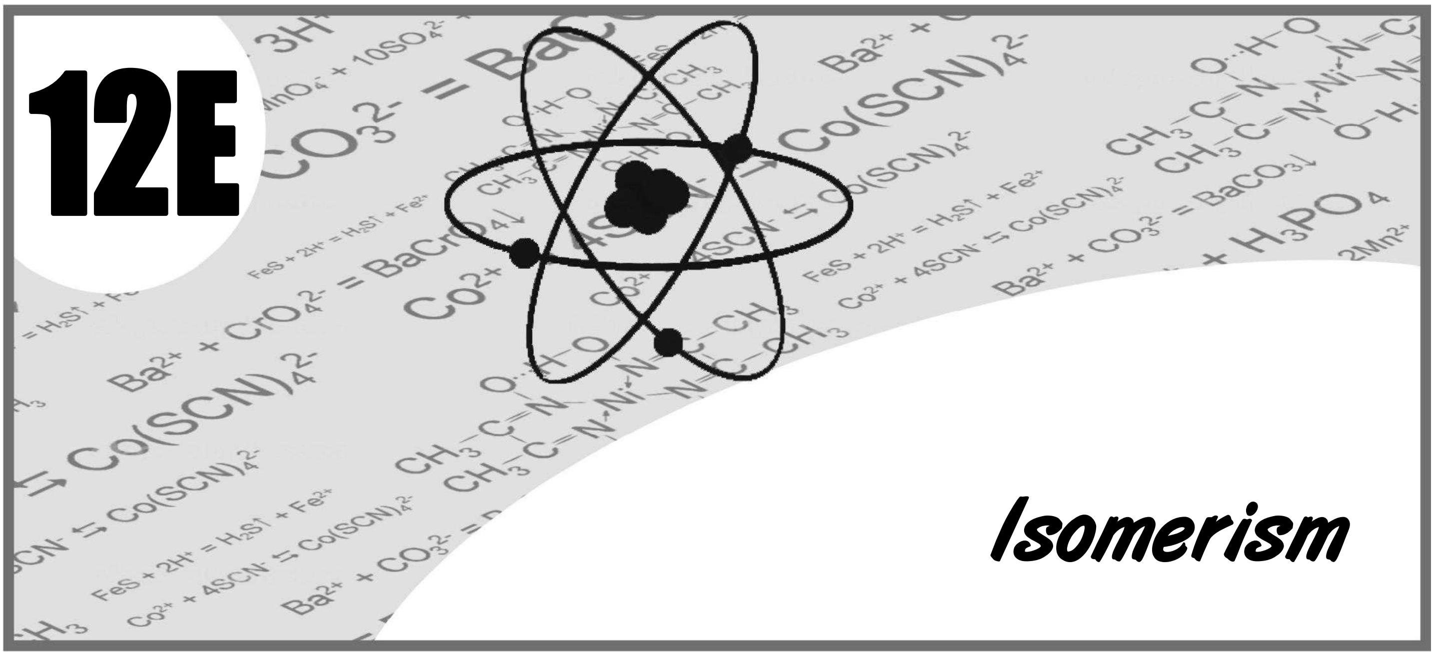
42. (a) $-CCl_3, -NO_2$ and $-\overset{+}{N}H_3$ are m - directing in nature.

43. (b) $CH_3\overset{-}{C}H_2 > HC \equiv C^- > CH_3CH_2O^-$ basic character. The acid character being

$CH_3CH_2OH > HC \equiv CH > CH_3CH_3$. The weaker the acid, the stronger the base (conjugate pair)

44. (b) (a),(c) and (d) are resonating structures.





12E

Isomerism

ISOMERISM

Berzelius introduced the term Isomer (Gr. Isos=Same, Mers=parts) to different compounds with the same molecular formula and the phenomenon was called Isomerism.

Types of isomerism : There are two main types of Isomerism

(i) ***Structural or constitutional isomerism :*** It is due to difference in the arrangement of atoms within the molecule.

(ii) ***Stereo isomerism or space isomerism :*** It is due to different spatial arrangement of some atoms and groups.

Types of structural isomerism

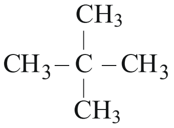
(i) ***Chain isomerism :*** This is due to difference in the structure of the carbon chains. Examples.

$CH_3CH_2.CH_2.CH_2–CH_3$

n-Pentane

$(CH_3)_2CH–CH_2–CH_3$

Iso-Pentane



$CH_3–C(CH_3)_2–CH_3$

Neo-Pentane

(ii) ***Functional isomerism :*** This is due to difference in the functional groups

C_2H_5OH ethyl alcohol — CH_3OCH_3 dimethyl ether

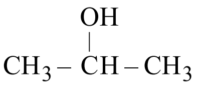
CH_3COOH Acetic acid — $HCOOCH_3$ Methyl formate

CH_3CH_2CHO Propionaldehyde — CH_3COCH_3 Acetone.

(iii) ***Position or region isomerism :*** This is due to difference in the positions of the same functional groups

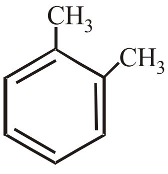
$CH_3 – CH_2 – CH_2OH$

n- Propyl alcohol

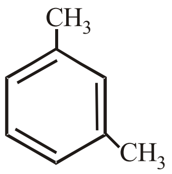


$CH_3 – CH(OH) – CH_3$

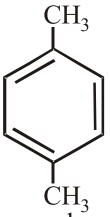
Iso - Propyl alcohol



o-xylene



m-xylene



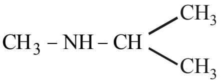
p-xylene

Position Isomers are also Known as **regiomers**.

(iv) ***Metamerism :*** This is due to different alkyl groups attached to the same functional group.

$CH_3–NH–CH_2CH_2CH_3$

Methyl n-propyl amine



$CH_3 – NH – CH(CH_3)_2$

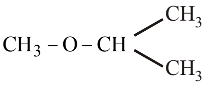
Methyl Isopropyl amine

$C_2H_5NH.C_2H_5$

Diethyl amine

$CH_3 – O – CH_2CH_2CH_3$

Methyl n-propyl ether



$CH_3 – O – CH(CH_3)_2$

Methyl Isopropyl ether

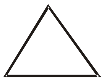
$C_2H_5 – O – C_2H_5$

Diethyl ether

(v) ***Ring chain isomerism :*** Cyclic/acyclic Isomerism

$CH_3 – CH = CH_2$

Propene



Cyclopropane

$CH_3 – CH_2 – CH = CH_2$

But–1–ene

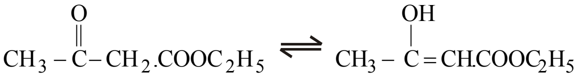
Cyclobutane

(vi) ***Tautomerism (Tauto = Same, Mers = Parts) :*** It is due to the presence of a mobile atom in the molecule and the same substance behaves in such a way as if it is a mixture of two or more compounds. Further we have *(a)* ***Dyad system*** *:* When the mobile atom oscillates between two adjascent atoms eg

$$H-C\equiv N \rightleftharpoons H-N\equiv C$$

Hydrocyanic acidIso-hydrocyanic acid

(b) ***Triad system*** *:* When the mobile atom oscillates between atoms one position ahead eg.



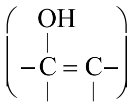
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2.COOC_2H_5 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CH.COOC_2H_5$$

93% Keto form 7% Enol form

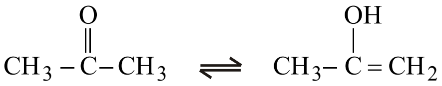
Aceto acetic ester Aceto acetic ester

Aceto acetic ester reacts with HCN, NH_2OH, $C_6H_5NHNH_2$ showing the properties of a ketone and also reacts with CH_3COCl, PCl_5, Na showing the properties of OH group.

It gives colour change with 1% $FeCl_3$ a characteristic

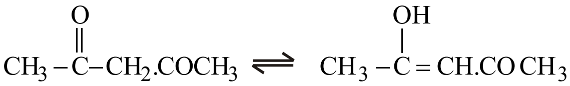
test of  $\left(\begin{array}{c}OH\\ |\\ -C=C-\\ |\quad\ |\end{array}\right)$ (enol group)

There exists an equilibrium between the two forms which is dynamic in nature.



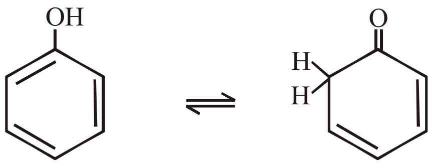
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CH_2$$

Acetone 99.5% Acetone (enol form) 0.5%



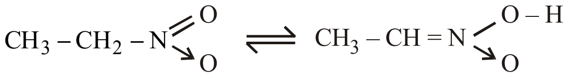
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2.COCH_3 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CH.COCH_3$$

Acetyl acetone (keto form) Acetyl acetone (enol form)



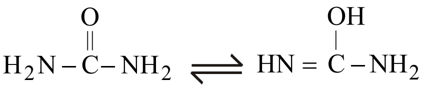
Phenol Keto form of Phenol

Triad system containing nitrogen



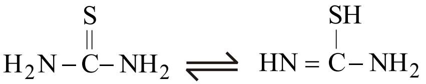
Nitro ethane Aci Nitro ethane

It dissolves in NaOH on account of aci form. Tautomeric form which is less stable is called **labile form.**



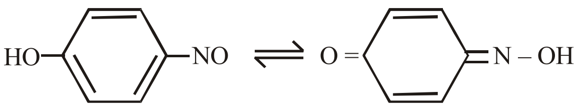
$$H_2N-\overset{\overset{O}{\|}}{C}-NH_2 \rightleftharpoons HN=\overset{\overset{OH}{|}}{C}-NH_2$$

Urea (Keto form) Enolic form



$$H_2N-\overset{\overset{S}{\|}}{C}-NH_2 \rightleftharpoons HN=\overset{\overset{SH}{|}}{C}-NH_2$$

Thio Urea Enolic form



p-Nitrosophenol Keto form

Types of stereo isomerism :

(I) Optical Isomerism

(II) Geometrical Isomerism and

(III) Conformational Isomerism

(I) ***Optical isomerism :*** The compounds having the same molecular formula, the same structural formula but different behaviour towards the plane polarised light are known as Optical Isomers.

Terminology used in optical isomerism.

- ***Plane polarised light :*** Light having vibrations restricted to one plane only is called plane polarised light.
- ***Optically active compounds*** : The compounds capable of rotating the plane of polarisation of plane polarised light are known as optically active compounds.
- ***Optical activity :*** It is the ability of a substance to rotate the plane of polarisation of plane polarised light.
- ***Dextrorotatory compounds (d or +) :*** The compounds which rotate the plane of polarisation of plane polarised light towards the right hand side are called dextro rotatory.
- ***Laevo rotatory compounds (l or –)*** *:* The compounds which rotate the plane of polarisation of plane polarised light towards the left hand side are called laevo rotatory.
- ***Specific rotation :*** The rotatory power of optically active compounds is compared in terms of specific rotation.

Specific rotation

$$=\frac{\text{Observed rotation in degrees}}{\text{Length of tube in decimeter}\times\text{Concentration of solution in g/ml}}$$

$$[\alpha]_D^t=\frac{\theta}{\ell\times C}$$

- D corresponds to D line of Sodium light ($\lambda = 5893Å$)
- t corresponds to temperature
- Rotation is observed and measured with a polarimeter The specific rotation varies with light λ and temperature.
- ***Optical activity due to crystalline strcuture :*** Some compounds are optically active only in crystalline form. They loss their optical activity when dissolved or fused e.g. Quartz.
- ***Optical activity due to molecular structure :*** Some compounds are optically active in solid as well as in solution e.g. tartaric acid. Hence their optical activity is due to their molecular structure which remains the same in solid form and in solution.

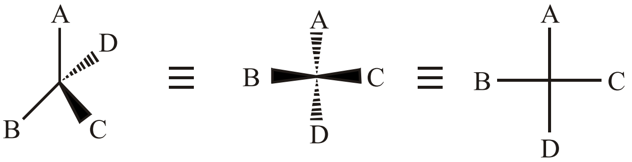
- ***Asymmetric carbon atom :*** A carbon atom attached to four different atoms and groups is called asymmetric carbon atom. e.g. $CH_3\overset{*}{C}HOHCOOH$.
- ***Chirality :*** If the mirror image of the molecule is different from the molecule it is said to be a chiral molecule. In such case if one configuration of the molecule is placed above its mirror image configuration, the similar atoms and groups do not fall over each other and the configurations are said to be **nonsuperimposable**.

If object and mirror image configurations are superimposable (similar atoms and groups fall over each other) the molecule is said to be ***"achiral"***.

Chirality is the necessary condition for a compound to be optically active.

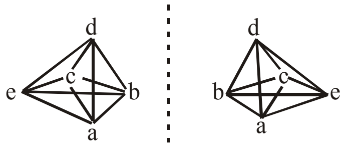
Enantiomers : Pairs of nonsuperimposable mirror images are called enantiomers.

Fischer Projections : Fischer projections are drawn with a cross, with chiral atom at the centre of the cross.

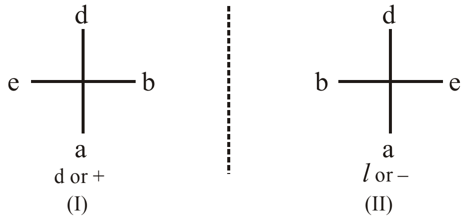


The horizontal line represents **wedges** (bonds) coming out of the plane of the paper. The vertical line represents dashed lines (bonds) in the plane of the paper (Bow-tie convention). The carbon chain is drawn along the vertical line of the projection with most highly oxidised carbon substituent at the top. Fischer projections are very useful to determine chirality of a compound.

Lebel and Van't Hoff's theory about optical isomerism : The tetrahedral structure of a compound containing asymmetric carbon atom (*Cabed) gives two configurations related to each other as object and its mirror image but are non-superimposable.

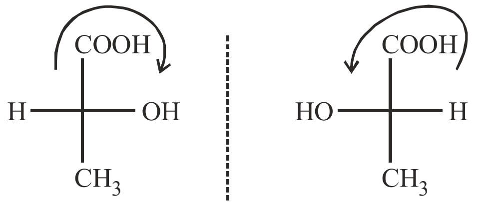


d or + Enantiomers   ℓ or – or Enantiomorphs



Enantiomers or Enantiomorphs

Optical isomerism of Lactic acid : $CH_3\overset{*}{C}HOH.COOH$

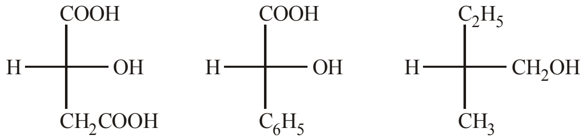


Dextrorotatory (d or +) Lactic acid (Source meat extract)

Laevorotatory ($l$or –) Lactic acid (Obtained during fermentation of Sucrose)

Racemic Lactic acid : It is an equimolar mixture of d- and l- forms. It is optically inactive due to external compensation of optical rotation. It is present in sour milk. It can be resolved.

Examples of optically active compounds containing one asymmetric C-atom.



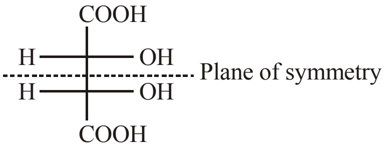
Malic acid   Mandelic acid   Amyl alcohol

Number of optically active forms is given by $\mathbf{2^n}$ where **n** is number of asymmetric C-atoms different in nature.

Resolution : The separation of d- and l- forms present in a racemic mixture is known as resolution.

Conditions for Chirality : Absence of *(I)* ***Plane of symmetry*** *(II)* ***Centre of symmetry*** and *(III)* ***Alternating axis of symmetry***.

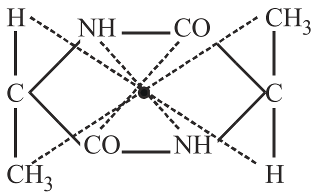
Plane of Symmetry : A plane which divides the molecule in two portions in such a way that one portion is the mirror image of the other eg. Tartaric acid.



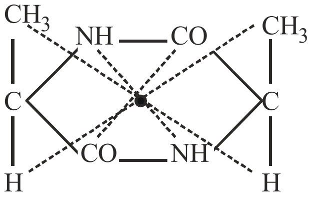
Meso tartaric acid

It is optically inactive due to internal compensation of optical rotation. It can not be resolved.

Centre of Symmetry : It is a point from which lines, when drawn on one side to meet the groups and produced to an equal distance on the other side of the point will meet the same original groups.

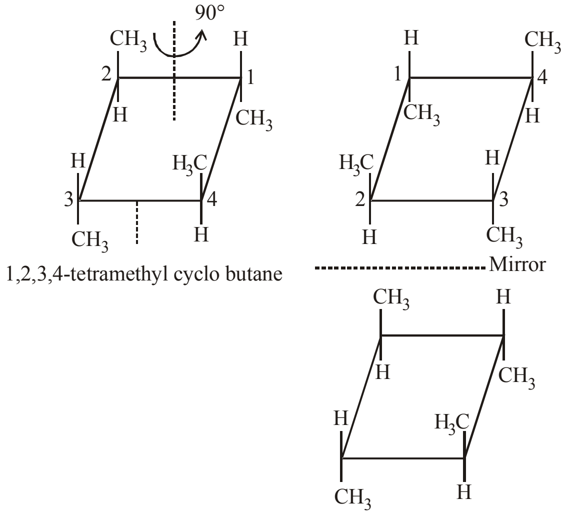


Trans:1,4-dimethyl diketo piperazino (Inactive)
Contains centre of symmetry



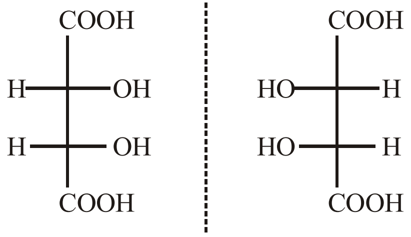
cis: 1,4-dimethyldiketo piperazino (Active)
No centre of symmetry

Alternating axis of symmetry : If a molecule is rotated through an angle of $\frac{360°}{n}$ about the axis and then reflected in a plane perpendicular to the axis, gives back the original molecule it is said to possess the n fold alternating axis of symmetry.

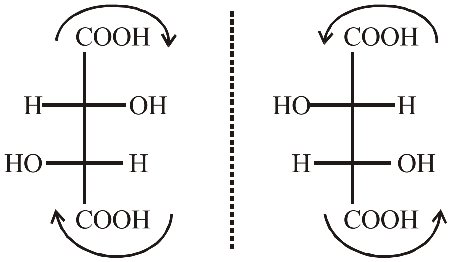


1,2,3,4-tetramethyl cyclo butane

Optical Isomerism of tartaric acid : (It contains two similar asymmetric C–atoms).



Meso tartaric acid
(I) (II)

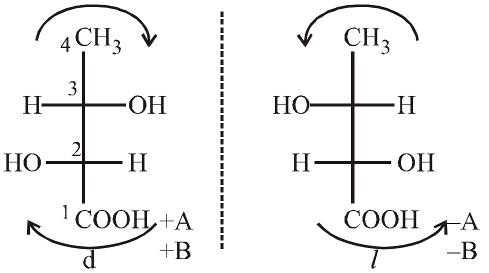


d-tartaric acid
(III)

l-tartaric acid
(IV)

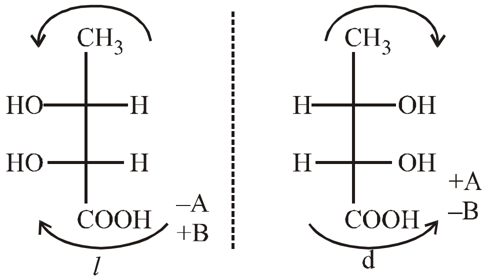
- When the configuration II is rotated through an angle 180° the configuration I is obtained hence they are not enantiomers but represent one single compound.
- d-tartaric acid is obtained from grapes and tamarind. Its mpt is 170°C.
- *l*-tartaric acid is prepared by resolving racemic acid. Its mpt is 170°C.
- Meso-tartaric acid is obtained by oxidation of maleic acid, heating d-tartaric acid with water at 170°C. Its mpt is 143°C.
- Racemic tartaric acid (d*l* or ±). It is obtained from Argol. Its mpt is 206°C. It is an equimolar mixture of d and *l* forms.
- Racemic tartaric acid can be resolved into d and *l* forms. It is a mixture of two compounds.
- Meso-tartaric acid cannot be resolved. It is a single compound.

Optical Isomerism of the compound containing two dissimilar C-atoms : Example α,β-dibromo cininamic acid and 2,3-dihydroxy butanoic acid.



(I)
Active (d, +)

(II)
Active (l, –)



(III)
Active (ℓ, –)

(IV)
Active (d, +)

Let optical rotation due to chiral centre C_3 and C_2 be A and B and further A > B. In the above case I-II and III-IV are pairs of enantiomers where as I-III; I-IV, II-III, and II-IV are pairs of diastereo-isomers.

Diastereo Isomers : Stereo isomers which are not mirror images of each other are called diastereo isomers. They have different physical properties (mpt, bpt, solubility) and are often easy to separate by distillation, recrystallisation, chromatography etc.)

The same compound pair are called the **meso diastereoisomer** (I-II in case of Tartaric acid see above). Most diastereoisomers are either geometric isomers or compounds with two or more chiral atoms.

Enantiomers : Enantiomers are non superimposable mirror image isomers. They have identical physical properties (bpt, mpt, density etc.) except for their rotation of plane polarised light. They are much more difficult to separate. In nature very often only one enantiomer is produced. Living organisms are one of the best sources of optically active compounds (plants, enzymes, animals, cells etc.).

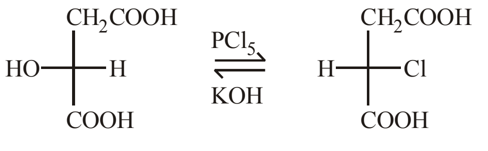
Asymmetric synthesis : The synthesis of an optically active compound from optically inactive compound under the influence of an optically active compound without resolution is known as asymmetric synthesis.

$$\underset{\text{Pyruvic acid}}{CH_3COCOOH}\xrightarrow[\text{Optically active alcohol}]{ROH}\underset{\text{Optically active ester}}{CH_3COCOOR}\xrightarrow{2H}$$

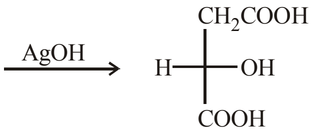
$$\underset{\text{Active lactic ester}}{CH_3CHOH.COOR}\xrightarrow{H_2O}\underset{l\text{-lactic acid}}{CH_3CHOH.COOH}$$

Racemisation : The transformation of an optically active isomer under the influence of heat, light or some reagents into an inactive isomer is called racemisation.

Walden inversion / Optical inversion : The conversion of an enantiomer into another is called Walden inversion.



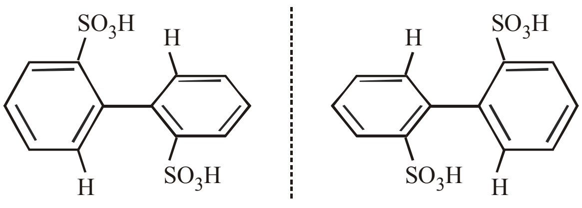
d-Malic acid   *l*-Chlorosuccinic acid



l-Malic acid

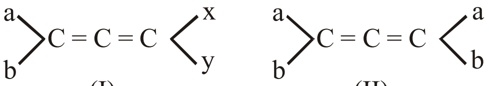
Optical isomerism due to restricted rotation :

(I) Diphenyls :

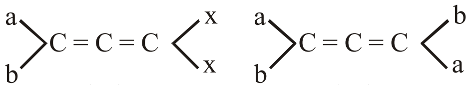


Enantiomers of diphenyl disulphonic acid

(II) Substituted allenes : Unsymmetrically substituted allene ($CH_2=C=CH_2$) are optically active.



(I) active   (II) Inactive



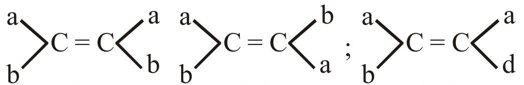
(III) Inactive   (IV) Active

Enantiomeric excess (Optical Purity) : It is given by Optical purity = O.P.

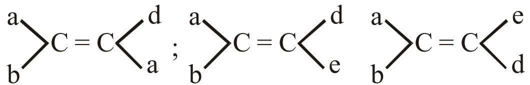
$$=\frac{\text{Observed rotation}}{\text{Pure enantiomer rotation}}\times 100\%\ \text{ Or }\ \text{O.P.}=\frac{d-l}{d+l}\times 100\%$$

where d and ℓ are ratio of two forms

Geometrical isomerism : Alkenes with double bonds cannot undergo free rotation and can have different geometrical shapes with two different groups on each end of the double bond. e.g. molecules $C_2a_2b_2$, C_2a_2bd or C_2abde.



(I)   (II)   (III)



(IV)   (V)   (VI)

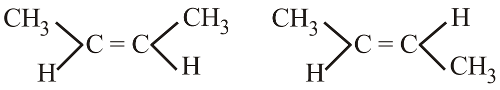
I-II, III-IV and V-VI are pairs of geometrical isomers.

Nomenclature :

Cis Isomer : Contains the similar atoms or groups on the same side.

Trans Isomer : Contains the similar atoms or groups on the opposite side.

Examples :

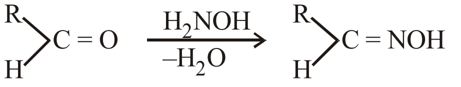


Cis-But-2-ene   Trans But-2-ene

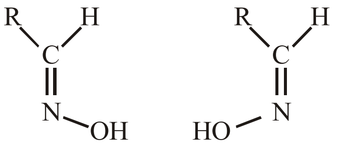
Maleic acid   Fumaric acid

Geometrical Isomerism of Oximes

Aldoximes :

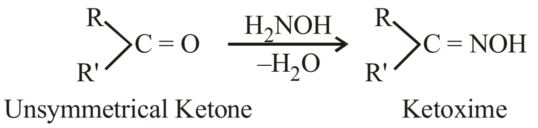


Aldehyde   Aldoxime

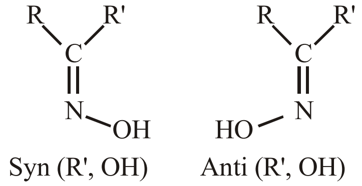


Syn Aldoxime   Anti Aldoxime

Ketoximes :

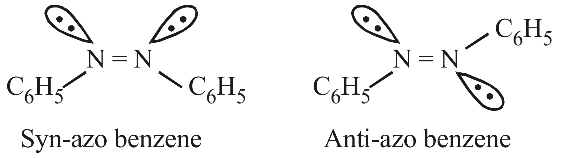


Unsymmetrical Ketone Ketoxime



Syn (R', OH) Anti (R', OH)

Geometrical isomerism of azo compounds : Example azobenzene



Syn-azo benzene Anti-azo benzene

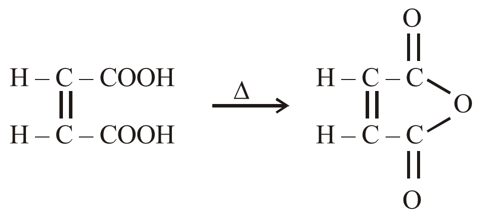
Geometrical isomerism in cyclo alkanes : Cyclo alkanes also cannot undergo free rotation.

cis-1,2-dimethyl cyclo pentane trans-1,2-dimethyl cyclo pentane

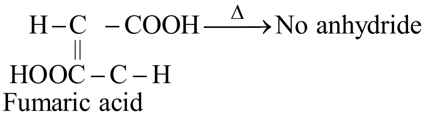
Determination of configuration of geometrical isomers :

(I) ***Physical methods :*** In general the *cis* isomer has low mpt, higher bpt, high density higher dipole moment, greater solubility, higher refractive index, higher heat of combustion.

(II) By Cyclisation :



Maleic acid Maleic anhydride

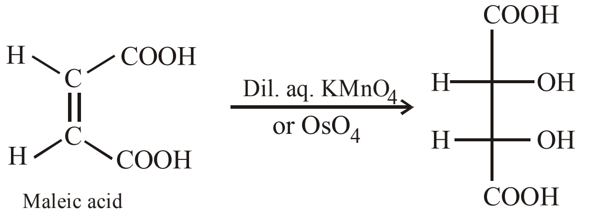


$$\begin{array}{l} \mathrm{H-C\ \ -COOH} \xrightarrow{\Delta} \text{No anhydride} \\ \quad\ \| \\ \mathrm{HOOC-C-H} \end{array}$$

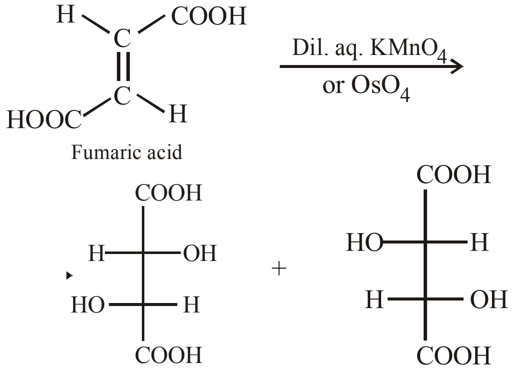
Fumaric acid

Hence Maleic acid must be *cis* isomer.

(III) By Oxidation :



Maleic acid meso-Tartaric acid

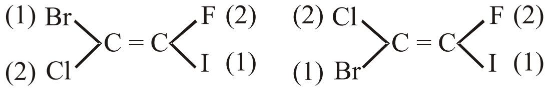


d-Tartaric acid *l*-Tartaric acid

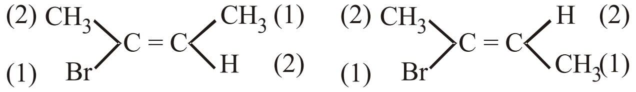
Hence Maleic must be *cis* and fumaric must be trans.

E,Z system of Nomenclature for Geometrical Isomers:

If two high-priority groups are on the same side, the configuration is Z (German, Zus ammen = togehter). If they are on opposite side, the configuration is E (German; entgegen = opposite)



E Z



trans or E *cis* or Z

Assignment of Priority : Atoms with higher atomic numbers receive higher priorites

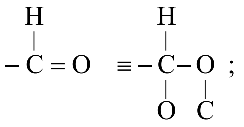
$$I > S > O > N > {}^{13}C > {}^{12}C > Li > {}^{3}H(T) > {}^{2}H(D) > H$$

R and S Assignments : By Cahn-Ingold-Prelog. Enantiomers are designated as (R) and (S) according to following rules

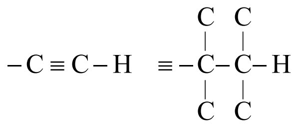
(I) Atoms with higher atomic numbers receive higher priorities.

(II) When the same atom is bound directly to the chiral carbon, we go to the next atom along the chain.

(III) Double and triple bonds are treated as if each bond were to a separate atom. e.g.



$$\begin{array}{c}\mathrm{H}\\|\\-\mathrm{C}=\mathrm{O}\end{array} \equiv \begin{array}{c}\mathrm{H}\\|\\-\mathrm{C}-\mathrm{O}\\|\qquad|\\\mathrm{O}\qquad\mathrm{C}\end{array};$$



$$-\mathrm{C}\equiv\mathrm{C}-\mathrm{H} \equiv \begin{array}{c}\mathrm{C}\quad\ \mathrm{C}\\|\qquad|\\-\mathrm{C}-\mathrm{C}-\mathrm{H}\\|\qquad|\\\mathrm{C}\quad\ \mathrm{C}\end{array}$$

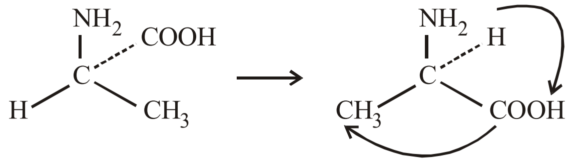
Thus between –CHO (O, O, H) and $-CH_2OH$ (O, H, H) the former will have priority.

(IV) The molecule is drawn in three dimensions in such a way that the bond between the chiral carbon and the lowest priority group heeds back into the paper.

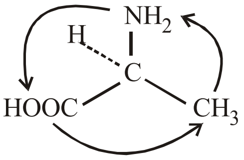
(V) Draw an arrow from the group of highest priority, to the second, to the third priority group.

(VI) If the arrow is clockwise, the chiral carbon is assigned (R). If the arrow is anticlockwise the chiral carbon is assigned (S).

Example : Alanine



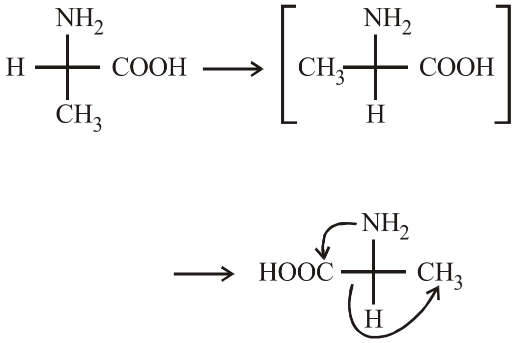
R-enantiomer



(S) enantiomer

(Always exchange the groups twice to get the same compound. If you exchange the groups once you get the enantiomer).

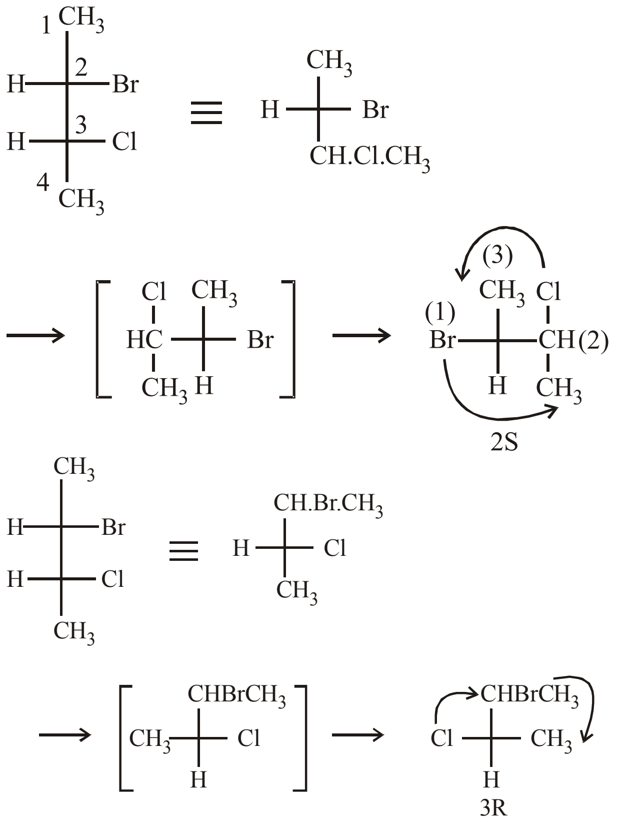
By using *Fischer Projections :*

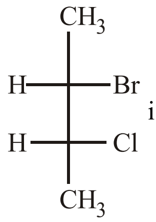


(S) enantiomer

Move the group of lowest priority to the bottom.

Molecules with two or more chiral atoms.



Hence the compound  is (2S, 3R).

Miscellaneous Solved Examples

1. Write down all possible isomers of $C_4H_8O_2$ and type of isomerism existing between them

Sol. **Acids :-**

$CH_3CH_2CH_2COOH$	$(CH_3)_2CH.COOH$
n - Butyric acid	Isobutyric acid

Esters :-

$HCOOC_3H_7$	$CH_3COOC_2H_5$	$C_2H_5COOCH_3$
Propyl formate	Ethyl acetate	Methyl propionate

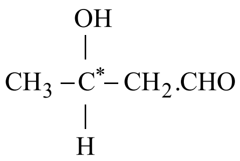
Aldol :- $CH_3\overset{*}{C}HOHCH_2CHO$

β - hydroxybutyric aldehyde

(i) Acids are chain isomers

(ii) Acids,esters and aldol are functional isomers

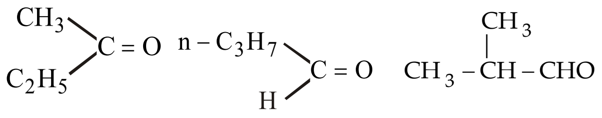
(iii) Aldol contains asymmetric C-atom and can exist in two optically active forms and one racemic form



$$CH_3-\overset{OH}{\underset{H}{C^*}}-CH_2.CHO$$

2. Write the possible isomers of C_4H_8O and type of isomerism

Sol.



(I)	(II)	(III)
Ethyl methyl Ketone	n -butyraldehyde	Isobutyraldehyde

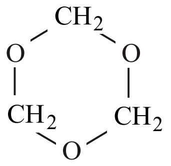
Functional isomers	I and II, I and III
Chain isomers	II and III

3. Write the possible isomers of $C_3H_6O_3$ and type of isomerism existing between them

Sol. $(HCHO)_3$ $CH_3CHOHCOOH$ $CH_2OH.CH_2COOH$

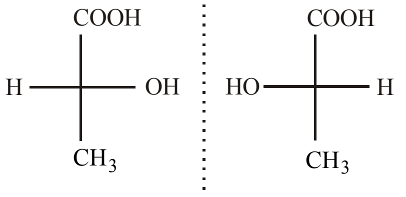
(I)	(II)	(III)
Meta formaldehyde	α - hydroxy propionic acid	β - hydroxy propionic acid

Functional isomers	I and II, I and III
Position isomers	II and III
Ring chain isomers	I and II, 1 and III



Trioxane (meta formaldehyde)

Stereoisomers :- II will show optical isomerism due to the presence of an asymmetric C- atom.



It will have the one racemic formed (dl, ±)

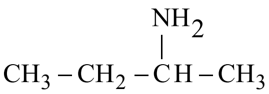
4 Write all possible isomers of each formula and report what type of isomerism exists in each

(a) $C_4H_{11}N$ (b) C_4H_8

Sol.

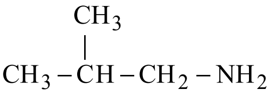
$CH_3-CH_2-CH_2-CH_2-NH_2$

1- amino butane (I)



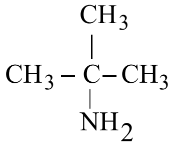
$$CH_3-CH_2-\overset{NH_2}{CH}-CH_3$$

2 - amino butane (II)



$$CH_3-\overset{CH_3}{CH}-CH_2-NH_2$$

1 - amino 2- methyl propane (III)

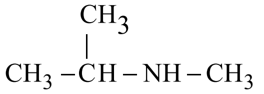


$$CH_3-\overset{CH_3}{\underset{NH_2}{C}}-CH_3$$

2- amino 2- methyl propane (IV)

$CH_3-CH_2-CH_2-NH-CH_3$

Methyl propylamine (V)

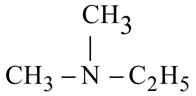


$$CH_3-\overset{CH_3}{CH}-NH-CH_3$$

methyl isopropylamine (VI)

$C_2H_5-NH-C_2H_5$

diethyl amine (VII)



$$CH_3-\overset{CH_3}{N}-C_2H_5$$

ethyl dimethylamine (VIII)

Position isomers	I and II, III and IV
Chain isomers	I and III, I and IV

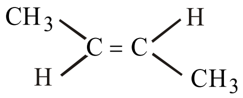
Functional isomers 1°, 2° and 3° amines are functional isomers

Metamers :- VI, V, VII

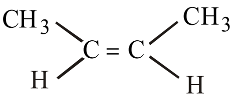
C_4H_8 :

(i) $CH_3CH_2.CH=CH_2$ but -1-ene

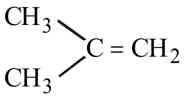
(ii) $CH_3CH=CHCH_3$ but - 2 - ene



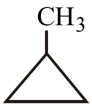
trans (A)



cis (B)

(iii)  2 - methyl propene

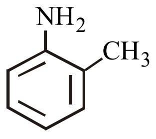
(iv)  Cyclobutane

(v)  methyl cyclopropane

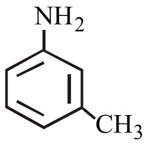
Chain isomers	I and III, II and III
Position isomers	I and II
Ring chain isomers	I and IV, II and IV
Geometrical isomers	A and B forms of II

5. Write are possible isomers of C_7H_9N

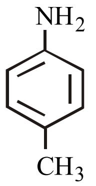
Sol.



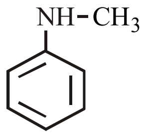
o- Toluidine



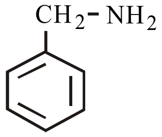
m - Toluidine



p- Toluidine



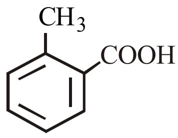
N -methyl aniline



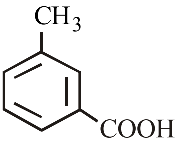
Benzylamine

6. Write possible isomers of $C_8H_8O_2$

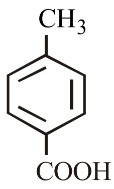
Sol.



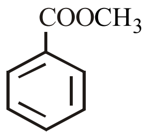
o- Toluic acid



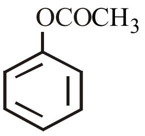
m - Toluic acid



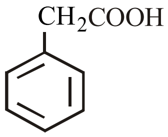
p - Toluic acid



methylbenzoate



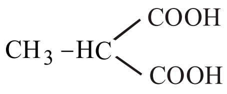
phenyl acetate



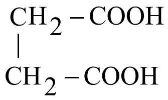
phenylacetic acid

7. Write all possible isomers of $C_4H_6O_4$

Sol.



methyl malonic acid



$$\begin{array}{l} CH_2-COOH \\ | \\ CH_2-COOH \end{array}$$

Succinic acid

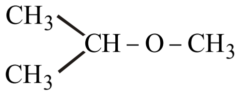
8. Write all possible metamers of $C_4H_{10}O$.

Sol. $C_2H_5-O-C_2H_5$

diethyl ether

$CH_3-CH_2-CH_2-O-CH_3$

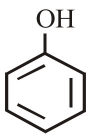
methyl n-propyl ether



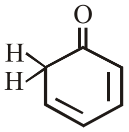
methyl iso-propyl ether

9. Write Keto-enol tautomers of phenol C_6H_5OH

Sol.



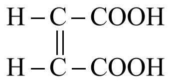
enol form



Keto form

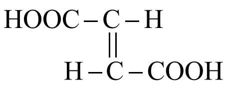
10. Write possible isomers of $C_4H_4O_4$ and type of isomerism exhibited by them

Sol.



$$\begin{array}{l} H-C-COOH \\ \quad\ \| \\ H-C-COOH \end{array}$$

Maleic acid

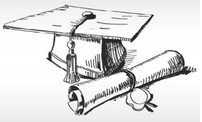


$$\begin{array}{l} HOOC-C-H \\ \qquad\quad\ \| \\ \qquad H-C-COOH \end{array}$$

Fumaric acid

These are Geometrical isomers.

Exercise-1 | NCERT BASED QUESTIONS



Very Short/ Short Answer Questions

1. What type of isomerism is shown by butane and isobutane?
2. A compound is formed by the substitution of two chlorine atoms for two hydrogen atoms in propane. What is the number of structural isomers possible ?
3. An alcohol with no carbon-carbon double bond has the formula C_4H_8O. What are the possible structures?
4. Draw all possible isomers for a compound with molecular formula C_8H_{10} containing benzene ring. Also, give IUPAC name to these isomers.
5. An aliphatic amine has a molecular mass of 59. Draw all its possible isomers.

Long Answer Questions

6. Draw all possible isomers of a compound with molecular formula, $C_4H_{10}O$. Classify them as chain and position isomers.

Multiple Choice Questions

7. In which of the following, functional group isomerism is not possible?

(a) Alcohols (b) Aldehydes
(c) Alkyl halides (d) Cyanides

8. Which of the following compounds will show metamerism?

(a) $CH_3–CO–C_2H_5$ (b) $C_2H_5–S–C_2H_5$
(c) $CH_3–O–CH_3$ (d) $CH_3–O–C_2H_5$

9. The number of possible open chain (acyclic) isomeric compounds for molecular formula C_5H_{10} would be

(a) 8 (b) 7
(c) 6 (d) 5

10. Which are isomers ?

(a) Ethyl alcohol and dimethyl ether
(b) Acetone and acetaldehyde
(c) Propionic acid and propanone
(d) Methyl alcohol and dimethyl ether

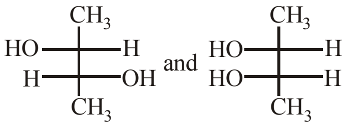
11. $C_6H_5C \equiv N$ and $C_6H_5N \overset{\rightarrow}{\equiv} C$ are which type of isomers?

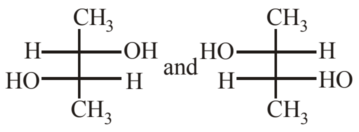
(a) Position (b) Functional
(c) Tautomerism (d) Linkage

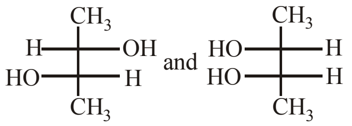
12. Which of the following compounds exhibits stereoisomerism ?

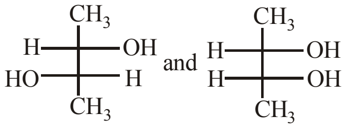
(a) 2-methylbutene-1
(b) 3-methylbutyne-1
(c) 3-methylbutanoic acid
(d) 2-methylbutanoic acid

13. Which of the following pairs of compounds are enantiomers?

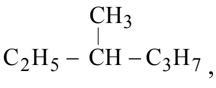
(a)


(b)


(c)


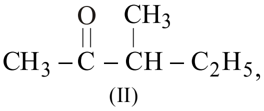
(d)


14. Among the following four structures I to IV,



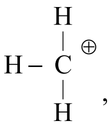
$C_2H_5-\overset{\overset{CH_3}{|}}{C}H-C_3H_7$,

(I)



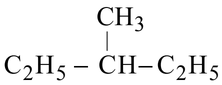
$CH_3-\overset{\overset{O}{||}}{C}-\overset{\overset{CH_3}{|}}{C}H-C_2H_5$,

(II)



,

(III)



$C_2H_5-\overset{\overset{CH_3}{|}}{C}H-C_2H_5$

(IV)

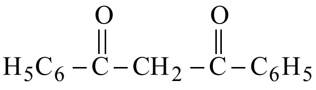
it is true that

(a) only I and II are chiral compounds
(b) only III is a chiral compound
(c) only II and IV are chiral compounds
(d) all four are chiral compounds

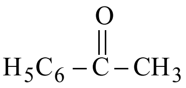
15. Which of the following compounds is optically active ?

(a) $CH_3CHClCOOH$ (b) $CH_3CH_2CH_2CH_3$
(c) $(CH_3)_2CHOH$ (d) $(CH_3)_3CCl$

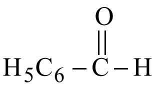
16. Keto-enol tautomerism is observed in :

(a)


$H_5C_6-\overset{\overset{O}{||}}{C}-CH_2-\overset{\overset{O}{||}}{C}-C_6H_5$

(b)


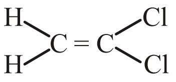
$H_5C_6-\overset{\overset{O}{||}}{C}-CH_3$

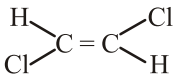
(c)


$H_5C_6-\overset{\overset{O}{||}}{C}-H$

(d) Both (a) and (b)

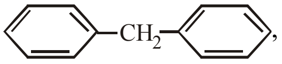
17. The following compounds differ in





(a) configuration (b) conformation
(c) structure (d) chirality

18. The molecular formula of diphenyl methane,



, is $C_{13}H_{12}$.

How many structural isomers are possible when one of the hydrogens is replaced by a chlorine atom?

(a) 6 (b) 4 (c) 8 (d) 7

Exercise-2 | CONCEPTUAL MCQs

1. Which organic structure among the following is not an isomer of the compound $CH_3–CO–CH_2CH_2CH_2CH_3$?

(a) $CH_3CH_2OCH=CHCH_2CH_3$
(b) $CH_3CH=CHCH_2CH_2CHO$
(c) $(CH_3)_2CH–CO–CH_2CH_3$
(d) $CH_3CH_2COCH_2CH_2CH_3$

2. The least number of carbon atoms in alkane showing isomerism is

(a) 3 (b) 1
(c) 2 (d) 4

3. The number of possible alkynes with molecular formula C_5H_8 is

(a) 2 (b) 3
(c) 4 (d) 5

4. The total number of isomers for C_4H_8 is

(a) 5 (b) 6
(c) 7 (d) 8

5. The number of possible open chain (acyclic) isomeric compounds for molecular formula C_5H_{10} would be

(a) 8 (b) 7
(c) 6 (d) 5

6. Consider the following statements : A hydrocarbon of molecular formula C_5H_{10} is a

I. monosubstituted alkene
II. disubstituted alkene
III. trisubstituted alkene

Which of the following statement(s) is(are) correct?

(a) I, II and III (b) I and II
(c) II and III (d) I and III

7. How many cyclic isomers of C_5H_{10} are possible?

(a) 4 (b) 3
(c) 2 (d) 5

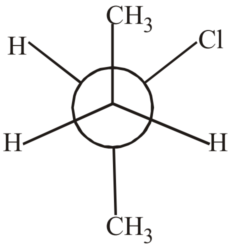
8. How many isomers can C_5H_{12} have ?

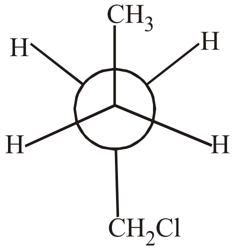
(a) 3 (b) 2
(c) 4 (d) 5

9. Which of the following compounds is isomeric with 2, 2, 4, 4- tetramethylhexane?

(a) 3-ethyl -2, 2- dimethylpentane
(b) 4-isopropylheptane
(c) 4-ethyl-3-methyl-4-n propyloctane
(d) 4, 4-diethyl-3-methylheptane

10. The pair of structures given below represent





(a) enantiomers
(b) diastereomers
(c) structural isomers
(d) two molecules of the same compound.

11. Which of the following compounds will show metamerism?

(a) $CH_3–CO–C_2H_5$ (b) $C_2H_5–S–C_2H_5$
(c) $CH_3–O–CH_3$ (d) $CH_3–O–C_2H_5$

12. The number of ether metamers represented by the formula $C_4H_{10}O$ is

(a) 4 (b) 3
(c) 2 (d) 1

13. A compound with molecular formula, C_7H_{16} shows optical isomerism, the compound will be

(a) 2, 3-dimethylpentane (b) 2, 2-dimethylpentane
(c) 2-methylhexane (d) None of these

14. Which are isomers ?

(a) ethyl alcohol and dimethyl ether
(b) acetone and acetaldehyde
(c) propionic acid and propanone
(d) methyl alcohol and dimethyl ether

15. Methoxyethane and propanol are the examples of isomerism of the type

(a) structural (b) position
(c) functional (d) tautomerism

16. The compound $C_4H_{10}O$ can show
(a) metamerism (b) functional isomerism
(c) position isomerism (d) All of these

17. Isomers of propionic acid are
(a) $HCOOC_2H_5$ and CH_3COOCH_3
(b) $HCOOC_2H_5$ and C_3H_7COOH
(c) CH_3COOCH_3 and C_3H_7OH
(d) C_3H_7OH and CH_3COCH_3

18. $C_6H_5C \equiv N$ and $C_6H_5N \equiv C$ are which type of isomers?
(a) Position (b) Functional
(c) Tautomerism (d) Linkage

19. A functional isomer of 1-butyne is
(a) 2-butyne (b) 1-butene
(c) 2-butene (d) 1, 3-butadiene

20. The number of primary amines of formula $C_4H_{11}N$ is
(a) 1 (b) 2
(c) 3 (d) 4

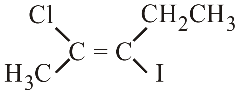
21. The number of isomers possible for C_7H_8O is
(a) 2 (b) 3
(c) 4 (d) 5

22. The total number of isomeric alcohols with the molecular formula C_4H_9OH is
(a) 2 (b) 3
(c) 4 (d) 5

23. The number of possible acyclic structural isomers of $C_4H_{10}O$ is
(a) 5 (b) 6
(c) 7 (d) 8

24. Tautomerism will be exhibited by
(a) $(CH_3)_3CNO$ (b) $(CH_3)_2NH$
(c) R_3CNO_2 (d) RCH_2NO_2

25. IUPAC name for the compound



is

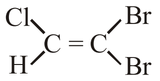
(a) E-2-chloro-3-iodopentene-2
(b) Z-2-chloro-3-iodo-2-pentene
(c) E-3-iodo-4-chloro-3-pentene
(d) Z-3-iodo-4-chloro-3-pentene

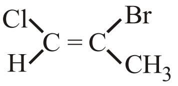
26. The prefixes ***syn*** and ***anti*** are used to denote
(a) structural isomers (b) conformational isomers
(c) geometrical isomers (d) optical isomers

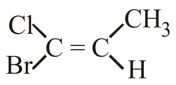
27. How many structural (including stereoisomers) isomers could be obtained by replacing one hydrogen of propene with chlorine ?
(a) 2 (b) 4
(c) 3 (d) 5

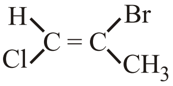
28. Which of the following compounds exhibits geometrical isomerism ?
(a) C_2H_5Br (b) $(CH)_2(COOH)_2$
(c) CH_3CHO (d) $(CH_2)_2(COOH)_2$

29. Which is a pair of geometrical isomers ?

I.


II.


III.


IV.


(a) I and II (b) I and III
(c) II,III and IV (d) III and IV

30. Which of the following compounds will exhibit geometrical isomerism ?
(a) 1-phenyl-2-butene (b) 3-phenyl-1-butene
(c) 2-phenyl -1-butene (d) 1,1-diphenyl-1-propene

31. But-2-ene exhibits cis-trans-isomerism due to
(a) rotation around $C_3 - C_4$ sigma bond
(b) restricted rotation around C = C bond
(c) rotation around $C_1 - C_2$ bond
(d) rotation around $C_2 - C_3$ double bond

32. The restricted rotation about carbon-carbon double bond in 2- butene is due to
(a) overlap of one s- and one sp^2-hybridized orbitals
(b) overlap of two sp^2-hybridized orbitals
(c) overlap of one p-and one sp^2-hybridized orbitals
(d) sideways overlap of two p-orbitals

33. Which of the following has zero dipole moment?
(a) cis-2-butene (b) trans-2-butene
(c) 1-butene (d) 2-methyl-1propene

34. Which of the following has zero dipole moment?
(a) 1, 1-dichloromethane
(b) cis-1, 2-dichloroethene
(c) trans-1, 2-dichloroethene
(d) 1-chloroethane

35. The number of geometrical isomers of $CH_3CH{=}CH{-}CH{=}CH{-}CH{=}CHCl$ is
(a) 2 (b) 4
(c) 6 (d) 8

36. The number of isomers for the compound with molecular formula $C_2BrClFI$ is
(a) 3 (b) 4 (c) 5 (d) 6

37. Fischer projection indicates
(a) horizontal substituents above the plane
(b) vertical substituents above the plane
(c) both horizontal and vertical substituents below the plane
(d) both horizontal and vertical substituents above the plane

38. An organic compound will show optical isomerism if
(a) four groups attached to C atom are different
(b) three groups attached to C atom are different
(c) two groups attached to C atom are different
(d) all the groups attached to C atom are same

39. Which of the following molecules contain asymmetric carbon atom ?
(a) $CH_3CHClCOOH$ (b) CH_3CH_2COOH
(c) $ClCH_2CH_2COOH$ (d) $Cl_2CHCOOH$

40. Which of the following compound is not chiral?
(a) $DCH_2CH_2CH_2Cl$ (b) CH_3CHDCH_2Cl
(c) $CH_3CHClCH_2D$ (d) CH_3CH_2CHDCl

41. Consider the following

$$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_2-\overset{7}{C}H_3$$

To make it a chiral compound, the attack should be on carbon
(a) 1 (b) 3 (c) 4 (d) 7

42. The (R)- and (S)- enantiomers of an optically active compound differ in
(a) their reactivity with achiral reagents
(b) their optical rotation of plane polarized light
(c) their melting points
(d) None of these

43. (+)-Mandelic acid has a specific rotation of + 158°. What would be the observed specific rotation of a mixture of 25% (–)- mandelic acid and 75% (+)-mandelic acid ?
(a) +118.5° (b) –118.5°
(c) – 79° (d) + 79°

44. Optical activity is measured by
(a) Polarimeter (b) Refractometer
(c) Spectrograph (d) Tracer technique

45. Which one of the following compounds is not optically active ?
(a) $CH_3CH_2CH(CH_3)CH_2Cl$ (b) $CH_3CH_2CH(CH_3)_2$
(c) CH_3–CHOH–COOH (d) CH_3–CHCl–CH_2Br

46. An optically active compound is
(a) 1-bromobutane
(b) β-bromobutyric acid
(c) 2-bromo-2-methylpropane
(d) 1-bromo -2-methylpropane

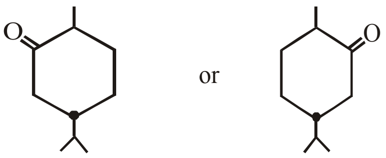
47. Which of the following is optically active ?
(a) butane (b) 4-methylheptane
(c) 3-methylheptane (d) 2-methylpentane

48. Which of the following compounds exhibits stereoisomerism ?
(a) 2-methylbutene-1 (b) 3-methylbutyne-1
(c) 3-methylbutanoic acid (d) 2-methylbutanoic acid

49. An organic molecule necessarily shows optical activity if it
(a) contains asymmetric carbon atoms
(b) is non-polar
(c) is non-superimposable on its mirror image
(d) is superimposable on its mirror image

50. Optically active isomers but not mirror images are called
(a) enantiomers (b) mesomers
(c) tautomers (d) diastereomers

51. The two compounds shown in the figure below are



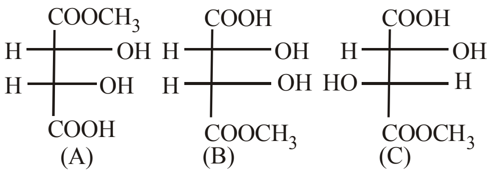
(a) diastereomers (b) enantiomers
(c) epimers (d) regiomers

52. Which of the following is optically active ?
(a) Oxalic acid (b) Ethylene glycol
(c) Glycerol (d) Tartaric acid

53. How many stereoisomers are possible for tartaric acid?
(a) 2 (b) 3
(c) 4 (d) 5

54. Meso- tartaric acid is optically inactive due to the presence of
(a) molecular symmetry (b) molecular asymmetry
(c) external compensation (d) two asymmetric C atoms

55. The correct statement about the compounds A, B, and C



is

(a) A and B are identical
(b) A and B are diastereomers
(c) A and C are enantiomers
(d) A and B are enantiomers

56. How many optically active stereoisomers are possible for butane-2, 3- diol ?
(a) 1 (b) 2
(c) 3 (d) 4

57. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methylbutane is
(a) 2 (b) 3
(c) 4 (d) 1

58. The number of enantiomers of the compound $CH_3CHBrCHBrCOOH$ is
(a) 0 (b) 1
(c) 3 (d) 4

59. Which of the following has a chiral carbon?

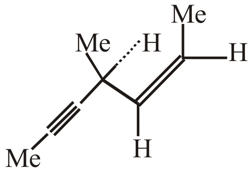
(a) 2,3-dimethylpentane

(b) $CH_3–CH_2–CH_2–CHO$

(c) $(CH_3)_3CCH_2CH_2CH_3$

(d) $(CH_3)_2CHCH_2CH_2CH_2CH_3$

60.



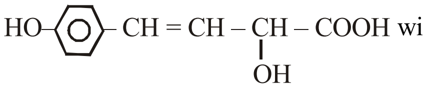
Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives

(a) optically active compound

(b) an optically inactive compound

(c) a racemic mixture

(d) a diastereomeric mixture

61.  will show.

(a) geometrical isomerism

(b) optical isomerism

(c) geometrical and optical isomerism

(d) neither geometrical nor optical isomerism

62. Number of stereoisomers of the compound, 2-chloro-4-methylhex-2-ene is/are

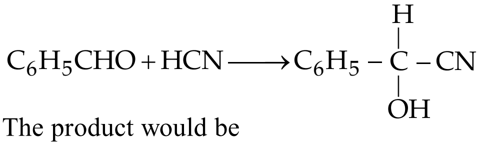
(a) 1 (b) 2

(c) 4 (d) 6

63. The number of stereoisomers for pent-3-en-2-ol is

(a) 2 (b) 4

(c) 3 (d) 5

64. 

$$C_6H_5CHO + HCN \longrightarrow C_6H_5-\underset{OH}{\overset{H}{C}}-CN$$

The product would be

(a) a racemate

(b) optically active

(c) a meso compound

(d) a mixture of diastereomers

65. The process of separation of a racemic modification into *d*- and *l*- enantiomers is called

(a) resolution (b) dehydration

(c) revolution (d) dehydrohalogenation

66. An important chemical method to resolve a racemic mixture makes use of the formation of

(a) a meso compound (b) enantiomers

(c) diastereomers (d) racemate

67. Which one of the following is the stablest structure of cyclohexatriene ?

(a) Chair form (b) Boat form

(c) Half chair form (d) Planar form

68. The isomers which can be converted into another form by rotation of the molecule around single bond are

(a) geometrical isomers (b) conformers

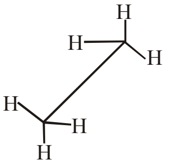
(c) enantiomers (d) diastereomers

69. The most stable conformation of n-butane is

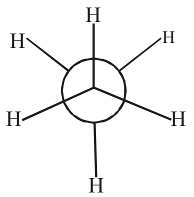
(a) skew-boat (b) eclipsed

(c) gauche (d) staggered -anti

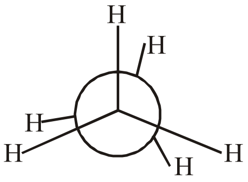
70. In the following structures, which two forms are staggered conformations of ethane ?



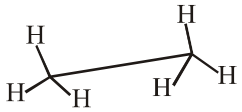
(1)



(2)



(3)



(4)

(a) 1 and 4 (b) 2 and 3

(c) 1 and 2 (d) 1 and 3

71. Which of the following is the most stable form of cyclohexane ?

(a) boat (b) chair

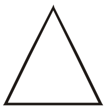
(c) twist boat (d) half chair

72. In the boat conformation of cyclohexane, the most destabilizing interaction is

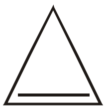
(a) eclipsing (b) 1, 3-diaxial

(c) 1, 3-diequatorial (d) flagpole -flagpole

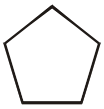
73. The stability of the compounds



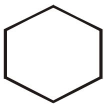
(i)



(ii)



(iii)



(iv)

(a) (iv) > (iii) > (i) > (ii) (b) (i) > (iii) > (ii) > (iv)

(c) (ii) > (iii) > (i) > (iv) (d) (iv) > (i) > (iii) > (ii)

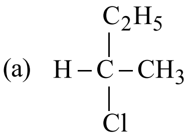
74. The Baeyer's angle strain is expected to be maximum in

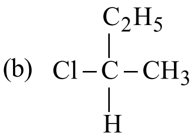
(a) cyclodecane (b) cyclopentane

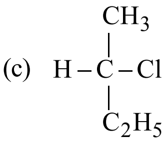
(c) cyclohexane (d) cyclooctane

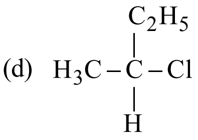
Exercise-3 | PAST COMPETITION MCQs

1. $CH_3-CHCl-CH_2-CH_3$ has a chiral centre. which one of the following represents its R-configuration? **[CBSE-PMT 2007]**

(a) 
$H-\overset{C_2H_5}{\underset{Cl}{C}}-CH_3$

(b) 
$Cl-\overset{C_2H_5}{\underset{H}{C}}-CH_3$

(c) 
$H-\overset{CH_3}{\underset{C_2H_5}{C}}-Cl$

(d) 
$H_3C-\overset{C_2H_5}{\underset{H}{C}}-Cl$

2. How many stereoisomers does this molecule have? **[CBSE-PMT 2008]**

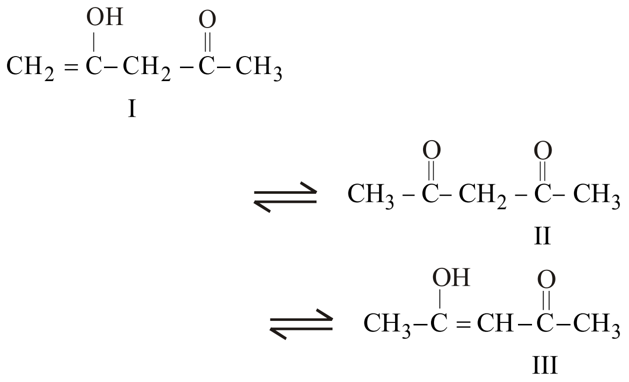
$CH_3CH=CHCH_2CHBrCH_3$

(a) 4 (b) 6 (c) 8 (d) 2

3. Which of the following compounds will exhibit cis-trans (geometrical) isomerism? **[CBSE-PMT 2009]**

(a) Butanol (b) 2-Butyne (c) 2-Butenol (d) 2-Butene

4. The order of stability of the following tautomeric compounds is : **[NEET 2013]**



$CH_2=\overset{OH}{C}-CH_2-\overset{O}{\overset{\parallel}{C}}-CH_3$ (I) $\rightleftharpoons CH_3-\overset{O}{\overset{\parallel}{C}}-CH_2-\overset{O}{\overset{\parallel}{C}}-CH_3$ (II) $\rightleftharpoons CH_3-\overset{OH}{C}=CH-\overset{O}{\overset{\parallel}{C}}-CH_3$ (III)

(a) III > II > I (b) II > I > III
(c) II > III > I (d) I > II > III

5. The type of isomerism present in nitropentamine chromium (III) chloride is **[AIEEE 2002]**

(a) linkage (b) ionization
(c) polymerisation. (d) optical

6. A similarity between optical and geometrical isomerism is that **[AIEEE 2002]**

(a) each forms equal number of isomers for a given compound
(b) if in a compound one is present then so is the other
(c) both are included in stereoisomerism
(d) they have no similarity.

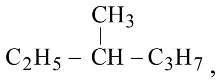
7. Which of the following does not show geometrical isomerism? **[AIEEE 2002]**

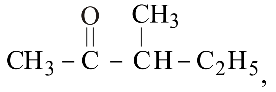
(a) 1,2-dichloro-1-pentene (b) 1,3-dichloro-2-pentene
(c) 1,1-dichloro-1-pentene (d) 1,4-dichloro-2-pentene

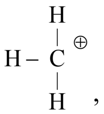
8. Racemic mixture is formed by mixing two **[AIEEE 2002]**

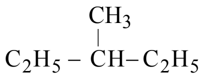
(a) isomeric compounds (b) chiral compounds
(c) meso compounds (d) optical isomers.

9. Among the following four structures I to IV, **[AIEEE 2003]**


$C_2H_5-\overset{CH_3}{CH}-C_3H_7$,
(I)


$CH_3-\overset{O}{\overset{\parallel}{C}}-\overset{CH_3}{CH}-C_2H_5$,
(II)

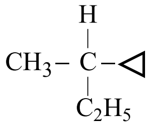

$H-\overset{H}{\underset{H}{C}}{}^{\oplus}$,
(III)

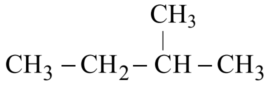

$C_2H_5-\overset{CH_3}{CH}-C_2H_5$
(IV)

it is true that

(a) only I and II are chiral compounds
(b) only III is a chiral compound
(c) only II and IV are chiral compounds
(d) all four are chiral compounds

10. Amongst the following compounds, the optically active alkane having lowest molecular mass is **[AIEEE 2004]**

(a) 

(b) 
$CH_3-CH_2-\overset{CH_3}{CH}-CH_3$

(c) $CH_3-CH_2-CH_2-CH_3$

(d) $CH_3-CH_2-C\equiv CH$

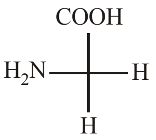
11. Which of the following compounds is not chiral? **[AIEEE 2004]**

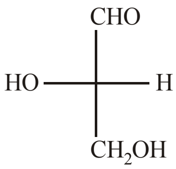
(a) 1-chloro-2-methyl pentane
(b) 2-chloropentane
(c) 1-chloropentane
(d) 3-chloro-2-methyl pentane

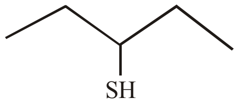
12. Increasing order of stability among the three main conformations (i.e. Eclipse, Anti, Gauche) of 2-fluoroethanol is **[AIEEE 2006]**

(a) eclipse, anti, gauche (b) anti, gauche, eclipse
(c) eclipse, gauche, anti (d) gauche, eclipse, anti

13. Which of the following molecules is expected to rotate the plane of plane-polarised light? **[AIEEE 2007]**

(a) 

(b) 

(c) 

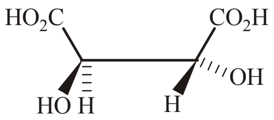
(d) 

14. Which one of the following conformations of cyclohexane is chiral? **[AIEEE 2007]**

(a) Boat (b) Twist boat

(c) Rigid (d) Chair.

15. The absolute configuration of **[AIEEE 2008]**



(a) S, S (b) R, R (b) R, S (c) S, R

(a) 3-methyl-2-pentene (b) 4-methyl-1-pentene

(c) 3-methyl-1-pentene (d) 2-methyl-2-pentene

16. The alkene that exhibits geometrical isomerism is : **[AIEEE 2009]**

(a) 2- methyl propene (b) 2-butene

(c) 2- methyl -2- butene (d) propene

17. The number of stereoisomers possible for a compound of the molecular formula

$CH_3-CH=CH-CH(OH)-Me$ is: **[AIEEE 2009]**

(b) 2 (c) 4 (d) 6 (d) 3

18. Out of the following, the alkene that exhibits optical isomerism is **[AIEEE 2010]**

(a) 3-methyl-2-pentene (b) 4-methyl-1-pentene

(c) 3-methyl-1-pentene (d) 2-methyl-2-pentene

19. The number of stereoisomers obtained by bromination of *trans*-2-*butene* is **[IIT-JEE 2007]**

(a) 1 (b) 2 (c) 3 (d) 4

Exercise-4 | Applied MCQs

1. The molecular formula of a saturated compound is $C_2H_4Br_2$. This formula permits the existence of

(a) functional isomers (b) optical isomers

(c) positional isomers (d) cis-trans isomers

2. The production of an optically active compound from a symmetric molecule without resolution is termed

(a) Walden inversion (b) Partial racemisation

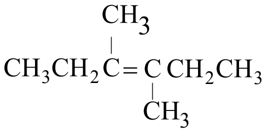
(c) Asymmetric synthesis (d) Partial resolution

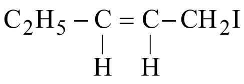
3. Which of the following is optically active

(a) n - propanol (b) 2 - chlorobutane

(c) n - butanol (d) 3 - hydroxy pentane

4. Geometrical isomerism is not shown by

(a) 
$CH_3CH_2\overset{CH_3}{C}=\underset{CH_3}{C}CH_2CH_3$

(b) 
$C_2H_5-\underset{H}{C}=\underset{H}{C}-CH_2I$

(c) $CH_2=C(Cl)CH_3$

(d) $CH_3-CH=CH-CH=CH_2$

5. The maximum number of stereoisomers possible for 3 - hydroxy - 2 -methyl butanoic acid is

(a) 1 (b) 2

(c) 3 (d) 4

6. The optically active tartaric acid is named as D - (+) - tartaric acid because it has a positive

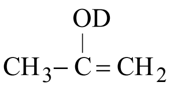
(a) optical rotation and is drived from D - glucose

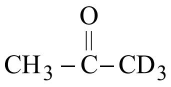
(b) pH in organic solvent

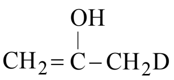
(c) optical rotation and is derived from D - (+) - glyceraldehyde

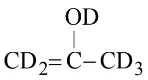
(d) optical rotation when substituted by deuterium

7. The enol form of acetone after treatment with D_2O gives:

(a) 
$CH_3-\overset{OD}{C}=CH_2$

(b) 
$CH_3-\overset{O}{\overset{||}{C}}-CD_3$

(c) 
$CH_2=\overset{OH}{C}-CH_2D$

(d) 
$CD_2=\overset{OD}{C}-CD_3$

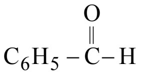
8. Two geometrical isomers are given by the following compound

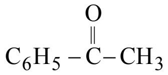
(a) ethylidene bromide (b) acetylene tetrachloride

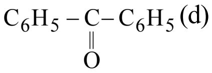
(c) acetylene tetrabromide (d) acetylene dibromide

9. Only two isomeric monochloro derivatives are possible for :
(a) n - butane
(b) 2, 4 - dimethylpentane
(c) benzene
(d) 2 - methylbutane

10. Keto-enol tautomerism is observed in

(a) 
$C_6H_5-\overset{O}{\overset{\|}{C}}-H$

(b) 
$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3$

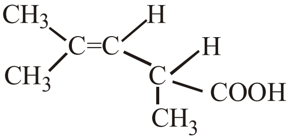
(c) 
$C_6H_5-\underset{O}{\underset{\|}{C}}-C_6H_5$ (d)

(d) None of these

11. Ethoxy ethane and methoxy propane are
(a) geometrical isomers (b) optical isomers
(c) functional group isomers (d) metamers

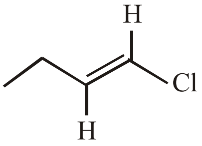
12. The number of structural and configurational isomers of a bromo compound, C_5H_9Br, formed by the addition of HBr to 2 - pentyne respectively are
(a) 1 and 2 (b) 2 and 4
(c) 4 and 2 (d) 2 and 1

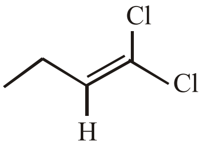
13. The structure,

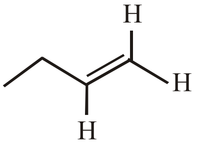


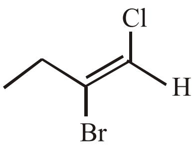
shows :
(a) geometrical isomerism
(b) optical isomerism
(c) geometrical and optical isomerism
(d) tautomerism

14. Which of the alkenes shown below are member of a pair of E - Z isomers ?

(A) 

(B) 

(C) 

(D) 

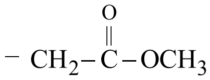
(a) A and C only (b) B and C only
(c) A and D only (d) None of these

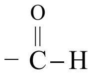
15. The correct priorities for the substituents shown below, according to the E-Z sequence rule is

I. $-CN$

II. $-CBr(CH_3)_2$

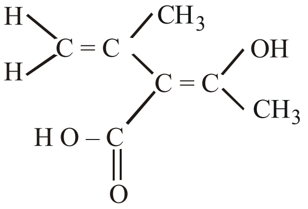
III. $-COOH$

IV. 
$-CH_2-\overset{O}{\overset{\|}{C}}-OCH_3$

V. 
$-\overset{O}{\overset{\|}{C}}-H$

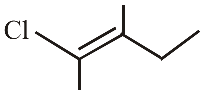
(a) II, III, V, I, IV (b) V, II, I, IV, III
(c) III, IV, I, II, V (d) II, V, I, IV, III

16. How many stereoisomers are possible for the molecule?



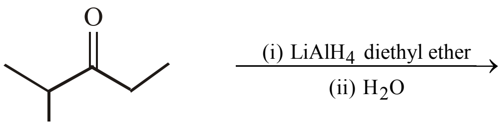
(a) 2 (b) 4
(c) 6 (d) 8

17. The configuration of the compound



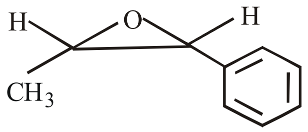
(a) E (b) Z
(c) Both (a) and (b) (d) Neither (a) nor (b)

18. The alcohol product(s) of the reduction of 2-methyl-3-pentanone with $LiAlH_4$ is (are)



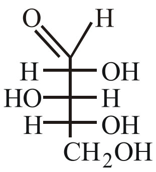
(a) a single enantiomer (b) racemic mixture
(c) two diastereoisomers (d) two structural isomers

19. How many stereoisomers of phenyl propylene oxide are there ?



(a) 1 (b) 2
(c) 4 (d) None of these

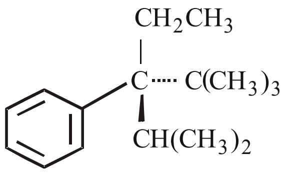
20. What is the R and S configuration for each stereogenic centre in this sugar from top to bottom ?



(a) R, R, S (b) R, S, S
(c) R, S, R (d) S, S, R

21. How many isomers have the compound bromomethyl cyclopentane (ignoring chirality) ?
(a) 4 (b) 5
(c) 6 (d) 7

22. The structure shown below has the configuration



(a) R (b) S
(c) Both (a) and (b) (d) Neither (a) nor (b)

23. The structure of allene is

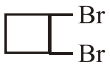
$CH_2=C=CH_2$

(a) staggered (b) planar

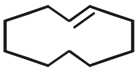
(c) eclipsed (d) None of these

24. The compound showing geometrical isomerism

(a) $C_6H_5CH = NOH$ (b)



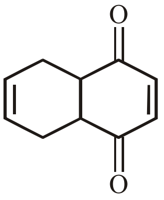
(c)



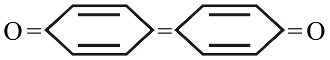
(d) All of these

25. Which of the following will show tautomerism ?

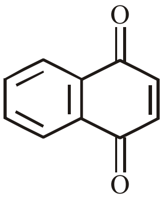
(a)



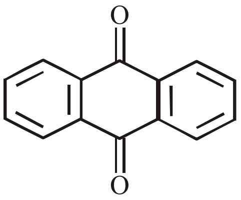
(b)



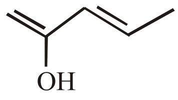
(c)



(d)



26. Identify the Keto form of the following enol



(a) 1-penten-3-one (b) (E)-3-penten-2-one

(c) 2-pentanone (d) (E)-3-pentanal

27. What is the relationship between keto and enol tautomers?

(a) Resonance forms

(b) Constitutional isomers

(c) Stereoisomers

(d) Different conformations of the same compound

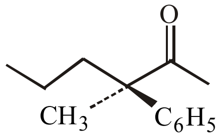
28. Which of the following has the highest percentage of enol in a Keto-enol equilibrium ?

(a) Hexanal (b) 2-hexanone

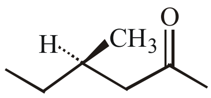
(c) 2, 4-hexanedione (d) 2, 5-hexanedione

29. Which of the following optically active compounds racemizes in dil. KOH/CH_3OH solution ?

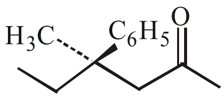
(a)



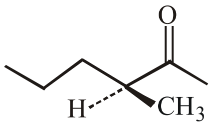
(b)



(c)



(d)



30. How many stereoisomeric aldohexoses are there ?

(a) four (b) eight

(c) sixteen (d) eighteen

31. What is the relationship between open chain forms of D-glucose and D-altrose ?

(a) enantiomers

(b) constitutional isomers

(c) diastereomers

(d) different conformations of the same compound

32. Which of the following compounds will not have diastereo isomers ?

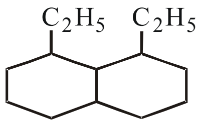
(a) $COOH(CHOH)_2COOH$

(b) $CH_3CHOH.COOH$

(c) $CH_2OH(CHOH)_4CHO$

(d) $CH_2OH(CHOH)_4CH_2OH$

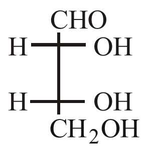
33. The correct number of chiral centres in



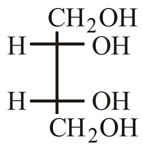
(a) 1 (b) 3

(c) 4 (d) 2

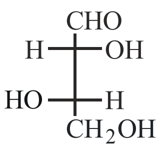
34. Give the correct relationship among the followings :



(A)



(B)



(C)

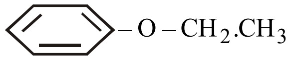
(a) A and B are identical

(b) A and B are diastereomers

(c) A and C are diastereo isomers

(d) A and C are enantiomers

35. The number of metamers given by the compound



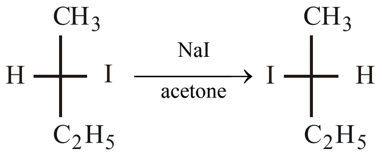
(a) 3 (b) 4

(c) 5 (d) 6

36. The number of asymmetric C-atom created and number of possible stereoisomers when benzil (Ph.CO.CO.Ph) is reduced with LiAl H_4.

(a) 2, 3
(b) 2, 2
(c) 2, 4
(d) 3, 2

37. An optically active compound (A) is treated with NaI/acetone (B) is obtained

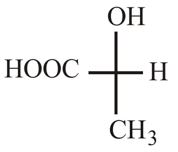


(A) (B)

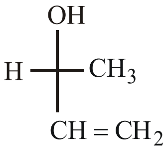
What is true about (B) ?

(a) optically active
(b) optically inactive and racemic form
(c) optically inactive
(d) None of these

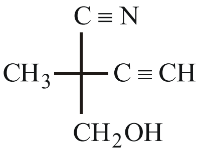
38. The following compounds A, B, C have R or S configurations



(A)



(B)



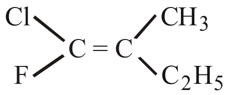
(C)

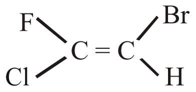
(a) R, R, S
(b) R, S, R
(c) R, R, R
(d) S, R, S

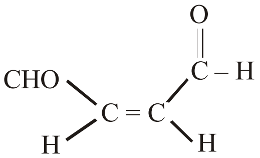
39. The stereo isomers formed when cis-2-butene is reacted with Br_2.

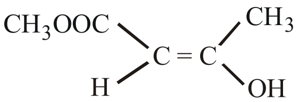
(a) meso-2, 3-dibromo butane
(b) racemic 2, 3-dibromo butane
(c) pair of diastereomers
(d) cannot be predicted

40. Which of the followings is Z-isomer ?

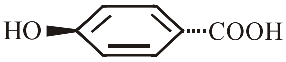
(a)


(b)


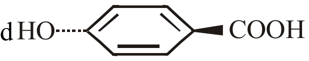
(c)


(d)


41. The two compounds given below are

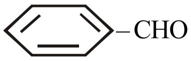


and



(a) identical
(b) enantiomers
(c) diastereo isomers
(d) regiomers

42. Which of the following have an enol form ?

(A)


(B) $(CH_3)_3C.CHO$

(C) $CH_3CCl_2.CHO$

(a) Only A
(b) Only B
(c) A and C only
(d) None have enol form

Hints & Solutions

EXERCISE 1

1. Chain or nuclear isomerism.
2. Four: 1, 1–dichloropropane ($CH_3CH_2CHCl_2$),
1, 2–dichloropropane ($CH_3CHClCH_2Cl$),
2, 2–dichloropropane ($CH_3CCl_2CH_3$) and
1, 3–dichloropropane ($ClCH_2CH_2CH_2Cl$).

7. (c)	**8. (b)**	**9. (c)**	**10. (a)**
11. (b)	**12. (d)**	**13. (b)**	**14. (a)**
15. (a)	**16. (d)**	**17. (a)**	**18. (b)**

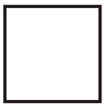
EXERCISE 2

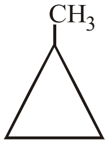
1. (b) Structures (*a*), (*c*) and (*d*) have the same molecular formula ($C_6H_{12}O$) while (*b*) has $C_6H_{10}O$ as molecular formula

2. (d)

3. (b) $CH_3CH_2CH_2C{\equiv}CH$, $(CH_3)_2CHC{\equiv}CH$, $CH_3CH_2C{\equiv}CCH_3$
I II III

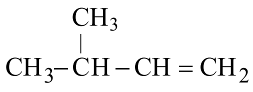
4. (b) $CH_3CH_2CH{=}CH_2$ $CH_3CH{=}CHCH_3$ $(CH_3)_2C{=}CH_2$
1-butene (*i*) 2- butene (*ii*), (*iii*) (*cis,- trans*) 2-methylpropene (*iv*)


cyclobutane (*v*)

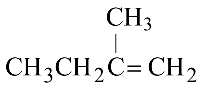

methylcyclopropane (*vi*)

5. (c) C_5H_{10} has 1° degree of unsaturation since the isomers are acyclic, all of these are alkenes. For writing the isomers, first introduce the double bond at different possible positions, and then consider the possibility of branching in the alkyl group.

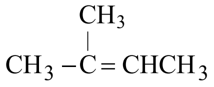
$CH_3CH_2CH_2CH{=}CH_2$ $CH_3CH_2CH{=}CHCH_3$
1-pentene (*i*) 2- pentene, (*cis,- trans*) (*ii*), (*iii*)


$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH=CH_2$

3-methyl-1-butene, (*iv*)


$CH_3CH_2\overset{CH_3}{\overset{|}{C}}=CH_2$

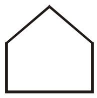
2-methyl-1-butene, (*v*)

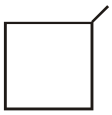

$CH_3-\overset{CH_3}{\overset{|}{C}}=CHCH_3$

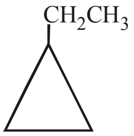
2-methyl-2-butene, (*vi*)

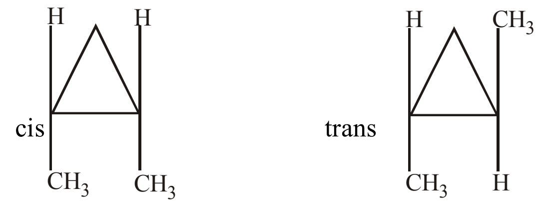
6. (a) As sketched in the above question , C_5H_{10} may be monosubstituted (i) and (iv), disubstituted as in (ii), (iii) and (v) and trisubstituted as in (vi)

7. (d) C_5H_{12} has 1° unstauration, so isomeric cyclic compounds (having 1° unsaturation) may be in the form of five-four, or three - membered ring compounds.


cyclopentane

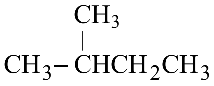

methylcyclobutane


ethylcyclopropane

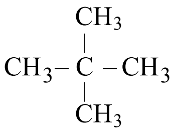


cis- and *trans* - 1, 2-dimethylcyclopropane

8. (a) $CH_3CH_2CH_2CH_2CH_3$
n- pentane


$CH_3-\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$

2-methylbutane


$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$

2, 2-dimethylpropane

9. (b) 2, 2, 4, 4 - Tetramethylhexane has 10 carbon atoms, only 4-isopropylheptane has also 10 carbon atoms so these two are isomers.

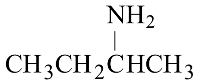
10. (c) Convert these Newmann projections into open chain structures.

Both structures have same molecular formula C_4H_9Cl, thus these are isomers. However, the two have different groups, viz CH_3 and CH_2Cl, so these are neither enantiomers nor diastereomers. Hence these are structural isomers.

11. (b)	**12. (b)**	**13. (a)**	**14. (a)**	**15. (c)**
16. (d)	**17. (a)**	**18. (b)**	**19. (d)**	

20. (d) Introduce - NH_2 at various possible positions to get different isomers which is possible only, on C_1 and C_2. Now observe isomerism in the alkyl part (C_4H_9–) of the amine which is three

$CH_3CH_2CH_2CH_2NH_2$



$CH_3CH_2\overset{NH_2}{\overset{|}{C}}HCH_3$

$(CH_3)_2CHCH_2NH_2$ $(CH_3)_3CNH_2$

21. (d) Molecular formula C_7H_8O points out the presence of one benzene ring (relatively less number of H atoms); so it can be $C_6H_5CH_2OH$ and its other isomers.

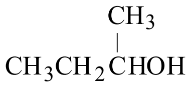
$C_6H_5CH_2OH$ $C_6H_5OCH_3$ $OH.C_6H_4.CH_3$

Benzylalcohol (*i*) Anisole (*ii*) *o* -, *m*-, *p*- Cresols, (*iii*), (*iv*) and (*v*)

22. (c) Alcohol may be 1°, 2° and 3°; further analyse the possibility of isomerism in each type of alcohol

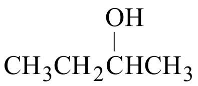
$CH_3CH_2CH_2CH_2OH$

1-butanol, 1°



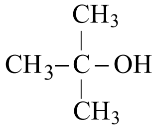
$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HOH$

2-methylpropanol, 1°



$CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_3$

2-butanol, 2°

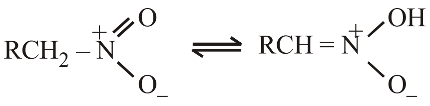


$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH$

2-methyl-2-propanol, 3°

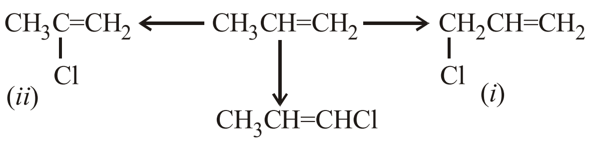
23. (c) There are four isomeric alcohols (mentioned in the above question) and three isomeric ethers corresponding to the formula $C_4H_{10}O$; $CH_3OC_3H_7$–*n*; $CH_3OC_3H_7$–*iso* and $C_2H_5OC_2H_5$

24. (d) Only RCH_2NO_2 has α -hydrogen atom



25. (a) **26. (c)**

27. (b) Replace three different types of hydrogen atoms,one by one.



cis- and *trans*, (*iii*) and (*iv*)

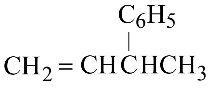
28. (b) $(CH)_2(COOH)_2$ is HOOCCH = CH COOH, hence here geometrical isomerism is possible.

29. (c)

30. (a) Draw the structure, and observe whether the two doubly bonded carbon atoms are differently substituted or not.

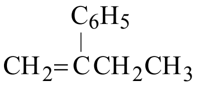
$C_6H_5CH_2CH = CHCH_3$

1-phenyl-2-butene



$CH_2 = CH\overset{C_6H_5}{\overset{|}{C}}HCH_3$

3-phenyl-1-butene



$CH_2 = \overset{C_6H_5}{\overset{|}{C}}CH_2CH_3$

2-phenyl-1-butene

$(C_6H_5)_2C=CHCH_3$

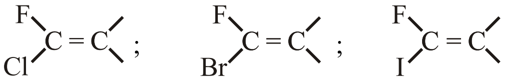
1, 1- diphenyl -1-propene

Note that only in first structure both of the doubly bonded carbon atoms have different groups.

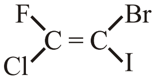
31. (b) **32. (d)** **33. (b)** **34. (c)**

35. (d) The given structure has three double bonds whose each carbon atom is differently substituted hence number of geometrical isomers will be $2^n = 2^{3'} = 8$, where *n* is the number of double bonds whose each carbon atom is differently substituted.

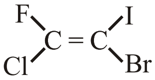
36. (d) Consider one doubly bonded carbon atom first, attach any one halogen atom (say F) on this C on one bond, and then attach the three remaining halogen atoms, of course one by one, on the other bond.



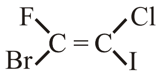
Now attach the remaining two halogen atoms in each of the above structures, for which there are two possibilities for every structure; so on the whole there will be 6 geometrical isomers.



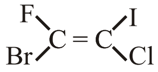
(I)



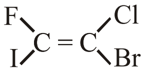
(II)



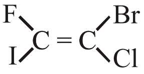
(III)



(IV)



(V)



(VI)

37. (a) **38. (a)** **39. (a)**

40. (a) None of the carbon atoms in $DCH_2CH_2CH_2Cl$ is chiral i.e., each carbon atom is achiral (symmetric).

41. (b) $\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_2-\overset{7}{C}H_3$

Replacement of one hydrogen atom at C_2,C_3,C_5 or C_6 can make the resulting compound chiral.

42. (c)

43. (d) Specific rotation of the mixture

$$=\left(\frac{75}{100}\times 158\right)+\left(\frac{25}{100}\times -158\right)=+79^\circ$$

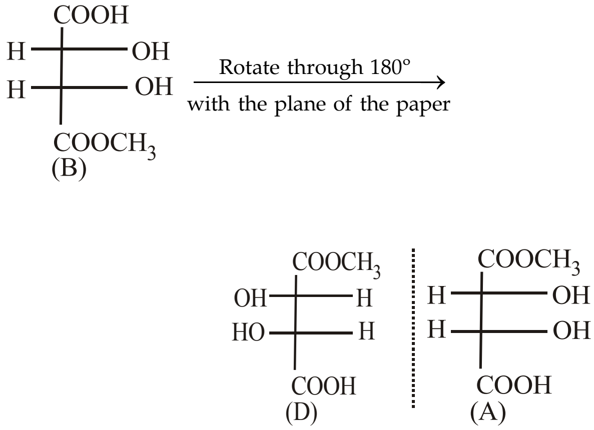
44. (a) **45. (b)** **46. (b)** **47. (c)** **48. (d)**

49. (c) **50. (d)**

51. (a) Since the configuration at the chiral centre is same , the two structures (optical isomers) are not mirror images, hence these are diastereomers.

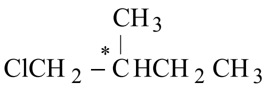
52. (d) **53. (b)** **54. (a)**

55. (d) Rotation of B through 180° within the plane of the paper gives D which is an enantiomer of A, hence A and B are enantiomers



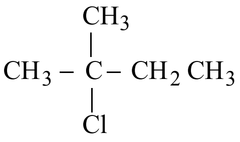
56. (b) Butane-2, 3-diol ($CH_3CHOHCHOHCH_3$) has two similar chiral carbon atoms (similar to tartartic acid), hence like tartaric acid it has three optical isomers (*d,-l-*, and *meso-*), of which only two (*d–* and *l–*) are optically active.

57. (d) First draw possible different structures obtained on monochlorination of 2-methylbutane, $CH_3CH(CH_3)CH_2CH_3$.

(i) 

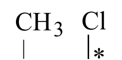
$\mathrm{ClCH_2-\overset{CH_3}{\overset{|}{\overset{*}{C}}}HCH_2CH_3}$

Optically active

(ii) 

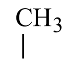
$\mathrm{CH_3-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2CH_3}$

Optically inactive

(iii) 

$\mathrm{CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{Cl}{\overset{|*}{C}}HCH_3}$

Optically active

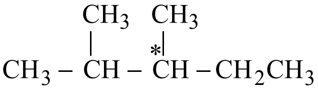
(iv) 

$\mathrm{CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2CH_2Cl}$

Optically inactive

Thus structures (i) and (iii) are optically active, each has one chiral carbon; so each structure will give one enantiomeric pair; thus total enantiomeric pairs will be two.

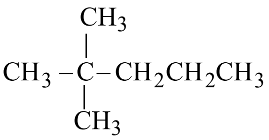
58. (d) The structure $\mathrm{CH_3\overset{*}{C}HBr\overset{*}{C}HBrCOOH}$ has two different chiral carbon atoms, hence number of enantiomers (optically active forms) is $2^n = 2^2 = 4$

59. (a) 

$\mathrm{CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{CH_3}{\overset{*|}{C}}H-CH_2CH_3}$

2,3 – dimethylpentane

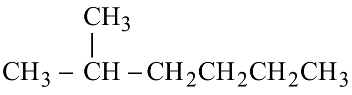
(has chiral C)



$\mathrm{CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2CH_2CH_3}$

2, 2 – dimethylpentane

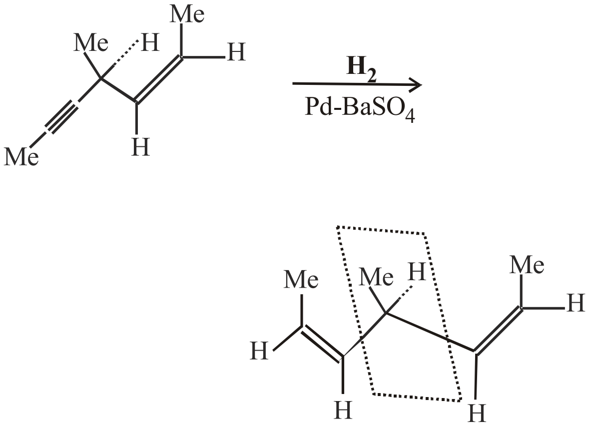
(No chiral carbon)



$\mathrm{CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2CH_2CH_2CH_3}$

2 – Methylhexane

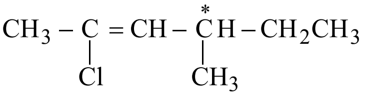
(No chiral carbon)

60. (b) 

Due to cis-addition of H_2 to the triple bond, the reduced product has a plane of symmetry and hence is optically inactive.

61. (c) Geometrical isomerism due to the presence of a double bond whose each carbon has two different substituents. Optical isomerism due to presence of a chiral carbon,

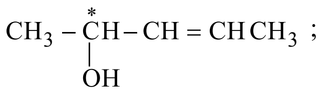
$-\overset{*}{C}HOHCOOH\cdot$

62. (c) 

$\mathrm{CH_3-\underset{Cl}{\underset{|}{C}}=CH-\underset{CH_3}{\underset{|}{\overset{*}{C}}}H-CH_2CH_3}$

2 – Chloro - 4 - methylhex - 2 - ene

Geometrical isomerism due to C = C, each C has two different groups. Each geometrical isomer (*cis–*, or *trans*) will show optical isomerism due to the presence of chiral C. Hence total number of isomers will be 2 × 2 = 4

63. (b) 

$CH_3-\overset{*}{C}H(OH)-CH=CHCH_3$;

Pent – 3 – en – 2 – ol

As in above question, total number of stereoisomers $=2\times2=4$

64. (a) Since during the reaction, a chiral carbon is created and further since the CN^- ion can attack the planar aldehyde group both from the top and the bottom face of the aldehyde group with equal ease, therefore, a 50:50 mixture of the two enantiomers, i.e. a racemic mixture is obtained.

65. (a)

66. (c) Diastereomers have different solubility, m.p. and b.p., hence they can be separated by fractional crystallisation.

67. (d) Since all the six carbon atoms of cyclohexatriene (benzene) are sp^2 hybridized, therefore its stablest structure is planar form.

68. (b) **69. (d)**

70. (c) Note that in structures 1 and 2, every two adjacent hydrogen atoms are at maximum possible distance from each other (staggered conformation).

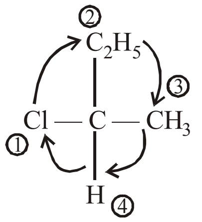
71. (b)

72. (d) Boat conformation of cyclohexane has two types of destabilizing interactions, i.e. eclipsing and flagpole-flagpole. Out of these flagpole-flagpole interaction is the most destabilizing.

73. (a) Cyclohexane (iv) is non-planar and has chair conformation. In this conformation, the bond angle is the normal tetrahedral angle (109°, 28') and thus has no angle strain and hence is most stable. The rest of the molecules are nearly planar and hence their stability depends upon the angle strain in accordance with *Baeyer's strain theory.* Since cyclopropane has higher angle strain $\left(\frac{109°28'-60°}{2}=24°,44'\right)$ than cyclopentane $\left(\frac{109°\ 28'-108°}{2}=0°,44'\right)$. Therefore cyclopentane (iii) is more stable than cyclopropane (i). Further, because of the presence of a double bond in a three membered ring, cyclopropene (ii) is the least stable. Thus the order of stability is (iv) > (iii) > (i) >(ii).

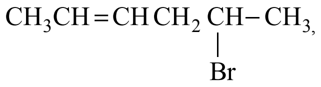
74. (a) As the size of the ring increases, the internal angle increases accordingly. As a result, the deviation from the tetrahedral angle and hence the angle strain increases as the size of the ring increases. Thus, planar cyclodecane is expected to have the maximum angle strain.

EXERCISE 3

1. (b) 

R-configuration

2. (a) In the molecule



$CH_3CH=CHCH_2CH(Br)-CH_3,$

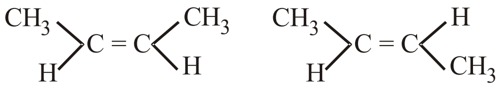
the number of stereoisomers is given by sum of geometrical isomers (because of presence of C = C) and optical isomers (because of presence of chiral carbon atom).

Number of geometrical isomers = 2 (one C = C is present).

Number of optical isomers = 2 (one chiral carbon atom).

Total number of stereoisomers = 2 + 2 = 4

3. (d) Alkenes with double bonds cannot undergo free rotation and can have different geometrical shapes with two different groups on each end of the double bond.



cis-But-2-ene *trans*-But-2-ene

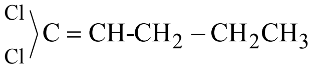
4. (a) Enolic form predominates in compounds containing two carbonyl groups separated by a $-CH_2$ group. This is due to following two factors.

(i) Presence of conjugation which increases stability.

(ii) Formation of intramolecular hydrogen bond between enolic hydroxyl group and second carbonyl group which leads to stablisation of the molecule. Hence the correct answer is III > II > I.

5. (b) The nitro group can attach to metal through nitrogen as $(-NO_2)$ or through oxygen as nitrito (–ONO).

6. (c) Optical and geometrical isomers are stereoisomers

7. (c) 

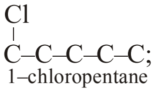
$Cl_2C=CH\text{-}CH_2-CH_2CH_3$ does not show geometrical isomerism due to presence of two similar Cl atoms on the same C-atom.

8. (d) Racemic mixture is formed when enantiomers are mixed in equimolar proportion

9. (a) A chiral object or structure has four different groups attached to the carbocation.

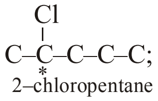
10. (a) Only 2- cyclopropyl butane has a chiral centre.

11. (c) 1-chloropentane is not chiral while others are chiral in nature



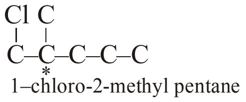
$$\overset{Cl}{C}-C-C-C-C;$$

1–chloropentane



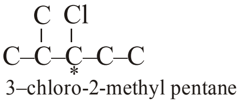
$$C-\overset{Cl}{\underset{*}{C}}-C-C-C;$$

2–chloropentane



$$\overset{Cl}{C}-\overset{C}{\underset{*}{C}}-C-C-C$$

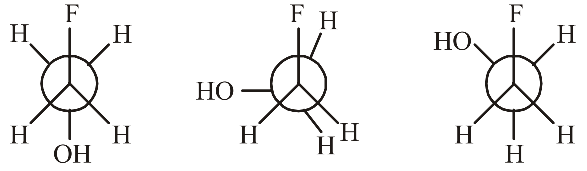
1–chloro-2-methyl pentane



$$C-\overset{C}{C}-\overset{Cl}{\underset{*}{C}}-C-C$$

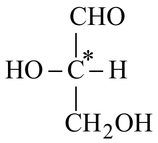
3–chloro-2-methyl pentane

12. (c) The greater the distance between the atoms or groups the more is the stability of conformers. Hence the order of stability is



anti or staggered   eclipsed   Skew or Gauche

13. (b) The organic compounds which have chiral carbon atom (a carbon atom attached to four different group or atoms and do not have plane of symmetry rotate plane polarised light.



$$HO-\overset{CHO}{\underset{CH_2OH}{C^*}}-H$$

(C* is asymmetric carbon)

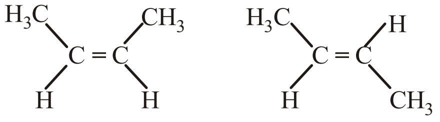
14. (b) Chiral conformation will not have plane of symmetry. Since twist boat does not have plane of symmetry it is chiral.

15. (b) The absolute configuration is (R, R)

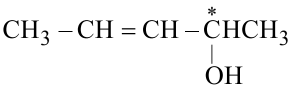
(using priority rules to get the absolute configuration)

So the correct answer is (b)

16. (b)



17. (b)



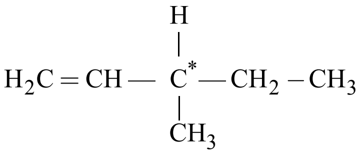
$$CH_3-CH=CH-\underset{OH}{\overset{*}{C}}HCH_3$$

exhibits both geometrical as well as optical isomerism.

cis - R   *cis* - S

trans - R   *trans* - S

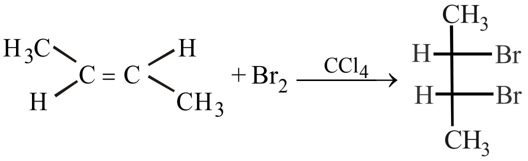
18. (c) For a compound to show optical isomerism, presence of chiral carbon atom is a necessary condition.



$$H_2C=CH-\overset{H}{\underset{CH_3}{C^*}}-CH_2-CH_3$$

3- methyl-1-pentene

19. (a) Anti addition of Br_2 on *trans* alkene provides meso compound.

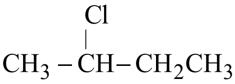


Therefore, no. of stereoisomers = 1

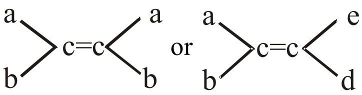
EXERCISE 4

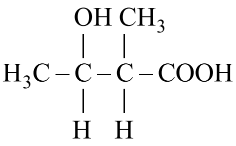
1. (c) $C_2H_4Br_2$ represents 1, 1-dibromoethane and 1, 2 - dibromethane which are position isomers

2. (c) It is definition of asymmetric synthesis

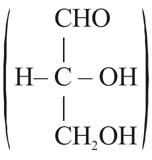
3. (b)  $CH_3-\overset{Cl}{C}H-CH_2CH_3$ contains asymmetric C - atom

4. (c) The condition for geometrical isomerism is

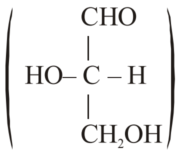


5. (d)  $H_3C-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{CH_3}{C}}-COOH$ contains two asymmetric C - atoms . Hence number of optical isomers is $2^2 = 4$

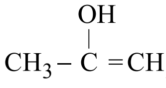
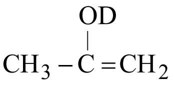
6. (c) Positive sign is for optical rotation (dextro rotatory) and D - is for configuration. It is derived from

D (+) glyceraldehyde 

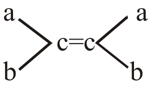
$$\left(H-\overset{CHO}{\underset{CH_2OH}{C}}-OH\right)$$

L (–)glyceraldehyde is 

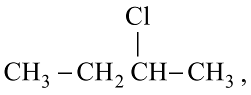
$$\left(HO-\overset{CHO}{\underset{CH_2OH}{C}}-H\right)$$

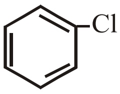
7. (a) The enol form of acetone is $CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2$ with D_2O it gives $CH_3-\overset{\overset{\displaystyle OD}{|}}{C}=CH_2$



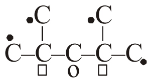
8. (d) $BrCH=CHBr$. It fulfills the condition of



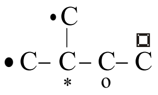
9. (a) $CH_3-CH_2\overset{\overset{\displaystyle Cl}{|}}{C}H-CH_3$, $CH_3CH_2CH_2CH_2-Cl$ (2 from n-butane)



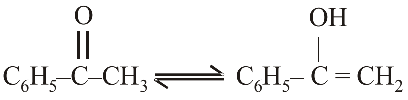
(1from benzene) (All positions are the same)



(3 from 2, 4 - dimethylpentane) (there are three different positions, •,□, and o)

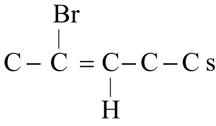


(4 from 2 - methyl butane) (there are 4 different positions, •,□,o and *)

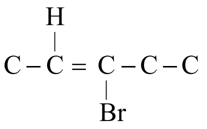


10. (b) $C_6H_5-\overset{\overset{\displaystyle O}{||}}{C}-CH_3 \rightleftharpoons C_6H_5-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2$

11. (d) There are metamers



12. (b) $C-\overset{\overset{\displaystyle Br}{|}}{C}=\underset{\underset{\displaystyle H}{|}}{C}-C-C$ structural : 1, geometrical : 2



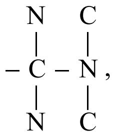
$C-\overset{\overset{\displaystyle H}{|}}{C}=\underset{\underset{\displaystyle Br}{|}}{C}-C-C$ structural : 1, geometrical : 2.

Hence 2 structural and 4 geometrical isomers

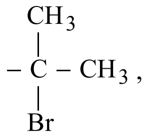
13. (b) It contains one asymmetric C- atom. Hence exhibits optical isomerism.

14. (c) The structures B and C contain similar atoms on ethylenic C-atoms. Hence do not exhibit isomerism.

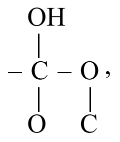
15. (a)



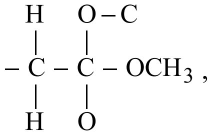
(i)



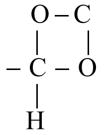
(ii)



(iii)



(iv)



(v)

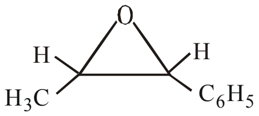
Arrange (NNN), (BrCC), (OOO), (CHH), (OOH) in increasing atomic number. The order is ii, iii, v, i, iv.

16. (a)

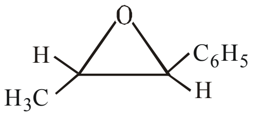
17. (a) The groups of higher priority Cl and $-C_2H_5$ are on opposite sides.

18. (b) The resulting compound is $C_3H_7.CHOH.C_2H_5$ which is optically inactive and reaction leads the racemisation.

19. (c)

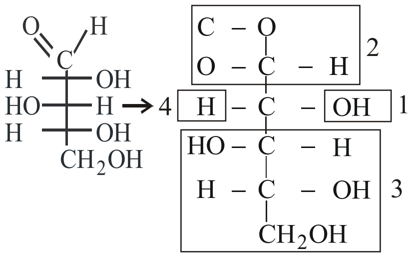


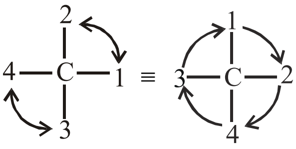
and



Each structure will have two configurations.

20. (c)

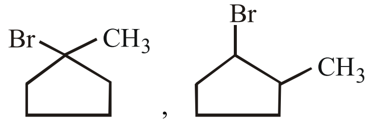




R configurations

Arrange the groups in order of priority by following the text.

21. (c) Each structure



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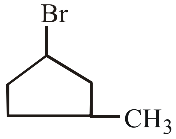
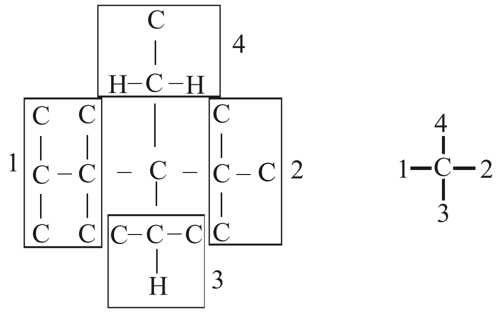
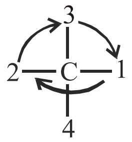


will give two configurations.

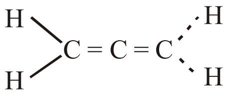
22. (a)





R configuration

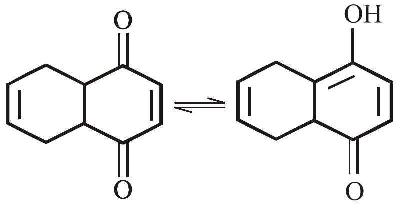
23. (a) Allene has the structure



staggered

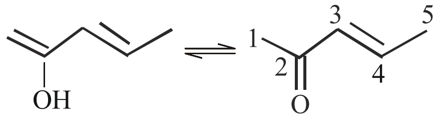
24. (d) Write cis and trans configuration for each.

25. (a)



are tautomers.

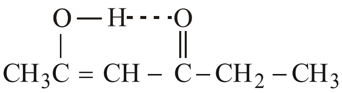
26. (b)



The keto form has E configuration.

27. (b) The keto enol tautomers are constitutional isomers.

28. (c) Enol form of 2, 4-hexane dione



$$\overset{\overset{O—H\cdots O}{|\qquad\quad\ \|}}{CH_3C = CH - C - CH_2 - CH_3}$$

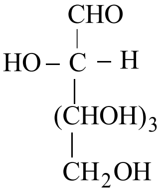
is stabilised by H-bonding.

29. (d) The compounds containing $-\overset{\overset{O}{\|}}{C}-$ group adjacent to asymmetric carbon atom carrying a hydrogen easily racemise.

30. (c) Aldohexose, contain four asymmetric carbon atoms and exist in $2^4 = 16$ stereo isomers.

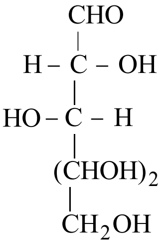
31. (b) Constitutional isomers

Altrose is



$$\begin{array}{c} CHO \\ | \\ HO - C - H \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}$$

, Glucose is



$$\begin{array}{c} CHO \\ | \\ H - C - OH \\ | \\ HO - C - H \\ | \\ (CHOH)_2 \\ | \\ CH_2OH \end{array}$$

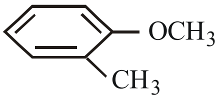
32. (b) For diastereo isomerism the compound must have two different asymmetric carbon atoms.

33. (d) The molecule contains two similar chiral centres.

34. (c) A and C are diastereo isomers.

35. (b) Metamers are

,



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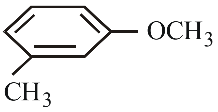

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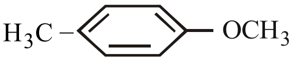
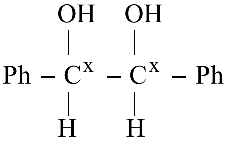


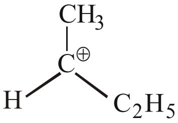
36. (a) Ph.CO.CO. Ph $\xrightarrow{LiAlH_4}$



$$\begin{array}{c} \quad OH \quad OH \\ \quad | \qquad | \\ Ph - C^x - C^x - Ph \\ \quad | \qquad | \\ \quad H \qquad H \end{array}$$

The product contains two similar asymmetric carbon atoms and two optically active and one optically inactive meso form.

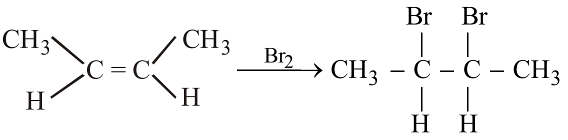
37. (b) The reaction proceeds through planar



leading to racemisation.

38. (d)

39. (b)



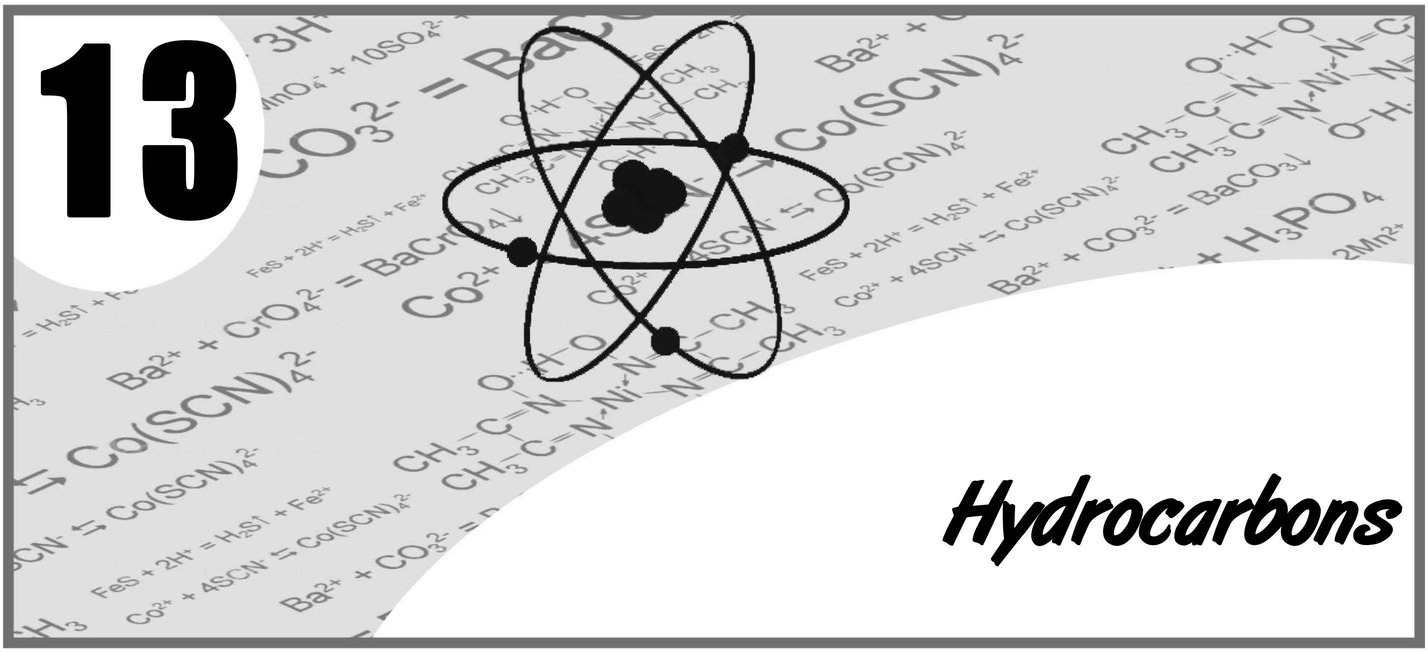
$$\begin{array}{c} CH_3 \quad CH_3 \\ C = C \\ H \qquad H \end{array} \xrightarrow{Br_2} \begin{array}{c} \qquad Br \quad Br \\ \qquad | \qquad | \\ CH_3 - C - C - CH_3 \\ \qquad | \qquad | \\ \qquad H \quad H \end{array}$$

Racemic form

40. (c)

41. (a) The given compounds are identical.

42. (d) None can have the enol form due to absence of H-atom on the carbon adjacent to $-\overset{\overset{O}{\|}}{C}-$ group.



13

Hydrocarbons

SATURATED HYDROCARBONS, PARAFFINS OR ALKANES :

They are open chain compounds of carbon and hydrogen having all the atoms linked together by single covalent bonds, least reactive in nature

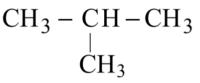
(Parum = little; affins = affinity) and having general formula C_nH_{2n+2}

NOMENCLATURE :

(I) Trivial names : The first four members have the trivial names derived from their preparation from corresponding alcohols containing same number of carbon atoms eg. methane from methyl alcohol, ethane from ethyl alcohol and so on. After butane they are named according to Latin or Greek numerals of the number of Carbon atoms present in them with class suffix-ane. eg. Pentane (penta = 5) : hexane (hexa = 6) and so on.

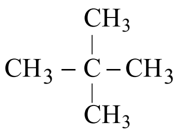
The straight chain hydrocarbons are called normal (n) and contain 1° or 1° & 2° carbon atoms. The branched chain hydrocarbons containing the group $(CH_3)_2CH-$ are called Iso and contain 1° & 3° or 1°, 2° and 3° carbon atoms. The hydrocarbons containing a quaternary carbon atom are called neo (new).

$\underset{\text{n–Butane}}{CH_3-CH_2-CH_2-CH_3}$;



$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$;

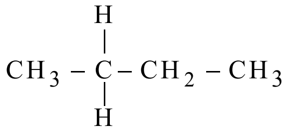
Iso–butane



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$;

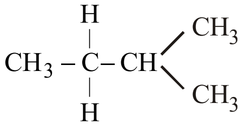
Neopentane

(II) Derived names : In this system the higher hydrocarbons are considered as derived from methane, eg.



$CH_3-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-CH_3$;

ethyl methyl methane



$CH_3-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-CH(CH_3)_2$;

methyl iso propyl methane

(III) IUPAC system

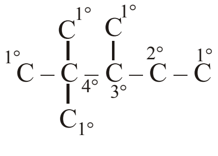
Types of carbon atoms :

(I) Primary (1°) - It is attached to one carbon atom only.

(II) Secondary (2°) - It is attached to two carbon atoms.

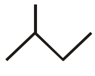
(III)Tertiary (3°) - It is attached to three carbon atoms.

(IV) Quaternary (4°) - It is attached to four carbon atoms.

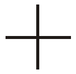


Isomerism : They exhibit chain isomerism

n-Pentane



Isopentane



Neopentane

Number of isomers of alkanes :

C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	$C_{10}H_{22}$
2	3	5	9	18	75

Occurrence : The crude petroleum and natural gas contain hydrocarbons from C_1 to C_{40}. Ozokerite (a neutral wax) is a mixture of higher solid hydrocarbons. Waxes of some plants and animals also contain some higher paraffins.

GENERAL METHODS OF PREPARATION OF ALKANES

(I) **From unsaturated hydrocarbons *:* (Sabatier and Senderen's reaction)**

$$C_nH_{2n} + H_2 \xrightarrow[200°-300°C]{H_2/Ni} C_nH_{2n+2}$$

$$C_nH_{2n-2} + 2H_2 \xrightarrow[300°C]{Ni/H_2} C_nH_{2n+2}$$

(II) By heating anhydrous sodium salt of fatty acid with soda lime (Lab method).

$$RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3$$

(III) **By reduction of alkyl halides with nascent hydrogen.**

$$RX + 2H \longrightarrow RH + HX$$

Reducing agents used are Na/C_2H_5OH; Zn/HCl;

Zn–Cu couple; Hg–Al couple, HI/P.

(IV) **Wurtz synthesis :**

$$RX + 2Na + XR \xrightarrow{ether} R-R + 2NaX$$

- Alkanes with odd number of carbon atoms can not be prepared by this method.
- Different alkyl halides give mixture of hydrocarbons viz. R – R, R' – R' & R – R'.
- 3° alkyl halides give alkenes by dehydrohalogenation.

(V) **By Frankland's method :**

$$R-I + Zn + I-R \longrightarrow R-R + ZnI_2$$

(VI) **From Grignard's reagent :**

$$\text{Compound H} + RMgX \longrightarrow \text{Compound MgX} + RH$$

H must be attached to O, N, S or sp hybridised C-atom. (*i.e.* active H-atom).

(VII) **Kolbe's electrolytic method :**

$$\begin{array}{l} RCOOK \rightleftharpoons \underset{\text{Anode}}{RCOO^-} + \underset{\text{Cathode}}{K^+} \\ \qquad\qquad \big\downarrow -e^- \\ \qquad\quad RCOO^\bullet \xrightarrow{\text{Fractionation}} R^\bullet + CO_2;\ R^\bullet + R^\bullet \longrightarrow R-R \end{array}$$

(VIII) **By Clemmensen's reduction :** From carbonyl compounds

$$>C=O + 4H \xrightarrow[\text{Conc. HCl}]{Zn-Hg} >CH_2 + H_2O$$

(IX) **By Wolf. Kishner reduction :** From Carbonyl compounds

$$>C=O + 4H \xrightarrow[\text{KOH/glycol}]{NH_2.NH_2} >CH_2 + H_2O$$

(X) **By Berthlot's reaction :**

$$C + 2H_2 \xrightarrow[1200°C]{\text{Electric arc}} CH_4$$

(XI) **From metal carbides :**

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

(XII) **From carbon monooxide**

$$CO + 3H_2 \xrightarrow[255°C]{Ni+C} CH_4 + H_2O$$

(XIII) **By reduction of alcohols, aldehydes, ketones and carboxylic acids :**

$$ROH + 2HI \xrightarrow[200°C]{\text{Red P}} RH + I_2 + H_2O$$

$$RCHO + 4HI \xrightarrow[150°C]{\text{Red P}} RCH_3 + 2I_2 + H_2O$$

$$RCOR + 4HI \xrightarrow[150°\,C]{\text{RedP}} RCH_2R + 2I_2 + H_2O$$

$$RCOOH + 6HI \xrightarrow[150°C]{\text{Red P}} RCH_3 + 3I_2 + 2H_2O$$

(XIV) **Corey-House alkane synthesis :**

$$RX + 2Li \xrightarrow{ether} \underset{\text{Alkyl lithium}}{RLi + LiX}$$

$$2RLi + CuI \longrightarrow \underset{\text{Lithium dialkyl copper}}{LiR_2Cu} + LiI$$

$$R'Br + LiR_2Cu \longrightarrow R'-R + RCu + LiBr$$

The reaction is particularly useful for preparing unsymmetrical alkanes.

Properties : C_1–C_4 gases; C_5–C_{17} colourless liquids, higher solids. Insoluble in water soluble in organic solvents

Branched chain alkanes boil at lower temperature than isomeric straight chain alkanes. The latter have higher van der Waals forces of attraction.

Melting points of hydrocarbons containing even number of C-atoms are relatively more than those containing odd number of carbon atoms.

RH
Alkane

$\xrightarrow[\text{UV light / or }\Delta]{\text{Halogenation }(Cl_2)}$ $CH_3Cl \,.\, CH_2Cl_2 \,.\, CHCl_3 \,.\, CCl_4$ (from methane)

$\xrightarrow[2Cl_2]{\text{Direct Sun Light}}$ $C + 4HCl$ (explosive reaction) (from methane)

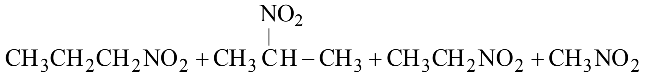
- Ease of replacement of hydrogen atom 3° > 2° > 1°. The relative rates being **5:3.8:1**
- Order of reactivity of halogens $F_2 > Cl_2 > Br_2 > I_2$
- Iodination is reversible $CH_4 + I_2 \rightleftharpoons CH_3I + HI$

  $5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$

  It requires the use of oxidising agent such as HNO_3, HIO_3 etc.
- Fluro compounds are obtained from bromo or chloro compounds
  $2RBr + HgF_2 \longrightarrow 2RF + HgBr_2$
- Chlorination and bromination proceed by free radical mechanism.

$\xrightarrow[SO_2Cl_2\text{+ light or peroxide}]{\text{Sulphuryl Chloride}}$ $R - Cl + SO_2 + HCl$ (Chlorination)

$\xrightarrow[450°C\text{ vapour phase}]{\text{Nitration }HNO_3}$



$CH_3CH_2CH_2NO_2 + CH_3\overset{\overset{\displaystyle NO_2}{|}}{C}H - CH_3 + CH_3CH_2NO_2 + CH_3NO_2$ (from propane)

$2CH_3COOH + CO_2 + H_2O$ (from neopentane)

$\xrightarrow[H_2SO_4\ \ 400°C]{\text{Sulphonation}}$ $RSO_3H \quad + H_2O$
Alkyl sulphonic acid

$\xrightarrow[200°C]{\text{Oxidation }O_2\text{, Cu tube 100 atm.}}$ CH_3OH

$\xrightarrow{MoO / O_2}$ $HCHO + H_2O$

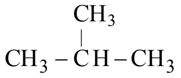
$\xrightarrow{(CH_3COO)_2\ Mn/O_2}$ $HCOOH + H_2O$

} From methane

$\xrightarrow{\text{Alk. }KMnO_4\ [O]}$ R_3COH (From Isobutane)
Alkanes containing 2° and 1° H atoms are generally not oxidised by $K_2Cr_2O_7$ and $KMnO_4$

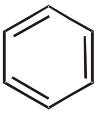
$\xrightarrow[O_2\text{ Excess }\Delta]{\text{Combustion}}$ $CO_2 + H_2O$

$\xrightarrow[\text{Anhy. }AlCl_3\text{ + Conc. HCl}]{\text{Isomerisation}}$



$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C}H - CH_3$ (from n – butane)

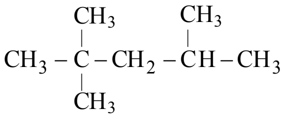
$\xrightarrow[450\text{–}500°C]{\text{Aromatisation }Cr_2O_3}$



$+ 4H_2$ (from n-Hexane)

$\xrightarrow[Cr_2O_3 / Al_2O_3\ \Delta]{\text{Dehydrogenation}}$ $CH_3 - CH = CH_2 + H_2$ (from propane)

$\xrightarrow[\text{Isobutane + Isobutylene}]{\text{Alkylation}}$

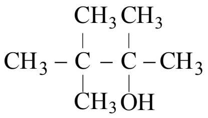


$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{C}H - CH_3$

2,2,4–trimethyl pentane (common name isoctane)

$\xrightarrow[\text{n-butane gives}]{\text{Cracking }\ \Delta}$ $CH_3 - CH = CH_2 + CH_4 + CH_2 = CH_2 + CH_3 - CH_3$

$\xrightarrow[\text{Conc. }H_2SO_4]{(CH_3)_3CH + CH_3COCH_3}$

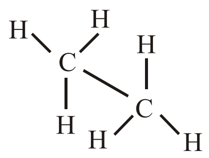


$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}} - CH_3$

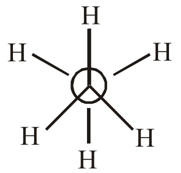
2,3,3–trimethyl butanol–2

CONFORMATIONAL ANALYSIS :

Ethane –

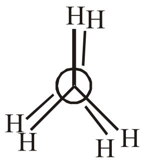


Sawhorse projection

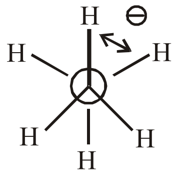


Newman projection

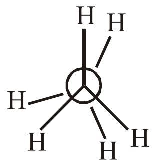
Different arrangements of atoms in a molecule convertible into one another by rotation about single bond are called **conformers** or **conformations**. Their study is known as **conformational analysis**. If the energy barrier to the rotation is nil or small, the rotation is said to be free or almost free. Ethane can exist in an infinite number of conformations. They are



Eclipsed



θ = 60° Staggered



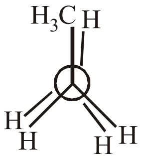
θ < 60° > 0 Skew

θ = It is dihedral angle between C–H bonds on the front of a Newman projection and those on the back.

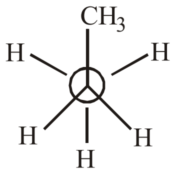
Order of stability : Staggered > Skew > Eclipsed

Energy barrier between eclipsed and staggered is 2.8 kcal/mol.

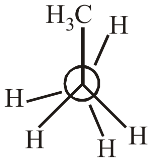
Conformations of Propane C_3H_8 :



Eclipsed



Staggered θ = 60°

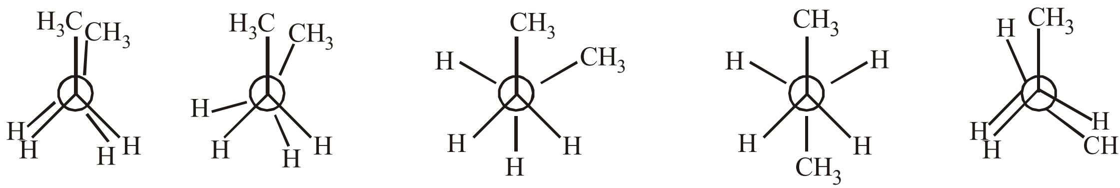


Skew θ < 60° > 0

Order of stability : Staggered > Skew > Eclipsed

Energy barrier between eclipsed and staggered is 3.3 kcal/mol

Conformations of n-Butane C_4H_{10} :



θ = 0° Fully Eclipsed

θ < 60° > 0 Skew

θ = 60° Gauche

θ = 180° Anti or Trans

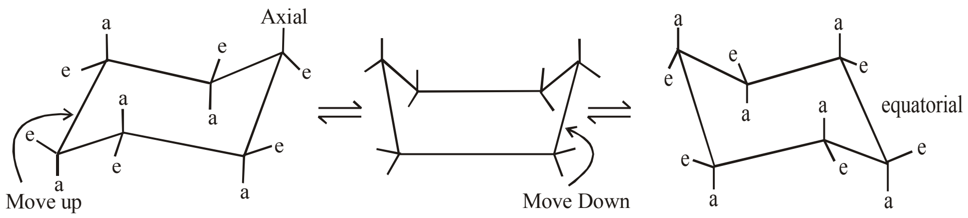
θ= 120 ° Eclipsed

Staggered

Order of stability : Anti > Gauche > Skew > Eclipsed > Fully Eclipsed

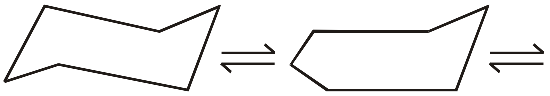
Energy barrier between fully eclipsed and fully staggered (anti) is 5.3 kcal / mol or 22 kJ/mol.

Conformations of Cyclohexane : It exists in two nonplanar, strainless forms, the boat and the chair form.

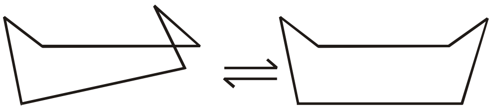


Chair form ***Boat form*** ***Chair form***

Equatorial hydrogens lie in the plane of the ring carbons. Axial hydrogens lie (up or down) the plane of the ring. There are six equatorial and six axial hydrogens. In the flipping and reflipping between conformations, axial becomes equatorial and vice versa. Chair form has the **lowest** energy. Cyclohexane can assume other shapes also.



Chair form Most Stable | Half Chair



Twist Boat | Boat form (Least Stable)

Baeyer's Strain Theory : When ring compounds are formed, the bonds deviate from normal positions which produces a condition of strain in the molecule. The strain is directly proportional to angle of deviation and can be calculated as follows. The more the angle of deviation, the less is the stability.

Angle of deviation of cyclic compound

$$= \frac{1}{2}(109°28' - \text{angle of cyclic compound})$$

For Cyclo propane $= \frac{1}{2}(109°28' - 60°) = 24°44'$

Cyclo butane $= \frac{1}{2}(109°28' - 90°) = 9°44'$

Cyclopentane $= \frac{1}{2}(109°28' - 108°) = 0.44'$

Cyclohexane

$$= \frac{1}{2}(109°28' - 120°) = -5°16' \text{ (deviation outside)}$$

Cycloheptane

$$= \frac{1}{2}(109°28' - 128°34') = -9°33' \text{ (deviation outside)}$$

Limitations : Baeyer's strain theory fails to explain the stability of large ring alicyclic compounds.

Sachse Mohr theory of Strainless rings :

A ring with six or more carbon atoms can assume "puckered" structure and there is a little distortion of normal tetrahedral angle. Thus there is little or negligible angle strain in the molecule.

UNSATURATED HYDROCARBONS, OLEFINS OR ALKENES :

They are open chain compounds of carbon and hydrogen having double bonds also known as **Olefins** (oil forming) Olefiant gas is Dutch name of ethylene which formed oily ethylene chloride with chlorine. Their general formula is C_nH_{2n}.

Nomenclature :

(I) Common System : The suffix -ane of alkane is replaced by -ylene, and named as Alkylenes eg. ethylene, propylene etc.

(II) IUPAC System : The suffix *-ane* of alkane is replaced by *-ene* and hence named as Alkenes.

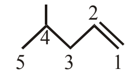
(III) Derived Names : They are named as substituted derivatives of ethylene. For example

	Common Name	*IUPAC Name*	*Derived name*
$CH_3-CH=CHCH_3$	α-Butylene	But-2-ene or 2-Butylene	s-Dimethyl ethylene

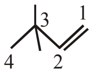
Isomerism : Alkenes show four types of isomerism

(I) Chain Isomerism :

Hex-1-ene



4-methyl pent-1-ene



3,3-dimethyl but-1-ene

(II) Position Isomerism :

But-1-ene

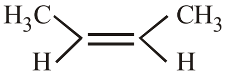
But-2-ene

(III) Ring Chain Isomerism :

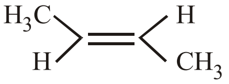
But-1-ene

Cyclo butane

(IV) Geometrical Isomerism :



cis But-2-ene



trans But-2-ene

GENERAL METHODS OF PREPARATIONS OF ALKENES

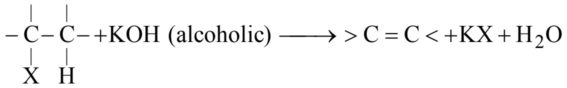
(I) By dehydration of alcohols :

$$ROH \xrightarrow{\text{Dehydrating agent}} \text{Alkene} + H_2O$$

Dehydrating agents Conc. H_2SO_4; P_2O_5; H_3PO_4; Al_2O_3. Anhy. $ZnCl_2$. Anhy. Oxalic acid.

Ease of dehydration of alcohols 3° > 2° > 1°.

(II) By Dehydrohalogenation of Alkyl halides.



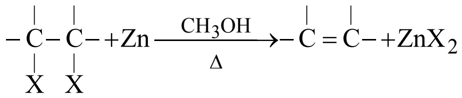
$$-\underset{X}{\overset{|}{\underset{|}{C}}}-\underset{H}{\overset{|}{\underset{|}{C}}}- + KOH \text{ (alcoholic)} \longrightarrow {>}C=C{<} + KX + H_2O$$

- Dehydrohalogenation and dehydration follows **Saytzeff's rule** (Hydrogen is removed from C-atom containing lesser number of H-atoms or more substituted alkene is formed)
- More substituted alkenes are more stable.

$$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 >$$
$$RCH=CHR > RCH=CH_2 > CH_2=CH_2$$

- Ease of dehydrohalogenation 3° > 2° > 1°.
- Ease of dehydrohalogenation : Iodides > Bromides > Chlorides

(III) By dehalogenation of vicinal halides :

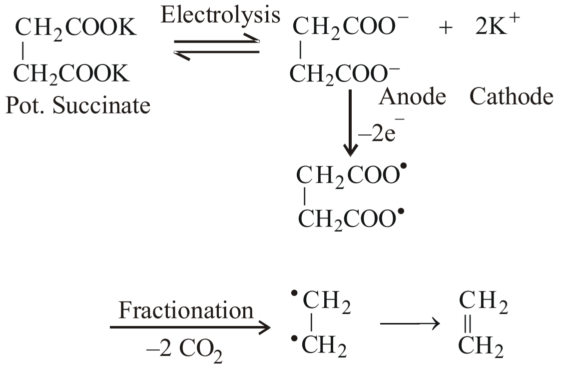


$$-\underset{X}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}- + Zn \xrightarrow[\Delta]{CH_3OH} -\overset{|}{C}=\overset{|}{C}- + ZnX_2$$

(IV) By dehalogenation of gem. halides :

$$RCHX_2 + 2Zn + X_2CHR \longrightarrow R-CH=CHR + 2ZnX_2$$

(V) By electrolysis of Sodium or potassium salt of succinic acid or its derivatives



$$\underset{\text{Pot. Succinate}}{\begin{array}{l}CH_2COOK\\ |\\ CH_2COOK\end{array}} \xrightleftharpoons{\text{Electrolysis}} \begin{array}{l}CH_2COO^-\\ |\\ CH_2COO^-\end{array} + 2K^+$$

Anode Cathode

$$\xrightarrow{-2e^-} \begin{array}{l}CH_2COO^\bullet\\ |\\ CH_2COO^\bullet\end{array} \xrightarrow[-2\,CO_2]{\text{Fractionation}} \begin{array}{l}^\bullet CH_2\\ |\\ ^\bullet CH_2\end{array} \longrightarrow \begin{array}{l}CH_2\\ \|\\ CH_2\end{array}$$

Alkenes with odd or even number of carbon atoms and having any position of double bond can be prepared.

(VI) By partial reduction of alkynes :

$$R-C\equiv CR + 2H \xrightarrow[\text{Quinoline}]{\text{Pd–CaCO}_3\text{ Lindlar's Catalyst}} R-CH=CHR$$

(always cis Isomer)

$$R-C\equiv C-R \xrightarrow[\text{Birch reduction}]{Na/liq.\ NH_3} RCH=CHR$$

(always trans Isomer)

(VII) Decomposition of quaternary ammonium hydroxide:

$$(C_2H_5)_4NOH \xrightarrow{\Delta} CH_2=CH_2 + (C_2H_5)_3N + H_2O$$

(VIII) By cracking of alkanes :

$$CH_3-CH_2-CH_2CH_3 \xrightarrow{600°C} CH_3-CH=CH_2 + CH_4$$

Properties : C_2–C_4 gases; C_4 – C_{15} liquids C_{16} onwards Solids. Less volatile than alkanes and possess anaesthetic properties.

Chemical Properties : Addition reactions given by alkenes are known as electrophilic addition reactions.

$R-CH=CH_2$

$\xrightarrow{H_2/Ni\ 200-300°C}$ CH_3-CH_3 **(Sabatier - Senderen reaction) (Syn addition)**

$\xrightarrow{Br_2/CCl_4 \text{ or } CHCl_3}$ $CH_2Br.CH_2.Br$ (Colour of bromine discharged) (**Anti addition**)

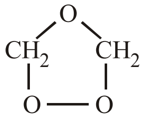
$\xrightarrow{HX}$ $CH_3.CH_2X$ (Order of reactivity of HX HI > HBr > HCl) **(Anti and Syn addition)**

$\xrightarrow{\text{HOX hypohalous acid}}$ $CH_2OH.CH_2Cl$ ethylene chlorohydrin

$\xrightarrow{\text{Cold conc. } H_2SO_4}$ $\underset{\text{Ethylhydrogen sulphate}}{CH_3.CH_2HSO_4} \xrightarrow{HOH} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$

$\xrightarrow{\text{NOCl Nitrosyl Chloride}}$ $CH_2Cl\ .\ CH_2NO$ Ethylene nitroso chloride

$\xrightarrow[\text{Ozone}]{O_3}$



$\xrightarrow{H_2O}$ $2HCHO + H_2O_2 \longrightarrow 2HCOOH$

$\xrightarrow{H_2/Zn}$ $2HCHO + H_2O$

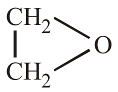
Addition of Zn powder removes H_2O_2 and aldehyde is obtained

$Zn + H_2O_2 \longrightarrow ZnO + H_2O$

$\xrightarrow{\text{Addition of } HNO_3}$ $CH_2(OH)CH_2NO_2$ β-Nitro ethyl alcohol

$\xrightarrow[\text{e.g. } CH_3COCl]{\text{Addition of acyl halide}}$ $CH_2(Cl)CH_2COCH_3$ Methyl β-chloro ethyl Ketone

$\xrightarrow[200-400°C]{\text{Addition of } O_2 \text{ Ag catalyst}}$



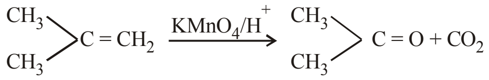
Ethylene Oxide

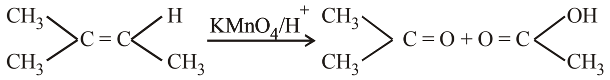
$\xrightarrow[\text{Baeyer's reagent Hydroxylation}]{1\% \text{ alk. } KMnO_4 \text{ Cold}}$ $\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$ (Test for unsaturation)

Ethylene glycol (Syn. addition)

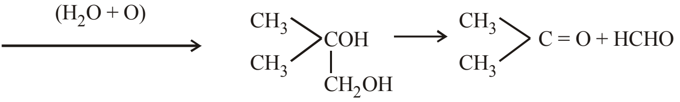
$$\xrightarrow{\text{[O]acid } KMnO_4 \text{ or acid } K_2Cr_2O_7} \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \xrightarrow{[O]} 2HCOOH$$

The double bond is completely cleaved; the molecule is split into two molecules. If carbon has two hydrogens it will become CO_2. If carbon has one hydrogen it will become carboxylic acid. If carbon has no hydrogens it will become a ketone. For example,



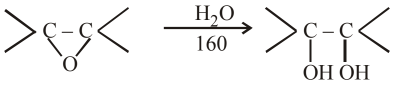


Periodic acid HIO_4 or lead tetra acetate $(H_2O + O)$



$$\xrightarrow{H_2O_2 / CH_3COOH} \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

$$\xrightarrow[\text{Perbenzoic acid}]{C_6H_5.CO.OOH}$$



Oxide Glycol

$$\xrightarrow[S_2Cl_2]{\text{Addition of sulphur monochloride}} Cl.\overset{\beta}{CH_2}.\overset{\alpha}{CH_2}-S-\overset{\alpha'}{CH_2}.\overset{\beta'}{CH_2}Cl+S$$

Mustard gas

$$\xrightarrow[\text{or } BH_3\text{- THF}]{\text{Hydroboration } B_2H_6 \text{ /ether}} (CH_3CH_2)_3B \xrightarrow[H_2O_2,OH^-]{\text{Hydrolysis}} 3CH_3CH_2OH$$

Triethyl borate

(Addition of H_2O anti to Markownikoff's rule)

$$\xrightarrow[CO + H_2\ [Co(CO)]_4]{\text{Oxo process carbonylation}} CH._3CH._2CHO$$

Propionaldehyde

$$\xrightarrow[\text{(i) } Hg(OAC)_2/THF,H_2O \text{ (ii) } NaBH_4,OH^-]{\text{Oxy-mercuration - demercuration}} \begin{matrix} R\text{-}CH\text{-}CH_3 \\ | \\ OH \end{matrix} \text{ (from R-CH= CH)}_2$$

or

H_2O + acid or Catalyst BF_3,M_n phosphate

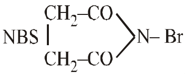
(Addition of H_2O according to Markownikoffs rule)

$$\xrightarrow[\text{(ii) } NaHSO_3 \text{ aq. Reflux}]{\text{(i) } OsO_4 \text{ Osmium tetraoxide}} \begin{matrix} R-CH-OH \\ | \\ R-CH-OH \end{matrix}$$

cis glycol

$$\xrightarrow[\text{Allylic substitution}]{Cl_2(500\text{–}600°C)} Cl\,CH_2-CH=CH_2 \text{ (from propene)}$$

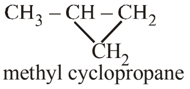
Allyl chloride



$$\xrightarrow[\text{Allylic substitution (Wohl - ziegler reaction)}]{} BrCH_2-CH=CH_2 \text{ (from propene)}$$

Allylbromide

$$\xrightarrow{\text{Addition of carbene } :CH_2}$$



methyl cyclopropane

$\xrightarrow[\text{or } \Delta \text{ above } 500^\circ - 700^\circ\text{ C}]{\text{Isomerisation } Al_2(SO_4)_3 \text{ at } 200-300^\circ C}$ $CH_3-CH_2-CH=CH_2 \longrightarrow CH_3-CH=CH-CH_3$

But-1-ene gives But-2-ene

$\xrightarrow[O_2\ \Delta]{\text{Polymerisation}}$ $-(CH_2-CH_2)_n$ polythene

$\xrightarrow{\text{Combustion}}$ $CO_2 + H_2O +$ heat

ALKYNES OR ACETYLENES : They are characterised by the presence of triple bond having general formula C_nH_{2n-2}.

NOMENCLATURE : According to trivial system they are regarded as derivatives of acetylene. In the IUPAC system their names are derived by replacing suffix **-ane** by **-yne**.

Formula	*Common Name*	*Derived name*	*IUPAC name*
$CH\equiv CH$	Acelylene	Acetylene	Ethyne
$CH_3C\equiv CH$	Allylene	Methyl acetylene	Propyne
$CH_3C\equiv C-CH_3$	Cretonylene	Dimethyl acetylene	But - 2- yne

ISOMERISM : They exhibit four types of Isomerism

(I) Chain Isomerism

Hex–1–yne

4–methyl pent –1– yne

(II) Position Isomerism

Hex – 1–yne

Hex – 3 – Yne

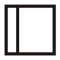
(III) Functional Isomerism

But – 1 –yne

But –1,3 – diene

(IV) Ring chain Isomerism

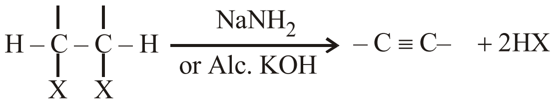
But – 2 –yne



cyclobutene

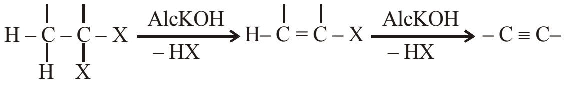
GENERAL METHODS OF PREPARATION :

(I) By dehydrohalogenation of vicinal halides



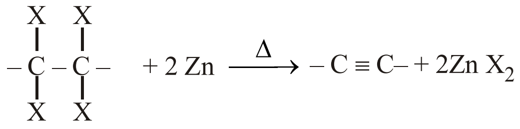
$$H-\underset{X}{C}-\underset{X}{C}-H \xrightarrow[\text{or Alc. KOH}]{NaNH_2} -C\equiv C- \quad +2HX$$

(II) By dehydrohalogention of gem halides



$$H-\underset{H}{C}-\underset{X}{C}-X \xrightarrow[-HX]{AlcKOH} H-C=C-X \xrightarrow[-HX]{AlcKOH} -C\equiv C-$$

(III) By dehalogenation of tetrahalides

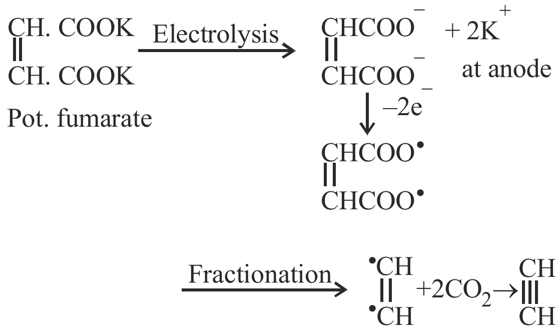


$$-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}- \quad +2\,Zn \xrightarrow{\Delta} -C\equiv C- + 2Zn\,X_2$$

(IV) From lower alkynes

$$HC\equiv CH \xrightarrow[liq.NH_3]{Na} NaC\equiv CNa \xrightarrow{2RX} R-C\equiv C-R + 2NaX$$

(V) Kolbe's electrolytic method



$$\begin{array}{l} CH.\,COOK \\ \parallel \\ CH.\,COOK \end{array} \xrightarrow{\text{Electrolysis}} \begin{array}{l} CHCOO^- \\ \parallel \\ CHCOO^- \end{array} + 2\overset{+}{K} \text{ at anode}$$

Pot. fumarate

$$\downarrow -2e$$

$$\begin{array}{l} CHCOO^\bullet \\ \parallel \\ CHCOO^\bullet \end{array} \xrightarrow{\text{Fractionation}} \begin{array}{l} {}^\bullet CH \\ \parallel \\ {}^\bullet CH \end{array} + 2CO_2 \rightarrow \begin{array}{l} CH \\ ||| \\ CH \end{array}$$

(VI) From haloform

$$CHI_3 + 6Ag + I_3CH \xrightarrow{\Delta} CH\equiv CH + 6AgI$$

(VII) Acetylene from calcium carbide (wohler's reaction)

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + CH\equiv CH$$

(VIII) Berthlot's reaction

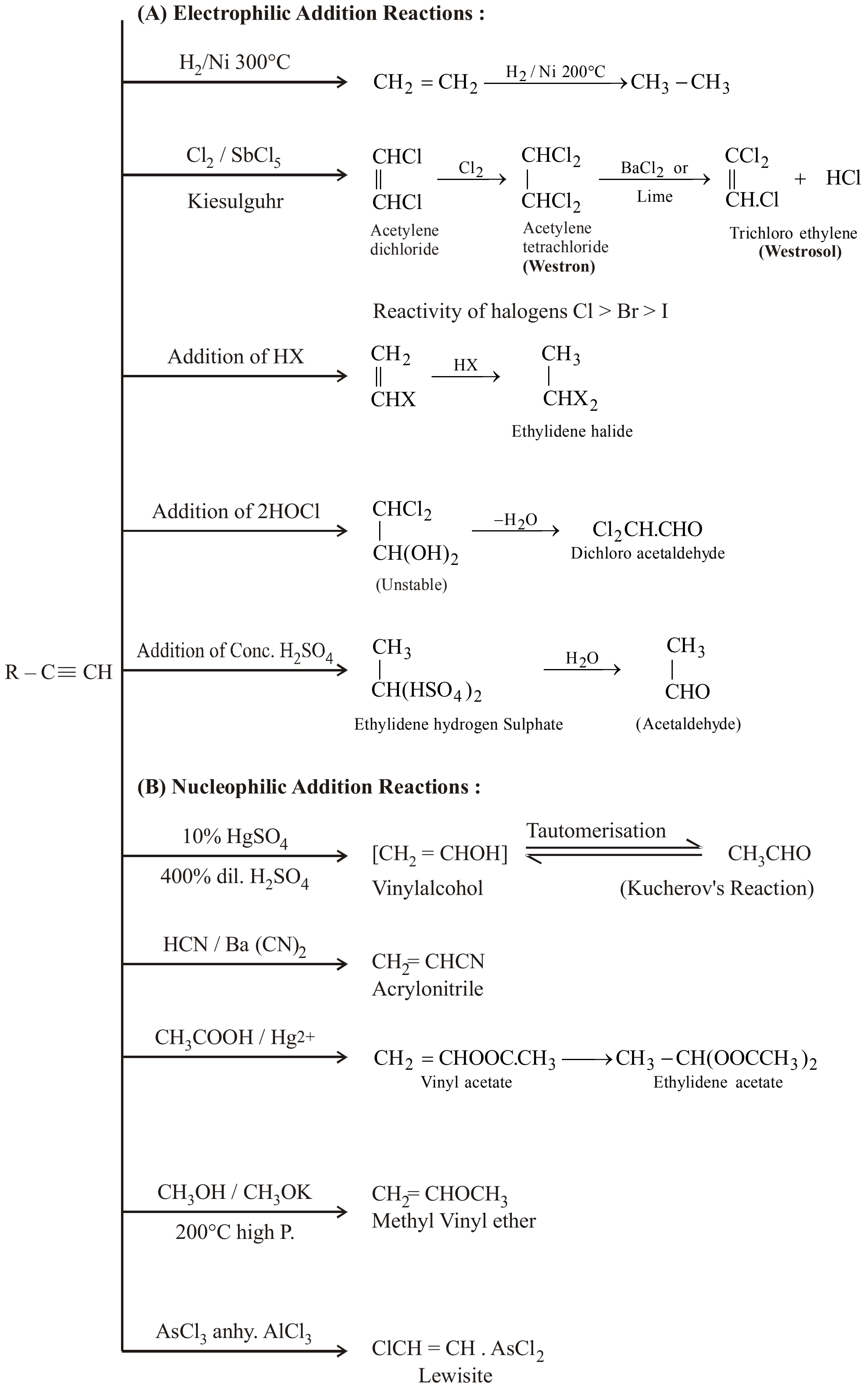
$$2C + H_2 \xrightarrow[\text{Arc.}]{1200^\circ C} HC\equiv CH$$

(IX) From methane :

$$2CH_4 \xrightarrow[\text{Electric arc.}]{1500^\circ C} HC\equiv CH + 3H_2$$

PROPERTIES : C_2–C_4 gases C_5–C_{12} liquids. C_{13} onwards solids. Acetylene has garlic odour due to phosphene and hydrogen sulphide impurity.

Chemical Properties: Alkynes are less reactive then alkenes for electrophilic addition reactions.



$R-C\equiv CH$

(A) Electrophilic Addition Reactions :

$$R-C\equiv CH \xrightarrow{H_2/Ni\ 300°C} CH_2=CH_2 \xrightarrow{H_2/Ni\ 200°C} CH_3-CH_3$$

$$R-C\equiv CH \xrightarrow[\text{Kiesulguhr}]{Cl_2/SbCl_5} \underset{\text{Acetylene dichloride}}{CHCl=CHCl} \xrightarrow{Cl_2} \underset{\text{Acetylene tetrachloride (Westron)}}{CHCl_2-CHCl_2} \xrightarrow[\text{Lime}]{BaCl_2\ \text{or}} \underset{\text{Trichloro ethylene (Westrosol)}}{CCl_2=CH.Cl} + HCl$$

Reactivity of halogens Cl > Br > I

$$R-C\equiv CH \xrightarrow{\text{Addition of HX}} CH_2=CHX \xrightarrow{HX} \underset{\text{Ethylidene halide}}{CH_3-CHX_2}$$

$$R-C\equiv CH \xrightarrow{\text{Addition of 2HOCl}} \underset{\text{(Unstable)}}{CHCl_2-CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{Dichloro acetaldehyde}}{Cl_2CH.CHO}$$

$$R-C\equiv CH \xrightarrow{\text{Addition of Conc. } H_2SO_4} \underset{\text{Ethylidene hydrogen Sulphate}}{CH_3-CH(HSO_4)_2} \xrightarrow{H_2O} \underset{\text{(Acetaldehyde)}}{CH_3-CHO}$$

(B) Nucleophilic Addition Reactions :

$$R-C\equiv CH \xrightarrow[400\%\ \text{dil. } H_2SO_4]{10\%\ HgSO_4} \underset{\text{Vinylalcohol}}{[CH_2=CHOH]} \overset{\text{Tautomerisation}}{\rightleftharpoons} CH_3CHO$$

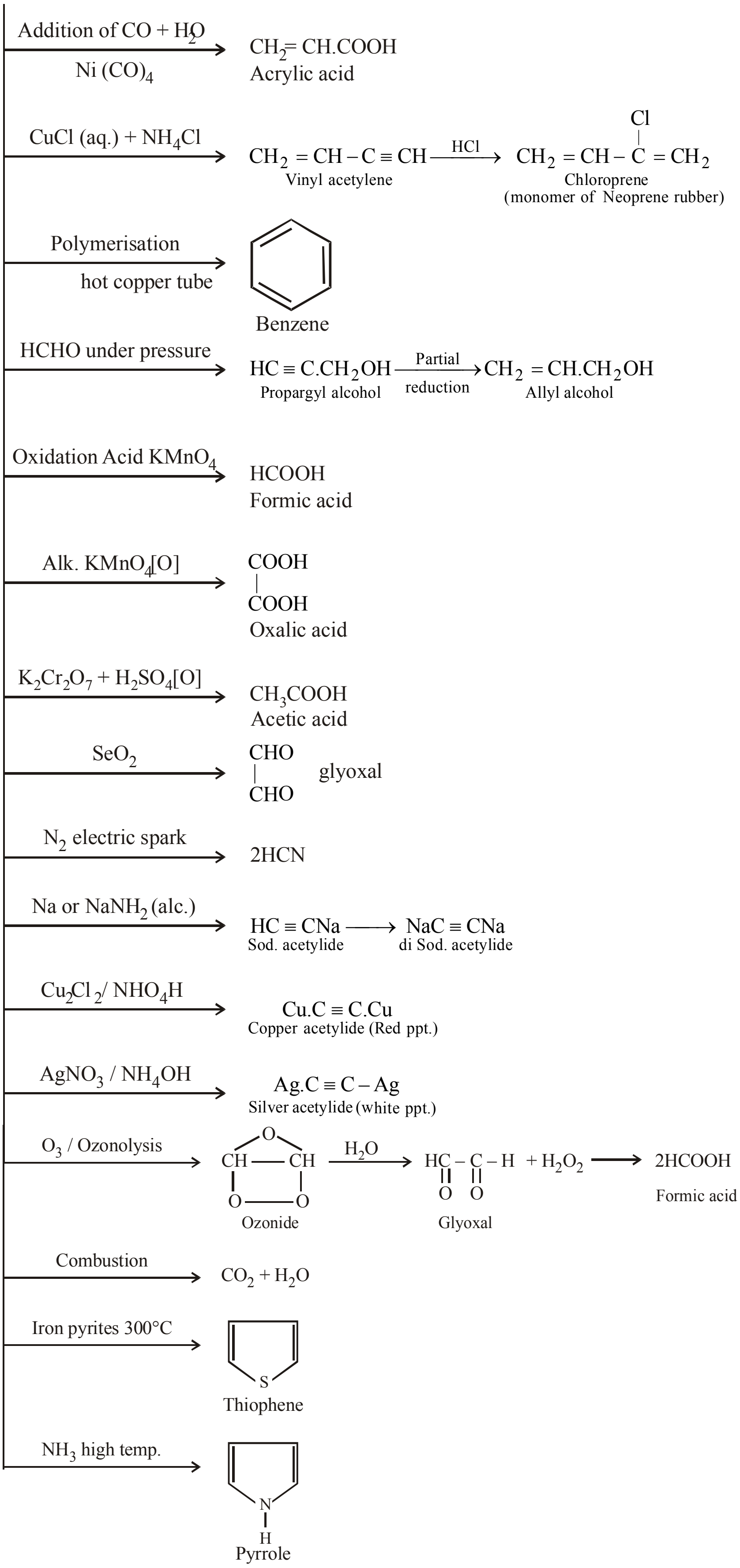
(Kucherov's Reaction)

$$R-C\equiv CH \xrightarrow{HCN/Ba(CN)_2} \underset{\text{Acrylonitrile}}{CH_2=CHCN}$$

$$R-C\equiv CH \xrightarrow{CH_3COOH/Hg^{2+}} \underset{\text{Vinyl acetate}}{CH_2=CHOOC.CH_3} \longrightarrow \underset{\text{Ethylidene acetate}}{CH_3-CH(OOCCH_3)_2}$$

$$R-C\equiv CH \xrightarrow[200°C\ \text{high P.}]{CH_3OH/CH_3OK} \underset{\text{Methyl Vinyl ether}}{CH_2=CHOCH_3}$$

$$R-C\equiv CH \xrightarrow{AsCl_3\ \text{anhy. } AlCl_3} \underset{\text{Lewisite}}{ClCH=CH.AsCl_2}$$



All the products obtained in the above reactions are from acetylene.

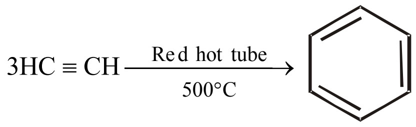
AROMATIC HYDROCARBONS :

Benzene C_6H_6

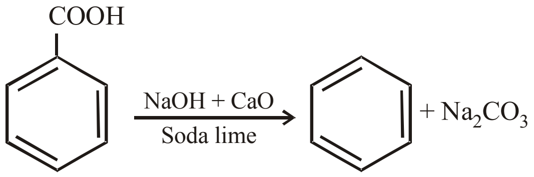
A Benzene

Preparation - A Small scale preparation :

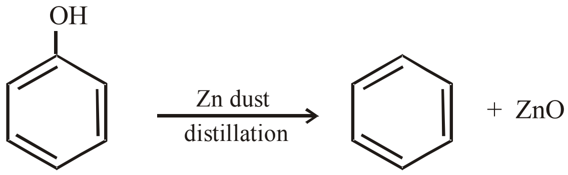
(I) From acetylene :



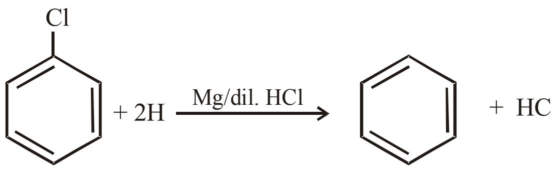
(II) From benzoic acid :



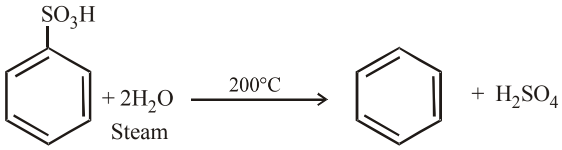
(III) From Phenol :



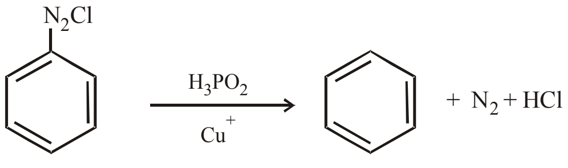
(IV) From Chlorobenzene :



(V) From benzene sulphonic acid :

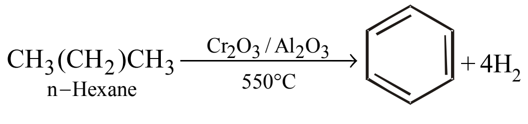


(VI) From benzene diazonium chloride :



(B) Large Scale preparation :

(I) From Petroleum : n-hexane fraction of petroleum



(II) From light-oil fraction of Coal tar

$$\text{Light oil fraction} \xrightarrow[-\text{ pyridene}]{\text{Conc. } H_2SO_4} \xrightarrow[-\text{ phenol}]{\text{NaOH}}.$$

$$\xrightarrow[110°C]{\text{distill}} \text{Benzene} + \text{Some toluene} + \text{Thiophene}$$

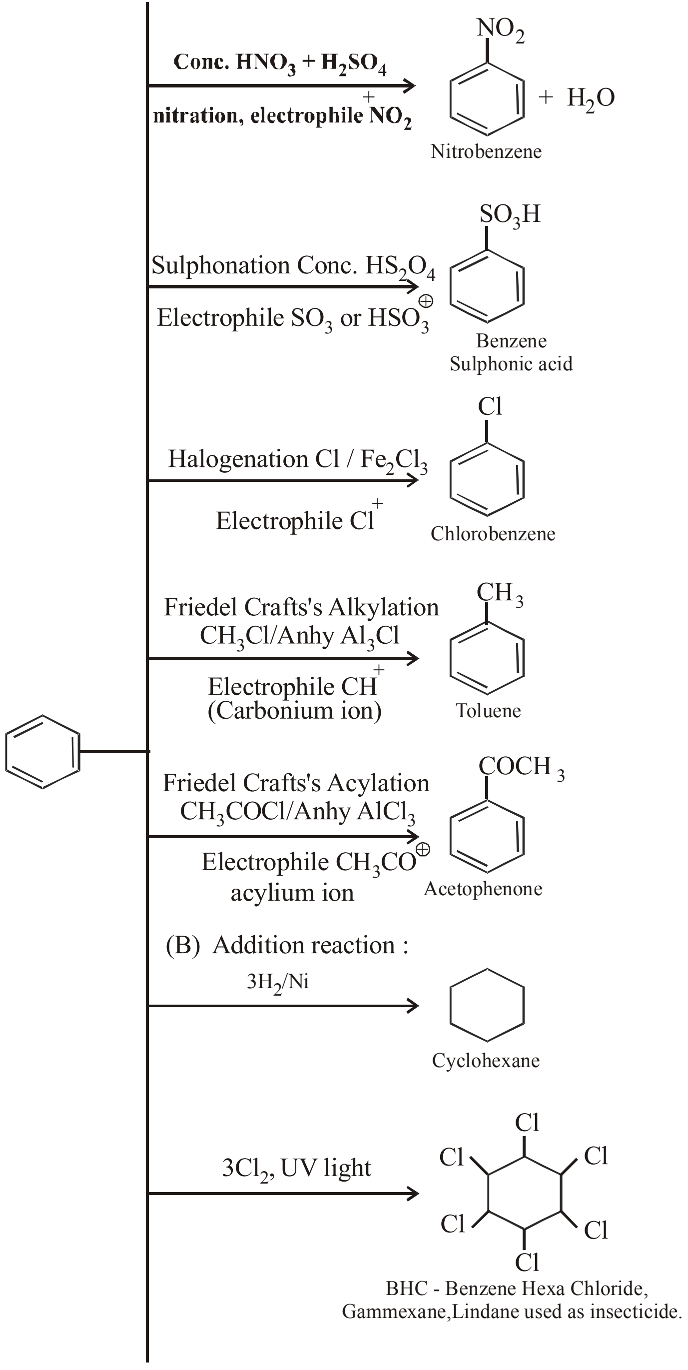
$$\xrightarrow[\text{at } 80–82°C]{\text{Again distill}} \text{Almost pure benzene}$$

Impurity of thiophene is removed by heating with hydrogen under pressure at 400°C in presence of catalyst.

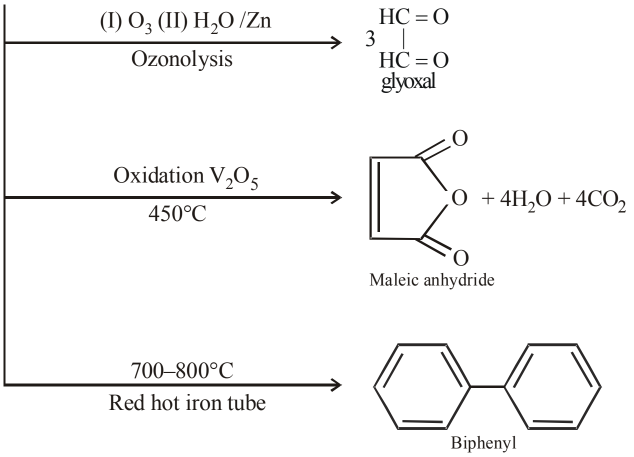
$$C_4H_4S + 4H_2 \xrightarrow[400°C]{\text{Catalyst}} \underset{\text{n–butane}}{C_4H_{10}} + H_2S$$

20. Properties - Colourless Liquid : bpt 80.1°C. Insoluble in H_2O.

(A) Electrophilic Substituton Reactions :



BHC - Benzene Hexa Chloride, Gammexane,Lindane used as insecticide.



STRUCTURE OF BENZENE :

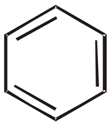
(I) **Open chain structures proposed.**

(a) $CH_2 = C = CH - CH = C = CH_2$

(b) $HC \equiv C - CH_2 - CH_2 - C \equiv CH$

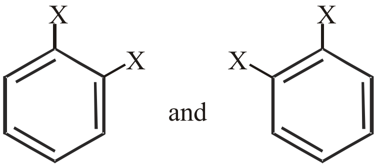
(c) $H_3C - C \equiv C - C \equiv C - CH_3$

(II) **Ring structure by Kekule *:***



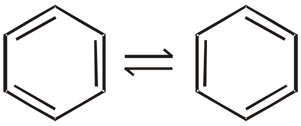
Objections against Kekule structure :

(a) Two ortho di substituted derivatives



(b) About Stability

(III) **Explanation against above objections :** Presence of two structures undergoing quick interconverson.



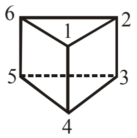
(IV) **Levine and Cole :** Levine and Cole confirmed the presence of above structures by ozonolysis of o-Xylene and obtaining the products.

(a) Dimethyl glyoxal

(b) Methyl glyoxal and

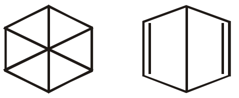
(c) Glyoxal

(V) **Ladenburg's prism structure :**

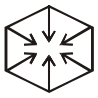


X-ray crystallographic methods showed benzene a planar compound whereas above structure is non planar.

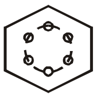
(VI) **Claus and Dewar's structures :**



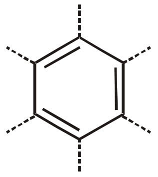
(VII) **Baeyer and Armstrong's centric structure :**



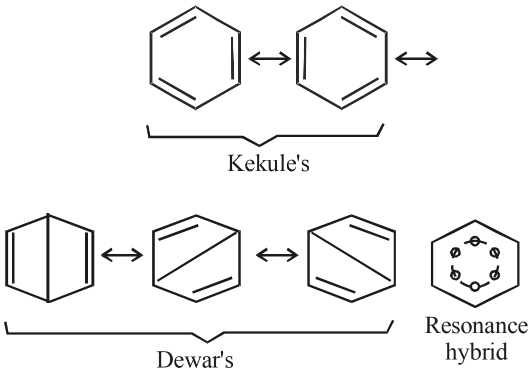
(VIII) **Robinson's sixtet structure *:***



(IX) **Thiele's structure of partial valency :**



(X) **Benzene and resonance :** Benzene is a resonance hybrid of the following structures.



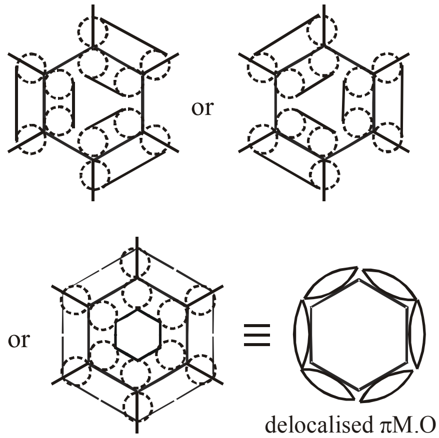
All C–C bonds in the benzene are of the same length 1.39Å.

(XI) **Benzene and aromaticity *:*** Benzene is an aromatic compond since it obeys Huckel rule of $(4n + 2)\pi$ electrons. The value of n must be an integer.

$4n + 2 = 6\pi$ electrons of benzene

$\therefore n = 1$

(XII) **Molecular orbital structure of benzene *:*** Each C-atom in benzene is sp^2 hybridised and forms 3σ bonds. The p_z atomic orbitals left on each C-atom form a delocalised π-molecular orbital which stabilises the structure and renders all C-C bonds equal in length.



delocalised πM.O.

PETROLEUM

Petroleum (petra = rock, oleum = oil). A thick dark coloured complex liquid, mixture of organic compounds obtained from below the surface of the earth is petroleum. The chief components of petroleum are hydrocarbons, aliphatic, alicyclic (naphthalenes) or aromatic in varying proportions and 1 to 6 percent of Sulphur, Nitrogen and Oxygen compounds.

Natural Gas : Found along with petroleum and roughly contains 60 to 80 percent methane 5 to 9 percent ethane, 3 to 18 percent propane, 2 to 14 percent higher hydrocarbons. It is used as fuel. Partial combustion of natural gas yields Carbon blocks (reinforcing agents for rubber).

Theories of origin :

(I) Mendeleef's Carbide Theory :

$$4Al + 3C \longrightarrow Al_4C_3\ ;$$

$$Ca + 2C \longrightarrow CaC_2$$

$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3\ ;$$

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

$$3C_2H_2 \xrightarrow{\text{Polymerisation}} C_6H_6\ ;$$

$$C_2H_2 + H_2 \longrightarrow C_2H_4 \xrightarrow{\text{Polymerisation}} C_6H_{12}$$

The theory was supported by Moissan, Sabatier and Senderens. It fails to explain the presence of optically active compounds, Compounds of N and S, chlorophyll and haemin derivatives.

(II) Engler's Theory : Petroleum is a product of slow decomposition of dead marine animals under high temperature and pressure. It explains the presence of brine, fossils, compounds of N and S.

It explains the presence of all the above mentioned compounds including chlorophyll. Hence petroleum is of animal as well as vegetable origin.

(III)Modern Theory : Petroleum is produced by partial decomposition of marine animals and sea weeds etc.

Mining and Refining : Recovery from oil wells and separation of individual components.

Products of Petroleum Fractionation

	Fractions	*Composition*	*Boiling Range*	*Uses*
1.	**Uncondensed gases**	C_1–C_4	0-30°C	
	(a) Cymogene			Used in the manufacture of Ice
	(b) Rhigolene			Used as local anaesthetic
2.	**Crude Naphtha** Refractionation	C_5–C_{10}	30-150°C	
	(a) Petroleum ether	C_5–C_6	30-70°C	Solvent for oils and fats and rubber, dry cleaning
	(b) Gasoline or Petrol	C_6–C_8	70-90°C	Fuel and dry cleaning
	(c) Ligroin or Light Petroleum	C_6–C_8	90-120°C	In drycleaning as solvent
	(d) Benzene or Benzolene	C_8–C_{10}	120-150°C	Solvent (oil and paints industry), dry cleaning
3.	**Kerosene Oil**	C_{11}–C_{18}	150-300°C	As fuel, for illumination, making oil gas
4.	**Diesel or Heavy Oil**	C_{18}–C_{42}	Above 300°C	Fuel in heavy automobiles
5.	**Residue** Refractionation under reduced pressure	C_{30}–C_{45}	Above 400°C	
	(a) Paraffin Wax			For Candles and boot polishes
	(d) Lubricating Oils			For lubrications
	(c) Vaseline			In ointments and toilet goods
	(d) Pitch			In paints and varnishes, as fuel
	(e) Petroleum Coke			As fuel.

Flash Point : The minimum temperature at which an oil gives off sufficient vapours to form an explosive mixture with air is called Flash Point.

Knocking : A sharp metallic sound emitted by internal combustion engine owing to immature ignition of the air gasoline mixture. Knocking is maximum in presence of straight chain hydrocarbons and minimum in presence of aromatic and branched chain hydrocarbons.

Anti Knock Compounds : 59% Tetra ethyl lead, 13% Ethylene bromide, 24% Ethylene chloride, 4% Kerosene and dye is anti knock mixture.

In presence of aromatic compounds tetramethyl lead is more effective.

Octane number : The percentage of iso octane (2, 2, 4-trimethyl pentane) in a mixture of iso octane and n-heptane having the same knocking properties as the fuel under consideration.

The higher the octane number, the better is the fuel.

Octane number of compunds : **Aromatic Compounds** > **Cyclo alkanes** > **Olefins** > **Branched chain alkanes** > **Straight Chain alkanes**.

Cetane number : It is the percentage of cetane (n-hexadecane) in a cetane and α-methylnaphthalene mixture that has the same ignition qualities as the fuel.

Cracking : The conversion of less valuable higher fraction to the more valuable lower fraction by the application of heat is known as cracking.

(I) Liquid Phase Cracking :

$$\text{Heavy Oil}(C_{18}-C_{43})\xrightarrow[\text{Catalyst 1000-1200 lbs psi}]{475°-530°C}(C_4-C_{10})$$

Catalyst : Silica, titanium dioxide, zinc oxide, ferric oxide, alumina etc. High pressure keeps the oil in liquid state. Octane number of product : 65-70.

(II) Vapour phase Cracking :

$$\text{Kerosene oil or gas oil}\xrightarrow[\text{50-150 lbs psi}]{600\text{-}800°C}\text{Lower fractions}$$

(III) Cracking in presence of hydrogen :

$$\left.\begin{array}{l} R-R+H_2\xrightarrow{\text{Catalyst}}2RH \\ ROH+H_2\longrightarrow RH+H_2O \\ R_2S+2H_2\longrightarrow 2RH+H_2S \\ R_2NH+2H_2\longrightarrow 2RH+NH_3 \end{array}\right\}\text{Product free from O,S \& N}$$

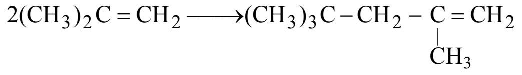
Reactions taking place during cracking :

(I) Carbonisation : $CH_4\xrightarrow{1000°C}C+2H_2$

(II) Dehydrogenation :

$$CH_3-CH_3\xrightarrow{450°C}CH_2=CH_2+H_2$$

(III) Polymerisation :



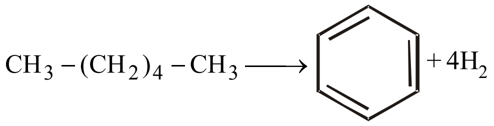
$$2(CH_3)_2C=CH_2\longrightarrow(CH_3)_3C-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$$

$$\xrightarrow{H_2}\underset{\text{Iso octane}}{(CH_3)_3C-CH_2CH(CH_3)_2}$$

(IV) Alkylation :

$$(CH_3)_2CH-CH_3+CH_2=CH_2\longrightarrow(CH_3)_3C-CH_2-CH_3$$

(V) Aromatisation :



$$CH_3-(CH_2)_4-CH_3\longrightarrow C_6H_6+4H_2$$

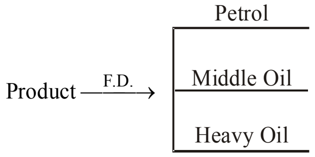
(VI) Chain Fission :

$$C_{16}H_{34}\longrightarrow C_8H_{18}+C_8H_{16}\ \text{ or }\ C_6H_{14}+C_{10}H_{20}$$

Synthetic Petrol :

(I) Bergins Process :

$$\text{Powdered Coal}+\text{Heavy Oil}\xrightarrow[H_2 400-500°C,\ 200-700\ \text{Atm}]{\text{Sn, Pb or Mo Compounds}}$$



Heavy oil is reused.

(II) Fischer-Tropsch Process :

$$\text{Steam}+\text{Coke (Red hot)}\longrightarrow\underset{\text{water gas}}{CO+H_2}$$

$$n(CO+H_2)+nH_2\xrightarrow[200-250\,°C]{\text{Catalyst}}C_nH_{2n}+nH_2O\ (\text{Olefin})$$

$$nCO+(2n+1)H_2\xrightarrow{910\text{afm.}}C_nH_{2n+2}+nH_2O\ (\text{Paraffin})$$

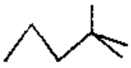
Catalyst Cobalt (100 parts), thoria (5 parts), magnesia (8 parts), Kieselguhr (200 parts).

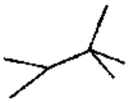
- **Reforming :** It is increasing of anti knock properties by special type of cracking which includes Alkylation, Isomerisation, Aromatisation, Cyclisation, Dehydrogenation, Fractionation etc.
- **No lead petrol :** It does not contain lead and obtained by reforming.
- **Petro chemicals :** Chemicals derived from petroleum sources.

Exercise-1 | NCERT BASED QUESTIONS

Very Short/Short Answer Questions

1. What does LPG stand for ?
2. Name the products formed when an ethereal solution containing ethyl iodide and methyl iodide is heated with sodium metal.
3. Out of ethylene and acetylene which is more acidic and why?
4. Can eclipsed and staggered conformations of ethane be isolated? Give reason.
5. Why is dipole moment of trans-1, 2-dichloroethene zero?
6. How will you distinguish between
   $CH_3CH_2C \equiv CH$ and $CH_3—C \equiv C—CH_3$
7. What is halogen carrier? Give one example.
8. Arrange the following in increasing order of their release of energy on combustion.

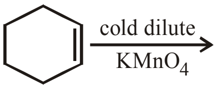
(i)


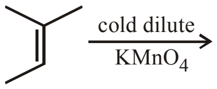
(ii)


(iii)


(iv)


9. Why is cyclopropane is more reactive as compared to cyclohexane?
10. What happens when
    (i) A mixture of steam and methane is passed over heated nickel (supported over catalyst at 1273 K)
    (ii) Methane is heated to high temperature (1500 K).
    (iii) Isobutane is treated with alkaline $KMnO_4$.
11. What is the role of red phosphorus in the reduction of alkyl halide using hydroiodic acid?
12. Write down the structural formulae of the product obtained in the following reaction:

(i)


(ii)


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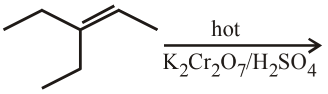
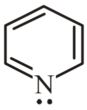


13. You are given three jars containing ethane, ethylene and acetylene, respectively. How will you identify each of them by chemical test?

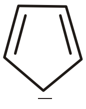
Long Answer Questions

14. (i) Why is the Wurtz synthesis not a good method for preparing propane?
    (ii) What alkanes would be expected from the reaction of sodium with 50 : 50 mixture of 1-chloropropane and 2-chloropropane ?
15. (i) Arrange the following compounds according to the increasing order of boiling point: Hexane, heptane, 3-methyl pentane, 2, 2-dimethyl butane.
    (ii) Account for the following :
       (a) The boiling points of hydrocarbon decreases with increase in branching.
       (b) Hydrocarbons with odd number of carbon atoms have a melting point lower than expected.
       (c) Boiling point of *n*-pentane is greater than that of neo-pentane but melting point of neo-pentane is greater than that of *n*-petane.
16. The ring systems having following characteristics are aromatic.
    (i) Planar ring containing conjugated π bonds.
    (ii) Complete delocalisation of the π-electrons in ring system i.e, each atom in the ring has unhybridised p-orbital, and
    (iii) Presence of (4n + 2) π-electrons in the ring where *n* is an integer (*n* = 0, 1, 2 ....) [Huckel rule]

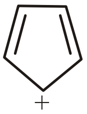
    Using this information classify the following compounds as aromatic/non-aromatic.



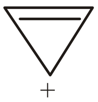
(A)



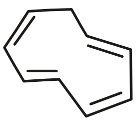
(B)



(C)



(D)


(E)

17. Convert the following :
    (a) Ethyne to ethanal
    (b) Tert. butyl chloride to 2,2,3,3 tetra methyl butane.
    (c) Ethyne to benzene.
    (d) Benzoic acid to benzene
    (e) But 1–ene to butane 1,2– diol.

Multiple Choice Questions

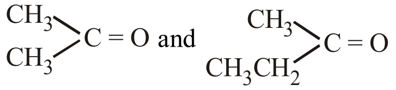
18. Arrange the following in decreasing order of their boiling points.

(A) n–butane	(B) 2-methylbutane
(C) n-pentane	(D) 2, 2–dimethylpropane
(a) A > B > C > D	(b) B > C > D > A
(c) D > C > B > A	(d) C > B > D > A

19. Arrange the halogens F_2, Cl_2, Br_2, I_2, in order of their increasing reactivity with alkanes.

(a) $I_2 < Br_2 < Cl_2 < F_2$	(b) $Br_2 < Cl_2 < F_2 < I_2$
(c) $F_2 < Cl_2 < Br_2 < I_2$	(d) $F_2 < I_2 < Cl_2 < F_2$

20. An alkene having molecular formula C_7H_{14} was subjected to ozonolysis in the presence of zinc dust. An equimolar amount of the following two compounds was obtained



The IUPAC name of the alkene is

(a) 3, 4-dimethyl-3-pentene	(b) 3, 4-dimethyl-2-pentene
(c) 2, 3-dimethyl-3-pentene	(d) 2, 3-dimethyl-2-pentene

21. Which of the following reactions of methane is incomplete combustion ?

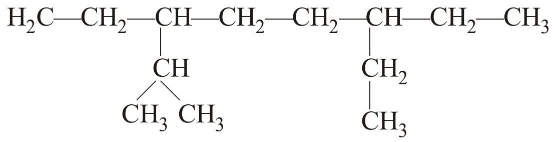
(a) $2CH_4 + O_2 \xrightarrow{Cu/523K/100atm} 2CH_3OH$

(b) $CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$

(c) $CH_4 + O_2 \rightarrow C(s) + 2H_2O(l)$

(d) $CH_4 + 2O_2 \rightarrow CO_2(g) + 2H_2O(l)$

22. The correct IUPAC name of following alkane is



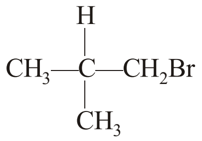
(a) 3,6 – Diethyl – 2 – methyloctane

(b) 5 – Isopropyl – 3 – ethyloctane

(c) 3 – Ethyl – 5 – isopropyloctane

(d) 3 – Isopropyl – 6 – ethyloctane

23. Arrange the following alkyl halides in decreasing order of the rate of β–elimination reaction with alcoholic KOH.

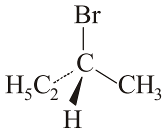
(A) 
$CH_3-\overset{H}{\underset{CH_3}{C}}-CH_2Br$

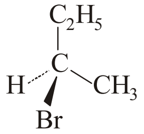
(B) CH_3-CH_2-Br

(C) $CH_3-CH_2-CH_2-Br$

(a) A > B > C	(b) C > B > A
(c) B > C > A	(d) A > C > B

24. The addition of HBr to 1-butene gives a mixture of products A, B and C

(A) 

(B) 

(C) $CH_3-CH_2-CH_2-CH_2-Br$

The mixture consists of

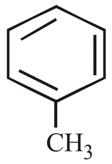
(a) A and B as major and C as minor products

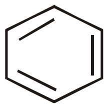
(b) B as major, A and C as minor products

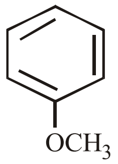
(c) B as minor, A and C as major products

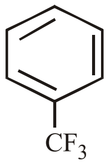
(d) A and B as minor and C as major products

25. Among the following compounds, the decreasing order of reactivity towards electrophilic substitution is


I


II


III


IV

(a) III > I > II > IV	(b) IV > I > II > III
(c) I > II > III > IV	(d) II > I > III > IV

Exercise-2 | CONCEPTUAL MCQs

1. Successive alkanes differ by

(a) CH_2	(b) CH
(c) CH_3	(d) C_2H_4

2. An alkyne has the general formula

(a) C_nH_{2n}	(b) C_nH_{2n+2}
(c) C_nH_{2n-2}	(d) C_nH_{2n+1}

3. Which of the following is not a mixture of hydrocarbons?

(a) Candle wax	(b) Kerosene
(c) Vegetable oil	(d) Paraffin oil

4. When petroleum is heated gradually, the first batch of vapours evolved will be rich in

(a) kerosene	(b) petroleum ether
(c) diesel	(d) lubricating oil

5. The order of appearance of the following with rising temperature during the refining of crude oil is

(a) kerosene oil, gasoline, diesel

(b) diesel, gasoline, kerosene oil

(c) gasoline, diesel, kerosene oil

(d) gasoline, kerosene oil, diesel

6. LPG contains

(a) methane (b) ethane

(c) butane (d) None of these

7. Petrol for aviation purposes must contain

(a) straight chain hydrocarbons

(b) aromatic hydrocarbons

(c) olefinic hydrocarbons

(d) highly branched chain paraffins

8. In commercial gasoline, the type of hydrocarbons which are desirable is

(a) Branched hydrocarbons

(b) Straight chain hydrocarbons

(c) Linear unsaturated hydrocarbons

(d) All of these

9. Fischer-Tropsch process is used in the manufacture of

(a) synthetic petroleum (b) ethanol

(c) benzene (d) ethanoic acid

10. Octane number is zero for

(a) isoheptane (b) n-heptane

(c) isooctane (d) n-octane

11. Which of the following has lowest octane number ?

(a) Iso-octane (b) n-Heptane

(c) n-Hexane (d) n-Hexadecane

12. Which of the following has highest octane number ?

(a) n-Hexane (b) n-Heptane

(c) n-Pentane (d) 2, 2, 4-Trimethylpentane

13. The process in which higher hydrocarbons are broken down into lower hydrocarbons by controlled pyrolysis is called

(a) Hydrolysis (b) Cracking

(c) reforming (d) Both (a) and (b)

14. A fuel has the same knocking property as a mixture of 70% isooctane (2,2,4-trimethylpentane) and 30% n-heptane by volume. The octane number of the fuel is

(a) 100 (b) 70

(c) 50 (d) 30

15. Cetane number of a diesel fuel will increase with the addition of

(a) n-Decane (b) n-Hexadecane

(c) n-Pentane (d) α-Methylnaphthalene

16. Which one is used as an antiknock in petrol fuel ?

(a) Basic lead carbonate (b) Lead tetraacetate

(c) Tetraethyl-lead (d) Basic lead sulphate

17. Wurtz reaction involves the interaction of alkyl halides in dry ether with

(a) sodium (b) zinc

(c) copper (d) platinum

18. Ethane is formed by the reaction of methyl iodide and sodium metal in dry ether solution. The reaction is known as

(a) Clemmensen reduction (b) Kolbe's reaction

(c) Wurtz reaction (d) Cannizzaro's reaction

19. Which one of the following cannot be prepared by Wurtz reaction ?

(a) CH_4 (b) C_2H_6

(c) C_3H_8 (d) C_4H_{10}

20. Formation of alkanes by action of Zn on alkyl halides is called

(a) Frankland's reaction (b) Cannizaro's reaction

(c) Wurtz's reaction (d) Kolbe's reaction

21. For preparing an alkane, a concentrated solution of sodium or potassium salt of a saturated carboxylic acid is subjected to

(a) hydrolysis (b) oxidation

(c) hydrogenation (d) electrolysis

22. Pure methane can be produced by

(a) Wurtz reaction

(b) Kolbe's electrolytic method

(c) Soda-lime decarboxylation

(d) Reduction with H_2

23. Which of the following liberates methane on treatment with water ?

(a) Silicon carbide (b) Calcium carbide

(c) Beryllium carbide (d) Magnesium carbide

24. Which of the following methods is most appropriate for the manufacture of methane ?

(a) Reduction of CH_2Cl_2

(b) Wurtz reaction

(c) Liquefaction of natural gas

(d) None of these

25. The reaction/method that does not give an alkane is

(a) catalytic hydrogenation of alkenes

(b) dehydrohalogenation of an alkyl halide

(c) hydrolysis of alkylmagnesium bromide

(d) Kolbe's electrolytic method

26. Ethyl bromide on treatment with alcoholic KOH gives

(a) ethylene (b) ethanol

(c) acetic acid (d) ethane

27. When n-propyl iodide is heated with alcoholic KOH, one of the products is

(a) Propene (C_3H_6) (b) Cyclopropane (C_3H_6)

(c) C_3H_4 (d) C_3H_8

28. 1-Chlorobutane, on reaction with alcoholic potash (KOH), gives

(a) 1-Butene (b) 1-Butanol

(c) 2-Butene (d) 2-Butanol

29. In preparation of alkene from alcohol using Al_2O_3 which is effective factor ?

(a) Porosity of Al_2O_3 (b) Temperature

(c) Concentration (d) Surface area of Al_2O_3

30. Which one of the following heptanols can be dehydrated to hept-3-ene only ?

(a) Heptan-3-ol (b) Heptan-4-ol

(c) Heptan-2-ol (d) Heptan-1-ol

31. Which of the principle is applied in the following reaction ?

$$CH_3CHBrCH_2CH_3 \xrightarrow{\text{alc. KOH}}$$

$$\underset{\text{(Major)}}{CH_3CH=CHCH_3} + \underset{\text{(Minor)}}{CH_2=CHCH_2CH_3}$$

(a) Markovnikov's rule (b) Saytzeff's rule

(c) Kharasch's effect (d) Hofmann's rule

32. The conversion of 2, 3-dibromobutane to 2-butene with Zn and alcohol is
(a) redox reaction
(b) α-elimination
(c) β-elimination
(d) Both (a) and (b)

33. Coal-tar is a main source of
(a) aromatic compounds
(b) aliphatic compounds
(c) cycloalkanes
(d) heterocyclic compounds

34. Which of the following metal powder is used to convert trichloromethane into acetylene by heating the latter with it ?
(a) Na
(b) Mg
(c) Ca
(d) Ag

35. Tetrabromoethane on heating with Zn gives
(a) ethyl bromide
(b) ethane
(c) ethene
(d) ethyne

36. What is formed when calcium carbide reacts with heavy water ?
(a) C_2D_2
(b) CaD_2
(c) Ca_2D_2O
(d) CD_2

37. Monosodium acetylide reacts with an alkyl halide to form
(a) an alkane
(b) an alkene
(c) an unsymmetric higher alkyne
(d) a symmetric higher alkyne

38. Fractional distillation of coal-tar produces the following fractions. Phenol is the main component of which fraction ?
(a) Light oil
(b) Middle oil
(c) Heavy oil
(d) Green oil

39. Benzene is obtained by fractional distillation of
(a) light oil
(b) middle oil
(c) anthracite oil
(d) heavy oil

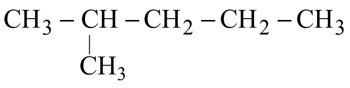
40. Heating a mixture of sodium benzoate or benzoic acid and soda-lime gives
(a) benzene
(b) methane
(c) sodium benzoate
(d) calcium benzoate

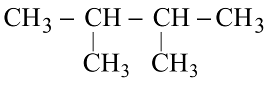
41. Crude naphtha is a mixture of
(a) alkanes
(b) conjugated dienes
(c) alkynes
(d) alkyl halides

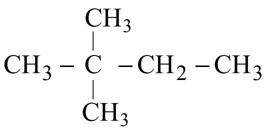
42. Hydrocarbon which is liquid at room temperature is
(a) pentane
(b) butane
(c) propane
(d) ethane

43. Which of the following isomers will have the highest boiling point ?

(a) $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

(b)

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

(c)

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(d)

$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2-CH_3$

44. How many monochlorobutanes will be obtained on chlorination of n-butane?
(a) 5
(b) 2
(c) 3
(d) 4

45. Conversion of CH_4 to CH_3Cl is an example of .... reaction
(a) electrophilic substitution
(b) nucleophilic substitution
(c) free radical substitution
(d) free radical addition

46. The molecule having dipole moment is
(a) 2,2-dimethylpropane
(b) trans-2-pentene
(c) hexane
(d) 2,2,3,3-tetramethylbutane

47. Olefins can be hydrogenated by
(a) zinc and hydrochloric acid
(b) raney nickel and hydrogen
(c) nascent hydrogen
(d) lithiumaluminium hydride in ether

48. Which one of the following compounds would have the highest heat of hydrogenation ?
(a) $CH_2=CH_2$
(b) $CH_3-CH_2-CH=CH_2$
(c) $CH_3CH=CHCH_3$
(d) $(CH_3)_2C=C(CH_3)_2$

49. The reaction,
$CH_2=CHCH_3+HBr\rightarrow CH_3CHBrCH_3$ is a type of
(a) electrophilic addition reaction
(b) nucleophilic addition reaction
(c) free radical addition reaction
(d) electrophilic substitution reaction

50. $CH_3-CH=CH_2+HI\longrightarrow X$, X is
(a) $CH_3–CH_2–CH_2–I$
(b) $CH_3–CHI–CH_3$
(c) $CH_3CH_2CH_3$
(d) None of these

51. When propene is treated with HBr in the dark and in absence of peroxide, the main product is
(a) 1-Bromopropane
(b) 2-Bromopropane
(c) 1,2-Dibromopropane
(d) 1,3-Dibromopropane

52. Pentene-1 with HCl gives
(a) 3-Chloropentane
(b) 2-Chloropentane
(c) 1,2-Dichloropentane
(d) 1-Chloropentane

53. Addition of HI to double bond of propene yields isopropyl iodide and not n-propyl iodide as the major product, because addition proceeds throughs
(a) a more stable carbonium ion
(b) a more stable carbanion
(c) a more stable free radical
(d) homolysis

54. Propene is reacted with HBr in presence of peroxides, the product is
(a) 2-Bromopropane
(b) 1-Bromopropane
(c) 3-Bromopropane
(d) None of these

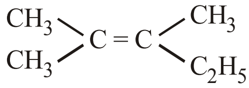
55. The principal organic product formed in the reaction,

$CH_2 = CH(CH_2)_8COOH + HBr \xrightarrow{\text{peroxide}}$ is

(a) $CH_3CHBr(CH_2)_8COOH$
(b) $CH_2 = CH(CH_2)_8COBr$
(c) $CH_2BrCH_2(CH_2)_8COOH$
(d) $CH_2 = CH(CH_2)_7CHBrCOOH$

56. Markovnikov's rule is applicable to

(a) $CH_2 = CH_2$ (b) $CH_3–CH_2–CH_3$
(c) $CH_3–CH = CH–CH_3$ (d)



57. Which of the following compound gives similar products obeying Markovnikov's rule and peroxide effect ?

(a) $CH_3–CH=CH_2$ (b) $CH_3CH = CH–CH_3$
(c) $C_2H_5–CH = CH–CH_3$ (d) $C_2H_5–CH = CH_2$

58. The addition of HBr is easiest in

(a) $CH_2=CHCl$ (b) $ClCH=CHCl$
(c) $CH_3–CH=CH_2$ (d) $(CH_3)_2C=CH_2$

59. 1, 3-Butadiene when treated with Br_2 gives

(a) 1, 4-dibromo-2-butene (b) 1, 3-dibromo-2-butene
(c) 3, 4-dibromo-1-butene (d) 2, 3-dibromo-2-butene

60. Ozonolysis of 2, 3-dimethyl-1-butene followed by reduction with zinc and water gives

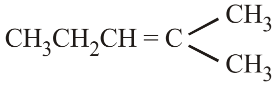
(a) methanoic acid and 3-methyl-2-butanone
(b) methanal and 2-methyl-2-butanone
(c) methanal and 3-methyl-2-butanone
(d) methanoic acid and 2-methyl-2-butanone

61. Position of double bond in alkenes can be identified by

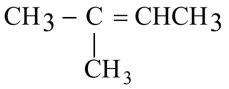
(a) bromine water
(b) ammonical silver nitrate solution
(c) ozonolysis
(d) None of these

62. Which alkene on ozonolysis gives CH_3CH_2CHO and CH_3COCH_3

(a)

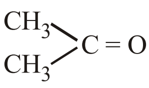


(b) $CH_3CH_2CH = CHCH_2CH_3$
(c) $CH_3CH_2CH=CHCH_3$
(d)

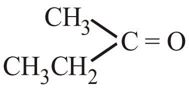


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CHCH_3$$

63. An alkene having molecular formula C_7H_{14} was subjected to ozonolysis in the presence of zinc dust. An equimolar amount of the following two compounds was obtained



and



The IUPAC name of the alkene is

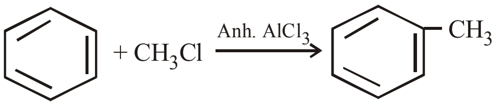
(a) 3, 4-dimethyl-3-pentene (b) 3, 4-dimethyl-2-pentene
(c) 2, 3-dimethyl-3-pentene (d) 2, 3-dimethyl-2-pentene

64. Ozonolysis of C_7H_{14} gave 2-methyl-3-pentanone. The alkene is

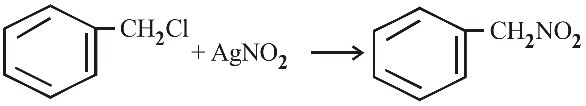
(a) 2-ethyl-3-methyl-1-butene
(b) 3-ethyl-2-methyl-3-butene
(c) 2,5-dimethyl-3, 4-dimethylhex-3-ene
(d) 3-ethyl-2-methyl-1-butene

65. Which one of the following is a free-radical substitution reaction ?

(a)

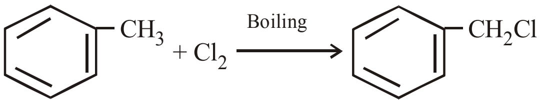


(b)



(c) $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$

(d)



66. Ethylene reacts with 1% cold alkaline $KMnO_4$ to form

(a) oxalic acid (b) ethylene glycol
(c) ethyl alcohol (d) HCHO

67. Baeyer's reagent is used in the laboratory for

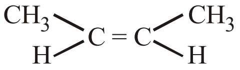
(a) detection of double bond
(b) reduction process
(c) oxidation process
(d) detection of glucose

68. Baeyer's reagent is

(a) saturated $KMnO_4$ soln. (b) neutral KMnO4 soln.
(c) alkaline $KMnO_4$ soln. (d) acidic $KMnO_4$ soln.

69. Which of the following has the lowest dipole moment ?

(a)



(b) $CH_3C \equiv CCH_3$
(c) $CH_3CH_2C \equiv CH$ (d) $CH_2 = CH - C \equiv CH$

70. 3-Hexyne reacts with Na/liq. NH_3 to produce

(a) cis-3-Hexene (b) trans-3-Hexene
(c) 3-Hexylamine (d) 2-Hexylamine

71. The most suitable catalyst for the hydrogenation of 2-Hexyne ⟶ 2-cis-Hexene is

(a) $Pd–BaSO_4$ (b) $(Ph_3P)_3RhCl$
(c) 10% Pd—C (d) Raney Ni

72. Lindlar's catalyst is

(a) Na in alcohol (b) Raney nickel
(c) $Pd/BaSO_4$ (d) Na/liq. NH_3

73. Acetylene when reacts with two molecules of HBr, then it gives

(a) $Br - C \equiv C - Br$ (b) $Br - CH = CH - Br$
(c) $Br_2CH - CHBr_2$ (d) $CH_3 - CHBr_2$

74. In the following reaction,

$$C_2H_2 \xrightarrow[HgSO_4/H_2SO_4,\ 60^\circ C]{H_2O} X \rightleftharpoons CH_3CHO$$

what is X ?

(a) CH_3CH_2OH (b) $CH_3–O–CH_3$

(c) CH_3CH_2CHO (d) $CH_2=CHOH$

75. When 2-pentyne is treated with dil. H_2SO_4 and $HgSO_4$, the product formed is

(a) 1-pentanol (b) 2-pentanol

(c) 2-pentanone (d) 3-pentanone

76. In which of the following hydrogen is most acidic?

(a) Acetylene (b) Methane

(c) Ethane (d) Ethylene

77. Match List I (Reagents used with ethyne) with List II (products) and select the correct answer using the codes given below in the lists.

List I	List II
I. Hydrogen chloride	A Benzene
II. Hydrogen in presence of Ni at 573 K	B Acetaldehyde
III. Hydrogen in presence of Pd and $BaSO_4$ at 473 K	C Ethene
IV. Water in presence of H_2SO_4 and $HgSO_4$	D Ethane

Codes :

(a) I-B, II-C, III-D, IV-A (b) I-A, II-D, III-C, IV-B

(c) I-A, II-D, III-B, IV-C (d) I-D, II-A, III-C, IV-B

78. In its reaction with silver nitrate, acetylene shows

(a) oxidising property (b) reducing property

(c) basic property (d) acidic property

79. When an alkyne, $RC\equiv CH$, is treated with cuprous ion in an ammonical medium, one of the products is

(a) $RC\equiv CCu$ (b) $CuC\equiv CH$

(c) $CuC\equiv CCu$ (d) $RC\equiv CR$

80. Which of the following does not give a white precipitate with $AgNO_3$ solution ?

(a) Propyne (b) 1-Butyne

(c) 2-Butyne (d) 1-Pentyne

81. A compound is treated with $NaNH_2$ to give sodium salt. Identify the compound

(a) C_2H_2 (b) C_6H_6

(c) C_2H_6 (d) C_2H_4

82. $KMnO_4$ will oxidise acetylene to

(a) ethylene glycol (b) ethyl alcohol

(c) oxalic acid (d) acetic acid

83. Which one of the following gives Tollen's reagent test ?

(a) 1-Butanol (b) 2-Butanol

(c) 1-Butyne (d) 2-Butyne

84. Propyne and propene can be distinguished by

(a) conc. H_2SO_4 (b) Br_2 in CCl_4

(c) dil. $KMnO_4$ (d) $AgNO_3$ in ammonia

85. Identify the reagent from the following list which can easily distinguish between 1-butyne and 2-butyne

(a) bromine, CCl_4

(b) H_2, Lindlar catalyst

(c) dilute H_2SO_4, $HgSO_4$

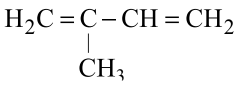
(d) ammonical Cu_2Cl_2 solution

86. An organic compound, on treatment with Br_2 in CCl_4 gives bromoderivative of an alkene. The compound will be

(a) $CH_3-CH=CH_2$ (b) $CH_3CH=CHCH_3$

(c) $HC\equiv CH$ (d) $H_2C=CH_2$

87. Which of the following will yield a mixture of 2-chlorobutene and 3-chlorobutene on treatment with HCl ?

(a) $CH_2=C=CH-CH_3$ (b)  $H_2C=C(CH_3)-CH=CH_2$

(c) $CH_2=CH-CH=CH_2$ (d) $HC\equiv C-CH=CH_2$

88. An unknown compound A has a molecular formula C_4H_6, when A is treated with an excess of Br_2, a new substance B with formula $C_4H_6Br_4$ is formed. A forms a white precipitate with ammonical silver nitrate solution. A may be

(a) Butyne-1 (b) Butyne-2

(c) Butene-1 (d) Butene-2

89. The hydrocarbon which decolourises alkaline $KMnO_4$ solution, but does not give any precipitate with ammonical silver nitrate is

(a) benzene (b) acetylene

(c) propyne (d) butyne-2

90. Select the true statement about benzene from amongst the following

(a) Because of unsaturation benzene easily undergoes addition

(b) There are two types of C—C bonds in benzene molecule

(c) There is cyclic delocalisation of pi-electrons in benzene

(d) Monosubstitution of benzene gives three isomeric products

91. Aromatic hydrocarbons undergo

(a) nucleophilic addition reactions

(b) electrophilic addition reactions

(c) electrophilic substitution reactions

(d) None of these

92. Benzene on treatment with a mixture of conc. HNO_3 and conc. H_2SO_4 at 100°C gives

(a) Nitrobenzene (b) m-Dinitrobenzene

(c) p-Dinitrobenzene (d) o-Dinitrobenzene

93. Which species represents the electrophile in aromatic nitration ?

(a) NO_2^- (b) NO_2^+

(c) NO_2 (d) NO_3^-

94. In the Friedel-Craft's synthesis of toluene, reactants in addition to anhydrous $AlCl_3$ are

(a) $C_6H_6+CH_4$ (b) $C_6H_6+CH_3Cl$

(c) $C_6H_5Cl+CH_3Cl$ (d) $C_6H_5Cl+CH_4$

95. When CH_3Cl and $AlCl_3$ are used in Friedel-Craft's reaction, the electrophile is
(a) Cl^+ (b) $AlCl_4^-$
(c) CH_3^+ (d) $AlCl_2^+$

96. Benzene reacts with $CH_3COCl + AlCl_3$ to give
(a) chlorobenzene (b) toluene
(c) benzyl chloride (d) acetophenone

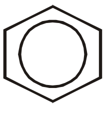
97. Which of the following is not a meta-directing group ?
(a) SO_3H (b) NO_2
(c) CN (d) NH_2

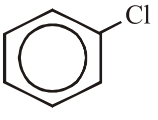
98. In the reaction of C_6H_5Y, the major product (> 60%) is m-isomer, so the group Y is
(a) —COOH (b) $—NH_2$
(c) —OH (d) —Cl

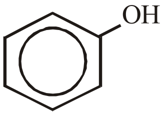
99. A group which deactivates the benzene ring towards electrophilic substitution but which directs the incoming group principally to the o- and p-positions is
(a) $-NH_2$ (b) –Cl
(c) $-NO_2$ (d) $-C_2H_5$

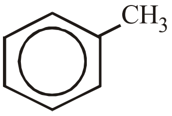
100. The most reactive compound for electrophilic nitration is
(a) benzene (b) nitrobenzene
(c) benzoic acid (d) toluene

101. Which of the following will be most easily attacked by an electrophile?

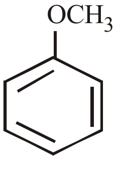
(a) 

(b) 

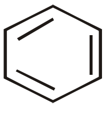
(c) 

(d) 

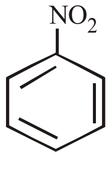
102. Among the followng compounds (I – III), the correct order in of reactivity with an electrophile is



I



II



III

(a) II > III > I (b) III < I < II
(c) I > II > III (d) I = II > III

103. The most reactive among the following towards sulphonation is
(a) toluene (b) chlorobenzene
(c) nitrobenzene (d) m-Xylene

104. Which of the following is the most reactive towards ring nitration ?
(a) Benzene (b) Mesitylene
(c) Toluene (d) m-Xylene

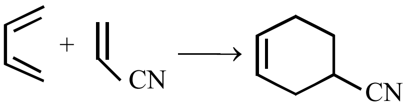
105. Aromatic compounds burn with a sooty flame because
(a) they have a ring structure of carbon atoms
(b) they have a relatively high percentage of hydrogen
(c) they have a relatively high percentage of carbon
(d) they resist reaction with oxygen of air

106. The correct order of reactivity towards the electrophilic substitution of the compounds aniline (I), benzene (II) and nitrobenzene (III) is
(a) II > III > I (b) I < II > III
(c) I > II > III (d) III > II > I

107. Addition of Br_2 to 1-butene would give 1, 2-dibromobutane which is
(a) achiral (b) racemic
(c) meso (d) optically active

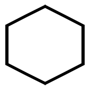
108. Addition of Br_2 to trans-2-butene would give a product which is
(a) chiral (b) meso
(c) racemic (d) optically active

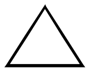
109. Name of following reaction is

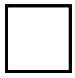


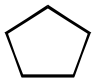
(a) Claisen Condensation
(b) Diel's Alder reaction
(c) Dieckmann cyclisation
(d) Michael addition reaction

110. The cycloalkane having the lowest heat of combustion per CH_2 group

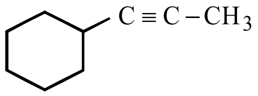
(a) 

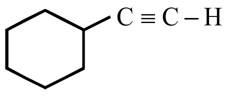
(b) 

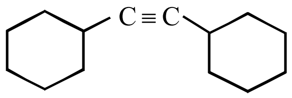
(c) 

(d) 

111. Which of the following will form alkynide ?

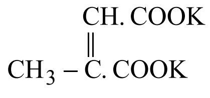
(a) 

(b) 

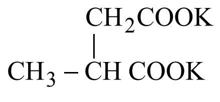
(c) 

(d) $CH_3 - C \equiv C - CH_3$

112. Which of the following will give alkene in Kolbe's electrolytic method ?

(a) 
$CH_3 - \overset{\overset{\displaystyle CH.COOK}{\|}}{C}.COOK$

(b) CH_3CH_2COOK

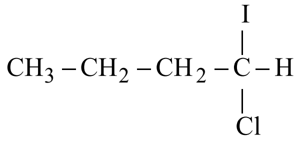
(c) 
$CH_3 - \overset{\overset{\displaystyle CH_2COOK}{|}}{CH}\ COOK$

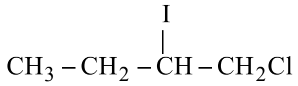
(d) All of these

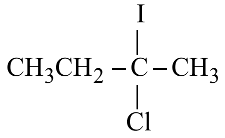
Exercise-3 | PAST COMPETITION MCQs

1. Predict the product C obtained in the following reaction of butyne-1. **[CBSE-PMT 2007]**

$$CH_3CH_2-C\equiv CH+HCl\longrightarrow B\xrightarrow{HI}C$$

(a) 
$CH_3-CH_2-CH_2-\overset{I}{\underset{Cl}{C}}-H$

(b) 
$CH_3-CH_2-\overset{I}{CH}-CH_2Cl$

(c) 
$CH_3CH_2-\overset{I}{\underset{Cl}{C}}-CH_3$

(d) 
$CH_3-\underset{Cl}{CH}-CH_2CH_2I$

2. Which of the compounds with molecular formula C_5H_{10} yields acetone on ozonolysis? **[CBSE-PMT 2007]**

(a) 3-methyl-1-butene (b) cyclopentane
(c) 2-methyl-1-butene (d) 2-methyl-2-butene.

3. The IUPAC name of the compound having the formula $CH\equiv C-CH=CH_2$ is: **[CBSE-PMT 2009]**

(a) 1-butyn-3-ene (b) but-1-yne-3-ene
(c) 1-butene-3-yne (d) 3-butene-1-yne

4. Liquid hydrocarbons can be converted to a mixture of gaseous hydrocarbons by : **[CBSE-PMT 2010]**

(a) oxidation
(b) cracking
(c) distillation under reduced pressure
(d) hydrolysis

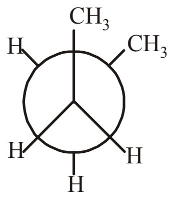
5 In the following reaction, $C_6H_5CH_2Br\xrightarrow[2.H_3O^+]{1.Mg,\ Ether}X$, the product 'X' is **[CBSE-PMT 2010]**

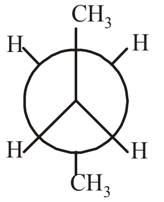
(a) $C_6H_5CH_2CH_2C_6H_5$ (b) $C_6H_5CH_2OCH_2C_6H_5$
(c) $C_6H_5CH_2OH$ (d) $C_6H_5CH_3$

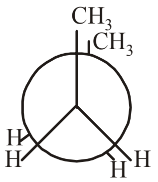
6. The IUPAC name of the compound $CH_3CH=CHC\equiv CH$ is **[CBSE-PMT 2010]**

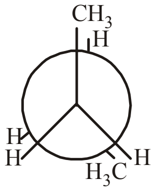
(a) Pent-l-yn-3-ene (b) Pent-4-yn-2-ene
(c) Pent-3-en-1-yne (d) Pent-2-en-4-yne

7. In the following the most stable conformation of *n*-butane is: **[CBSE-PMT 2010]**

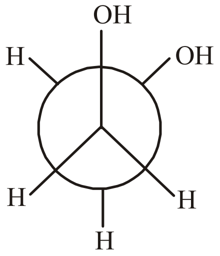
(a) 

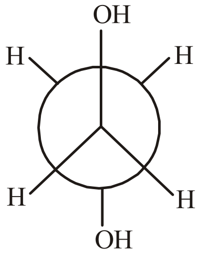
(b) 

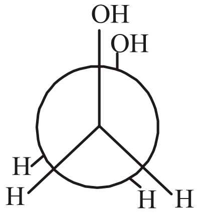
(c) 

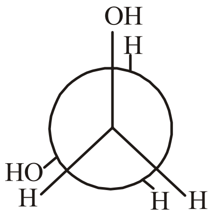
(d) 

8. Which of the following conformers for ethylene glycol is most stable? **[CBSE-PMT 2010]**

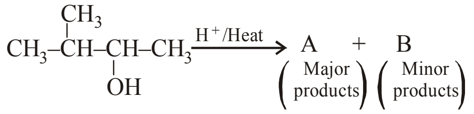
(a) 

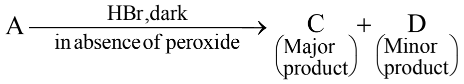
(b) 

(c) 

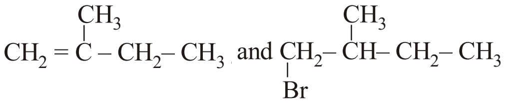
(d) 

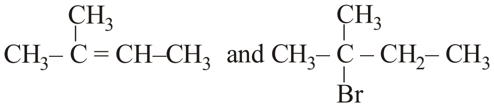
9. In the following reactions, **[CBSE-PMT 2011]**

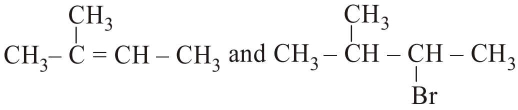
(a) 
$CH_3-\overset{CH_3}{CH}-\underset{OH}{CH}-CH_3\xrightarrow{H^+/Heat}\underset{\left(\text{Major products}\right)}{A}+\underset{\left(\text{Minor products}\right)}{B}$

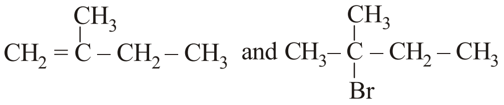
(b) 
$A\xrightarrow[\text{in absence of peroxide}]{\text{HBr,dark}}\underset{\left(\text{Major product}\right)}{C}+\underset{\left(\text{Minor product}\right)}{D}$

the major products (A) and (C) are respectively :

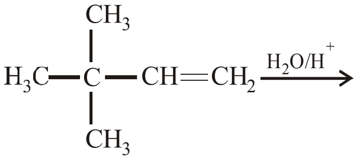
(a) 
$CH_2=\overset{CH_3}{C}-CH_2-CH_3$ and $\underset{Br}{CH_2}-\overset{CH_3}{CH}-CH_2-CH_3$

(b) 
$CH_3-\overset{CH_3}{C}=CH-CH_3$ and $CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_2-CH_3$

(c) 
$CH_3-\overset{CH_3}{C}=CH-CH_3$ and $CH_3-\overset{CH_3}{CH}-\underset{Br}{CH}-CH_3$

(d) 
$CH_2=\overset{CH_3}{C}-CH_2-CH_3$ and $CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_2-CH_3$

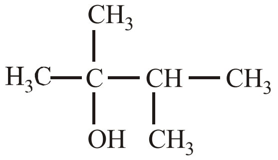
10. In the following reaction : **[CBSE-PMT 2012 S]**



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH=CH_2 \xrightarrow{H_2O/\overset{+}{H}} \underset{\text{Minor Product}}{A} + \underset{\text{Major Product}}{B}$$

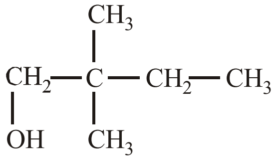
The major product is :

(a)



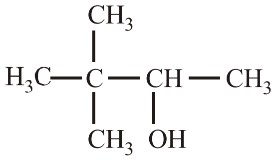
$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

(b)



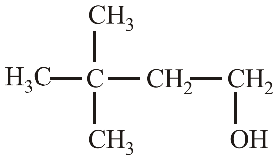
$$\underset{\underset{OH}{|}}{CH_2}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$$

(c)



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{CH}-CH_3$$

(d)



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\underset{\underset{OH}{|}}{CH_2}$$

11. Which of these will not react with acetylene? **[AIEEE 2002]**
(a) NaOH (b) ammonical $AgNO_3$
(c) Na (d) HCl.

12. What is the product when acetylene reacts with hypochlorous acid? **[AIEEE 2002]**
(a) CH_3COCl (b) $ClCH_2CHO$
(c) Cl_2CHCHO (d) ClCHCOOH.

13. On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be **[AIEEE 2003]**
(a) pentane (b) isopentane
(c) neopentane (d) propane

14. Butene-1 may be converted to butane by reaction with **[AIEEE 2003]**
(a) Sn – HCl (b) Zn – Hg
(c) Pd/H_2 (d) Zn – HCl

15. Which one of the following has the minimum boiling point ? **[AIEEE 2004]**
(a) 1 - Butene (b) 1 - Butyne
(c) n- Butane (d) isobutane

16. 2-Methylbutane on reacting with bromine in the presence of sunlight gives mainly **[AIEEE 2005]**
(a) 1-bromo-3-methylbutane
(b) 2-bromo-3-methylbutane
(c) 2-bromo-2-methylbutane
(d) 1-bromo-2-methylbutane

17. Acid catalyzed hydration of alkenes except ethene leads to the formation of **[AIEEE 2005]**
(a) mixture of secondary and tertiary alcohols
(b) mixture of primary and secondary alcohols
(c) secondary or tertiary alcohol
(d) primary alcohol

18. Which one of the following conformations of cyclohexane is chiral? **[AIEEE 2007]**
(a) Boat (b) Twist boat
(c) Rigid (d) Chair.

19. The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is **[AIEEE 2007]**
(a) benzyl alcohol (b) benzophenone
(c) acetophenone (d) benzoic acid.

20. Which of the following reactions will yield 2, 2-dibromopropane? **[AIEEE 2007]**
(a) $CH_3-CH=CH_2+HBr \rightarrow$
(b) $CH_3-C\equiv CH+2HBr \rightarrow$
(c) $CH_3CH=CHBr+HBr \rightarrow$
(d) $CH\equiv CH+2HBr \rightarrow$

21. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives predominantly **[AIEEE 2007]**
(a) *m*-chlorobenzene (b) benzoyl chloride
(c) benzyl chloride (d) *o*- and *p*-chlorotoluene.

22. Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated wth cuprous bromide. The reaction mixture so formed contains **[AIEEE 2008]**
(a) mixture of *o*- and *p*-bromotoluenes
(b) mixture of *o*- and *p*-dibromobenzenes
(c) mixture of *o*- and *p*-bromoanilines
(d) mixture of *o*- and *m*-bromotoluenes

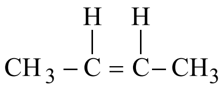
23. In the following sequence of reactions, the alkene affords the compound 'B'

$$CH_3-CH=CH-CH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B.$$

The compound B is **[AIEEE 2008]**
(a) CH_3CH_2CHO (b) CH_3COCH_3
(c) $CH_3CH_2COCH_3$ (d) CH_3CHO

24. The hydrocarbon which can react with sodium in liquid ammonia is **[AIEEE 2008]**
(a) $CH_3CH_2CH_2C\equiv CCH_2CH_2CH_3$
(b) $CH_3CH_2C\equiv CH$
(c) $CH_3CH=CHCH_3$
(d) $CH_3CH_2C\equiv CCH_2CH_3$

25. The treatment of CH_3MgX with $CH_3C\equiv C-H$ produces **[AIEEE 2008]**
(a) $CH_3-CH=CH_2$
(b) $CH_3C\equiv C-CH_3$
(c)



$$CH_3-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-CH_3$$

(d) CH_4

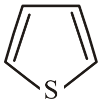
26. One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is **[AIEEE 2010]**

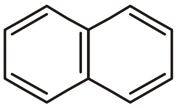
(a) propene (b) 1-butene
(c) 2-butene (d) ethene

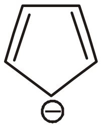
27. Ozonolysis of an organic compound 'A' produces acetone and propionaldhyde in equimolar mixture. Identify 'A' from the following compounds: **[AIEEE 2011]**

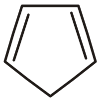
(a) 1 – Pentene
(b) 2 – Pentene
(c) 2 – Methyl – 2 – pentene
(d) 2 – Methyl – 1 – pentene

28. The non aromatic compound among the following is : **[AIEEE 2011RS]**

(a)


(b)


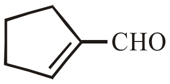
(c)


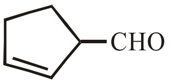
(d)


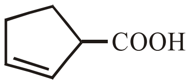
29. 2-Hexyne gives *trans*-2-Hexene on treatment with :

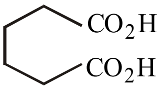
(a) Pt/H_2 (b) Li / NH_3 **[AIEEE 2012]**
(c) Pd/$BaSO_4$ (d) LiAlH_4

30. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound **E**. Compound **E** on further treatment with aqueous KOH yields compound **F**. Compound **F** is **[IIT-JEE 2007]**

(a)


(b)


(c)


(d)


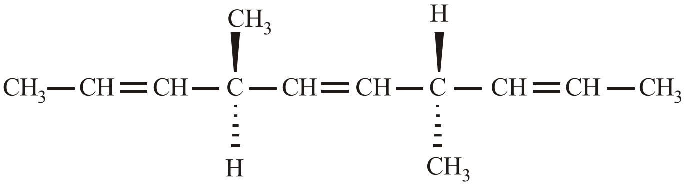
31. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are **[IIT-JEE 2010]**

(a) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2C\equiv CH$
(b) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2C\equiv CH$
(c) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C\equiv CH$
(d) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C\equiv CH$

32. The bond energy (in **kcal mol^{-1}**) of a C–C single bond is approximately **[IIT-JEE 2010]**

(a) 1 (b) 10
(c) 100 (d) 1000

33. The number of optically active products obtained from the **complete** ozonolysis of the given compound is : **[IIT-JEE 2012]**



$$CH_3-CH=CH-\underset{H}{\overset{CH_3}{C}}-CH=CH-\underset{CH_3}{\overset{H}{C}}-CH=CH-CH_3$$

(a) 0 (b) 1
(c) 2 (d) 4

Exercise-4 | Applied MCQs

1. To prepare a pure sample of n-hexane using sodium metal as one reactant, the other reactant will be

(a) Ethyl chloride and n-butyl chloride
(b) Methyl bromide and n-pentyl bromide
(c) n-Propyl bromide
(d) Ethyl bromide and n-butyl bromide

2. Indicate the expected structure of the organic product when ethyl magnesium bromide is treated with heavy water (D_2O)

(a) C_2H_5–C_2H_5 (b) C_2H_5OD
(c) Sodium benzoate (d) C_2H_5D

3. $(CH_3)_3CMgCl$ on reaction with D_2O produces

(a) $(CH_3)_3CD$ (b) $(CH_3)_3COD$
(c) $(CD)_3CD$ (d) $(CD)_3COD$

4. The reagent used for the conversion,

$CH_3CH_2COOH \rightarrow CH_3CH_2CH_3$ is

(a) $LiAlH_4$
(b) Soda-lime
(c) Red P and concentrated HI
(d) Zn – Hg/conc. HCl

5. An alkane C_7H_{16} is produced by the reaction of lithium di(3-pentyl) cuprate with ethyl bromide. The structural formula of the product is

(a) 3-ethylpentane (b) 2-ethylpentane
(c) 3-methylhexane (d) 2-methylhexane

6. When ethyl alcohol is heated with conc. H_2SO_4 at 443 K, ethylene is formed by

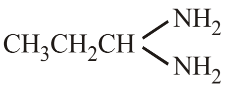
(a) intramolecular hydration
(b) intermolecular hydration
(c) intermolecular dehydration
(d) intramolecular dehydration

7. Electrolysis of cold concentrated aqueous solution of potassium succinate yields

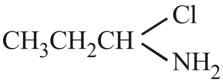
(a) ethane (b) ethyne
(c) ethene (d) ethane-1, 2-diol

8. When $CH_3CH_2CHCl_2$ is treated with $NaNH_2$, the product formed is

(a) $CH_3-CH=CH_2$ (b) $CH_3-C\equiv CH$

(c)


$CH_3CH_2CH\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}$

(d)


$CH_3CH_2CH\begin{smallmatrix}Cl\\NH_2\end{smallmatrix}$

9. 1,2-Dibromopropane on treatment with X moles of $NaNH_2$ followed by treatment with ethyl bromide gave pentyne. The value of X is
(a) 1 (b) 2
(c) 3 (d) 4

10. In the reaction,

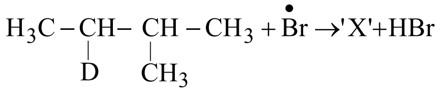
$$C_6H_5CH_3 \xrightarrow{\text{oxidation}} A \xrightarrow{\text{NaOH}} B \xrightarrow[\Delta]{\text{Soda-lime}} C,$$

the product C is
(a) C_6H_5OH (b) C_6H_6
(c) C_6H_5COONa (d) C_6H_5ONa

11. Reactivity of hydrogen atoms attached to different carbon atoms in alkanes has the order
(a) Tertiary > Primary > Secondary
(b) Primary > Secondary > Tertiary
(c) Tertiary > Secondary > Primary
(d) Both (a) and (b)

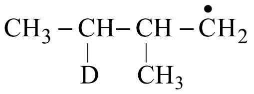
12. In the free radical chlorination of methane, the chain initiating step involves the formation of
(a) chlorine atom (b) hydrogen chloride
(c) methyl radical (d) chloromethyl radical

13. Consider the following reaction,

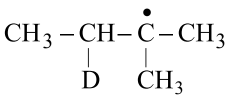


$$H_3C-\underset{|\atop D}{CH}-\underset{|\atop CH_3}{CH}-CH_3+\dot{Br}\rightarrow\text{'X'}+HBr$$

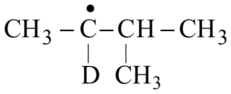
Identify the structure of the major product 'X'

(a) 

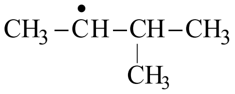
$$CH_3-\underset{|\atop D}{CH}-\underset{|\atop CH_3}{CH}-\dot{C}H_2$$

(b) 

$$CH_3-\underset{|\atop D}{CH}-\underset{|\atop CH_3}{\dot{C}}-CH_3$$

(c) 

$$CH_3-\underset{|\atop D}{\dot{C}}-\underset{|\atop CH_3}{CH}-CH_3$$

(d) 

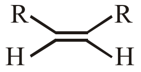
$$CH_3-\dot{C}H-\underset{|\atop CH_3}{CH}-CH_3$$

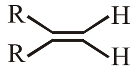
14. A hydrocarbon with molecular formula C_8H_{18} gives only one monochloro derivative. The hydrocarbon is
(a) n-Octane
(b) 2-Methylheptane
(c) 2,2,4-Trimethylpentane
(d) 2,3,3,3-Tetramethylbutane

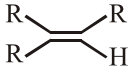
15. Which of the following compounds has the lowest boiling point ?
(a) $CH_3CH_2CH_2CH_2CH_3$
(b) $CH_3CH=CHCH_2CH_3$
(c) $CH_3CH=CH-CH=CH_2$
(d) $CH_3CH_2CH_2CH_3$

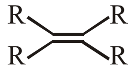
16. Among the following alkenes : 1-butene(I), cis-2-butene(II), trans-2-butene(III), the decreasing order of stability is
(a) III > II > I (b) III > I > II
(c) I > II > III (d) II > I > III

17. Which of the following alkenes will react fastest with H_2 under catalytic hydrogenation conditions ?

(a) 

(b) 

(c) 

(d) 

18. The conversion of ClCH=CHCl to $Cl_2CH-CHCl_2$ can be carried out with
(a) Cl_2 (b) $Cl_2/h\nu$
(c) $Cl_2/AlCl_3$ (d) Cl_2/aq. NaOH

19. The products formed by the action of chlorine on ethene in saturated solution of KBr is/are
(a) $ClCH_2CH_2Cl + ClCH_2CH_2Br$
(b) $ClCH_2CH_2Cl$
(c) $ClCH_2CH_2Cl + BrCH_2CH_2Br$
(d) $ClCH_2CH_2Cl + BrCH_2CH_2Br + ClCH_2CH_2Br$

20. In methyl alcohol solution, bromine reacts with ethylene to yield $BrCH_2CH_2OCH_3$ in addition to 1, 2-dibromoethane because
(a) the ion formed initially may react with Br^- or CH_3OH
(b) the methyl alcohol solvates the bromine
(c) the reaction follows Markovnikov's rule
(d) this is a free-radical mechanism

21. The intermediate during the addition of HCl to propene in the presence of peroxide is
(a) $CH_3\dot{C}HCH_2Cl$ (b) $CH_3\overset{+}{C}HCH_3$
(c) $CH_3CH_2\dot{C}H_2$ (d) $CH_3CH_2\overset{+}{C}H_2$

22. In presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov's addition to alkenes because
(a) both are highly ionic
(b) one is oxidising and the other is reducing
(c) one of the steps is endothermic in both cases
(d) all steps are exothermic in both cases

23. Arrange the following compounds in increasing order of reactivity towards the addition of HBr.
$RCH=CHR, CH_2=CH_2, R_2C=CHR, R_2C=CR_2$
(a) $CH_2=CH_2 < RCH=CHR < R_2C=CHR < R_2C=CR_2$
(b) $R_2C=CHR < RCH=CHR < CH_2=CH_2 < R_2C=CR_2$
(c) $RCH=CHR < R_2C=CR_2 < R_2C=CHR < CH_2=CH_2$
(d) $R_2C=CR_2 < R_2C=CHR < RCH=CHR < CH_2=CH_2$

24. Which of the following is the predominant product in the reaction of HOBr with propene?
(a) 2-Bromo-1-propanol (b) 3-Bromo-1-propanol
(c) 2-Bromo-2-propanol (d) 1-Bromo-2-propanol

25. The reaction of propene with HOCl proceeds via the addition of
(a) H^+ in the first step
(b) Cl^+ in the first step
(c) OH^- in the first step
(d) Cl^+ and OH^- in a single step

26. The products obtained via oxymercuration ($HgSO_4 + H_2SO_4$) of 1-butyne would be

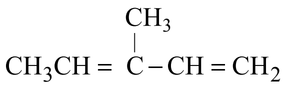
(a) $CH_3-CH_2-CO-CH_3$

(b) $CH_3-CH_2-CH_2-CHO$

(c) $CH_3-CH_2-CHO+HCHO$

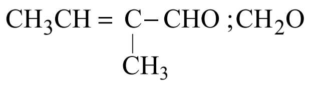
(d) $CH_3CH_2COOH+HCOOH$

27. Which set of products is expected on reductive ozonolysis of the following diolefin ?



$$CH_3CH=\overset{CH_3}{\overset{|}{C}}-CH=CH_2$$

(a) $CH_3CHO;CH_3COCH=CH_2$

(b)  $CH_3CH=\underset{CH_3}{\underset{|}{C}}-CHO;CH_2O$

(c) $CH_3CHO;CH_3COCHO;CH_2O$

(d) $CH_3CHO;CH_3COCH_3;CH_2O$

28. The alkene C_6H_{10} producing $OHC(CH_2)_4CHO$ on ozonolysis is

(a) Hexene-1

(b) Hexene-3

(c) Cyclohexene

(d) 1-Methylcyclohexene

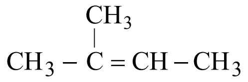
29. 2.8 g of pure alkene containing only one double bond per molecule, react completely with 8 g of bromine (in an inert solvent). What is the molecular formula of the alkene ?

(a) C_2H_4

(b) C_4H_8

(c) C_3H_4

(d) C_6H_{12}



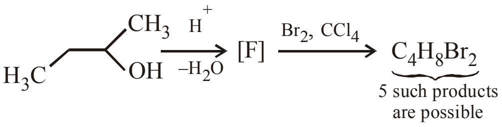
30. The compound $CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3$ on reaction with $NaIO_4$ in the presence of $KMnO_4$ gives

(a) $CH_3COCH_3+CH_3COOH$

(b) $CH_3COCH_3+CH_3CHO$

(c) $CH_3CHO+CO_2$

(d) CH_3COCH_3

31. 

How many structures of F are possible ?

(a) 2

(b) 5

(c) 6

(d) 3

32. When $CH_2 = CH - COOH$ is reduced with $LiAlH_4$, the compound obtained will be

(a) $CH_3–CH_2–COOH$

(b) $CH_2=CH–CH_2OH$

(c) $CH_3–CH_2–CH_2OH$

(d) $CH_3–CH_2–CHO$

33. Ethyne can be oxidised to oxalic acid by using

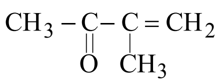
(a) chromic acid

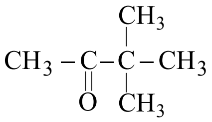
(b) alkaline $KMnO_4$

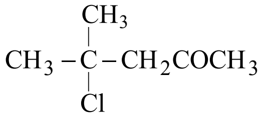
(c) hypochlorous acid

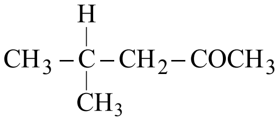
(d) Any of these

34. Indicate the organic structure for product expected when 2-methylpropene is heated with acetyl chloride in the presence of anhydrous $ZnCl_2$?

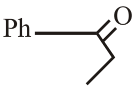
(a)  $CH_3-\underset{O}{\underset{||}{C}}-\underset{CH_3}{\underset{|}{C}}=CH_2$

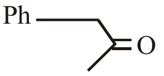
(b)  $CH_3-\underset{O}{\underset{||}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

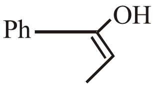
(c)  $CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_2COCH_3$

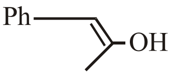
(d)  $CH_3-\overset{H}{\underset{CH_3}{C}}-CH_2-COCH_3$

35. $Ph-C\equiv CCH_3 \xrightarrow{Hg^{2+}/H^+} A$, A is

(a) 

(b) 

(c) 

(d) 

36. Excess of CH_3COOH is reacted with $CH\equiv CH$ in presence of Hg^{2+}, the product is

(a) $CH_3CH(OOCCH_3)_2$

(b) $CH_2=CH(OCOCH_3)$

(c) $(CH_3COO)CH_2-CH_2(OOCCH_3)$

(d) None of these

37. When acetylene reacts with arsenic trichloride in the presence of anhydrous aluminium chloride it produces

(a) β-Chlorovinyldichloroarsine

(b) Lewisite

(c) Nitrobenzene

(d) Both (a) and (b)

38. Which one of the following compounds will react with methylmagnesium iodide ?

(a) $CH_3CH_2CH_2CH_2CH_3$

(b) $CH_3CH=CH–CH=CH_2$

(c) $CH_3C\equiv CCH_2CH_3$

(d) $CH_3CH_2CH_2C\equiv CH$

39. Propyne on polymerization gives

(a) mesitylene

(b) benzene

(c) ethylbenzene

(d) propylbenzene

40. 1-Butyne reacts with cold alkaline $KMnO_4$ to produce

(a) CH_3CH_2COOH

(b) $CH_3CH_2CH_2COOH$

(c) $CH_3CH_2COOH+CO_2$

(d) $CH_3CH_2COOH+HCOOH$

41. Two gases, P and Q decolourise aqueous bromine but only one of them gives a white precipitate with aqueous ammonical silver nitrate solution. P and Q are likely to be

(a) ethane and ethyne

(b) But-1-yne and but-2-yne

(c) ethane and but-2-yne

(d) ethyne and propyne

42. The compound X (C_5H_8) reacts with ammonical $AgNO_3$ to give a white precipitate, and on oxidation with hot alkaline $KMnO_4$ gives the acid, $(CH_3)_2CHCOOH$. Therefore, X is

(a) $CH_2=CHCH=CHCH_3$

(b) $CH_3(CH_2)_2C\equiv CH$

(c) $(CH_3)_2CH-C\equiv CH$

(d) $(CH_3)_2C=C=CH_2$

43. Choose the compound which can react with $[Ag(NH_3)_2]^+$ and on treatment with alk. $KMnO_4$ gives $(CH_3)_3CCOOH$

(a) $CH_3CH_2CH_2-C\equiv C-CH_3$

(b) $(CH_3)_2CHCH_2-C\equiv CH$

(c) $(CH_3)_3C-C\equiv CH$

(d) $(CH_3)_3C-C\equiv C-CH_3$

44. Which of the following possesses the highest melting point ?

(a) Chlorobenzene (b) o-Dichlorobenzene

(c) m-Dichlorobenzene (d) p-Dichlorobenzene

45. The function of $AlCl_3$ in the Friedel-Craft's reaction is

(a) to absorb water (b) to absorb HCl

(c) to produce electrophile (d) to produce nucleophile

46. Which one of the following will undergo metasubstitution on monochlorination ?

(a) Ethoxybenzene (b) Chlorobenzene

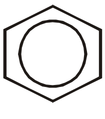
(c) Ethyl benzoate (d) Phenol

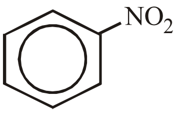
47. Which of the following deactivates benzene towards further substitution reaction ?

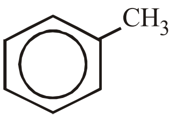
(a) —NHR (b) —OH

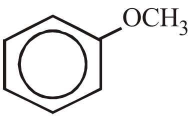
(c) —COOR (d) —OR

48. Which of the following will have fastest rate of reaction with $Br_2/FeBr_3$?

(a) 

(b) 

(c) 

(d) 

49. The order of activity of the various o- and p-directors is

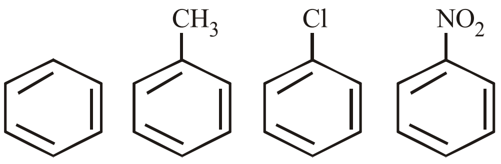
(a) $-O^- > -OH > -OCOCH_3 > -COCH_3$

(b) $-OH > -O^- > -OCOCH_3 > -COCH_3$

(c) $-OH > -O^- > -COCH_3 > -OCOCH_3$

(d) $-O^- > -COCH_3 > -OCOCH_3 > -OH$

50. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds :



1 2 3 4

(a) $1>2>3>4$ (b) $4>3>2>1$

(c) $2>1>3>4$ (d) $2>3>1>4$

51. n-Butylbenzene on oxidation will give

(a) benzoic acid (b) butanoic acid

(c) benzyl alcohol (d) benzaldehyde

52. Two organic compounds A and B both containing only carbon and hydrogen, on quantitative analysis gave the same percentage composition by weight :

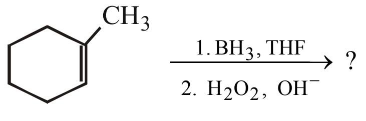
$C = (12/13) \times 100\%, H = (1/13) \times 100\%$

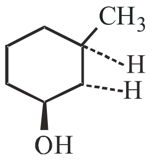
A decolourises bromine water but B does not. A and B respectively are

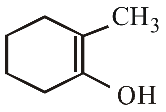
(a) C_2H_2 and C_6H_6 (b) C_6H_6 and C_2H_2

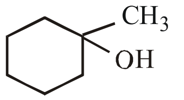
(c) C_2H_4 and C_2H_6 (d) C_2H_2 and C_2H_6

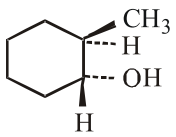
53. What is the correct product of reaction ?



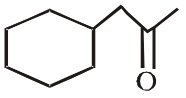
(a) 

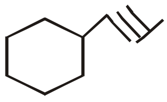
(b) 

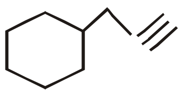
(c) 

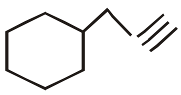
(d) 

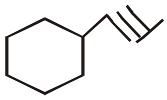
54. Choose the correct alkyne and reagents for the preparation

of 

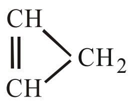
(a)  , $HgSO_4$, H_2SO_4, H_2O

(b)  , $HgSO_4$, H_2SO_4, H_2O

(c)  , BH_3, H_2O_2, NaOH

(d)  , BH_3, H_2O_2, NaOH

55. Of the three isomeric C_3H_4 hydrocarbons shown below how many can exist with all carbon and hydrogen nuclei located in a single plane

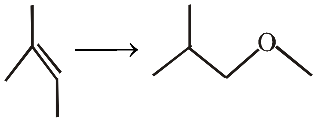
$H_2C=C=CH_2$,  , $H_3C-C\equiv CH$

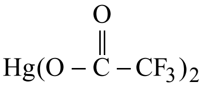
$\begin{array}{l} CH \\ \| \quad \rangle CH_2 \\ CH \end{array}$

(a) 0 (b) 1

(c) 2 (d) 3

56. Which sets of reagents would give the correct product ?



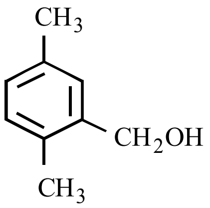
(a) 
$Hg(O-\overset{\overset{O}{\parallel}}{C}-CF_3)_2$

(b) $Hg(OAC)_2$ in THF/H_2O , $NaBH_4$

(c) BH_3, $NaOH/H_2O_2$

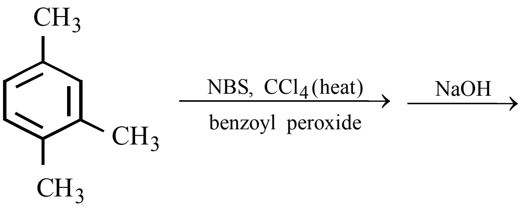
(d) BH_3, H_2O_2/OH^-, NaH, CH_3I

57. For the synthesis of the following compound :

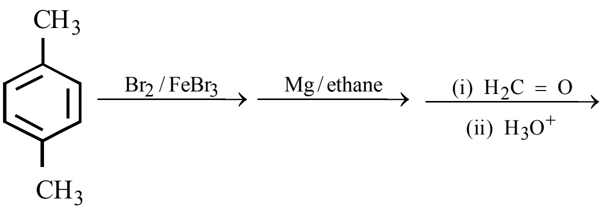


Which method is best ?

Method I :



Method II :



(a) Method I

(b) Method II

(c) Both (I) and (II) are equally good

(d) Neither (I) nor (II)

58. The reaction of cis-2-butene with CH_2I_2 and Zn(Cu) to give cis-1, 2-dimethyl cyclopropane is

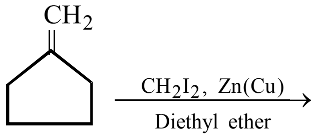
(a) stereospecific reaction

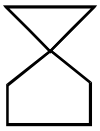
(b) enantiospecific reaction

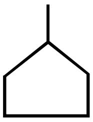
(c) diastereoselective reaction

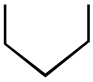
(d) regioselective reaction

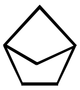
59. The product of the following reaction



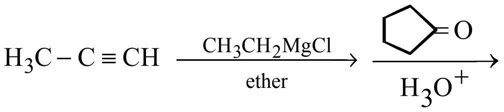
(a) 

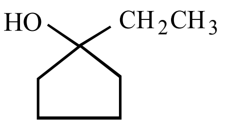
(b) 

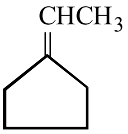
(c) 

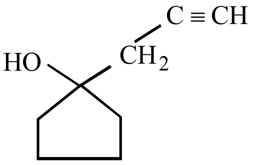
(d) 

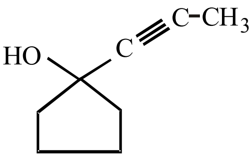
60. The major product of the following reaction



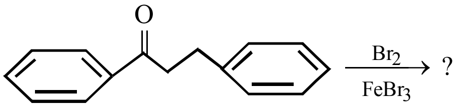
(a) 

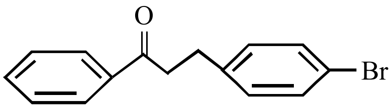
(b) 

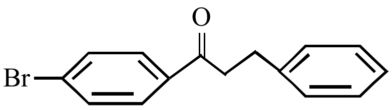
(c) 

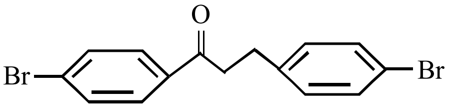
(d) 

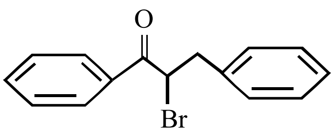
61. The major product obtained in the following reaction



(a) 

(b) 

(c) 

(d) 

62. The unsaturated hydrocarbon which on ozonolysis gives one mole each of formaldehyde, acetaldehyde and methyl glyoxal ($CH_3CO.CHO$)

(a) $CH_3-CH=C(CH_3)-CH_3$

(b) $CH_2=CH-CH_2-CH=CH_2$

(c) $CH_2=CH-C(CH_3)=CH-CH_3$

(d) $(CH_3)_2C=CH-CH_3$

63. Which of the following is not the mechanistic step during chlorination of methane by $Cl_2/h\nu$?

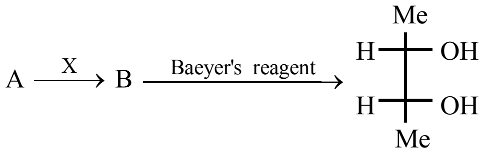
(a) $Cl_2 \rightarrow 2\dot{Cl}$

(b) $\dot{Cl} + CH_4 \rightarrow \dot{C}H_3 + HCl$

(c) $\dot{Cl} + CH_4 \rightarrow CH_3Cl + \dot{H}$

(d) $\dot{Cl} + \dot{C}H_3 \rightarrow CH_3Cl$

64. Which is correct for the following changes ?



(a) X is Lindlar Catalyst, B is Cis-2-butene

(b) A is 2-butyne, X is Na-liq. NH_3

(c) B is trans-2-butene, X is Na-liq. NH_3

(d) A is 2-butene, X is SeO_2

65.  NH_2 + (excess) of Et. MgBr → ?

(a) 1 mol of Ethane (b) 3 mol of ethane

(c) $EtC\equiv C.CH_2CH_2NHEt$ (d) 4 mole of ethane

66. Addition of Br_2 to alkene proceeds by the intermediate formation of

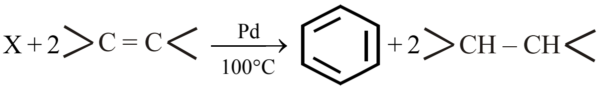
(a) carbonium ion

(b) carbanium ion

(c) bridged (non classical) carbonium ion

(d) All of these

67. In the following change,



The X may be

(a) cyclohexene (b) cyclohexadiene

(c) cyclogexatriene (d) None of these

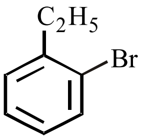
68. $R-CH=CH_2 \xrightarrow[Et.\ OH]{Na\ liquid\ NH_3} R.CH_2.CH_3$

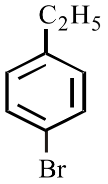
The reaction is called

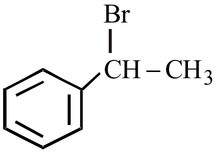
(a) Birch's reduction (b) Clemensen's reduction

(c) Catalytic reduction (d) None of these

69. Bromination of ethyl benzene in presence of light gives

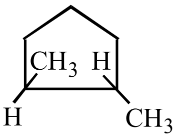
(a) 

(b) 

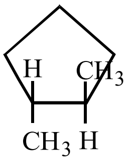
(c) 

(d) Both (a) and (b)

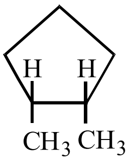
70. Pair of enantiomers of 1, 2-dimethylcyclopentane having structures



(I)



(II)

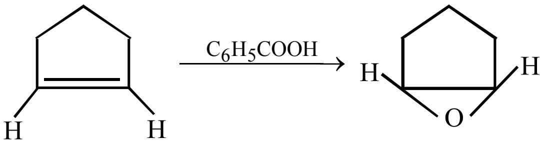


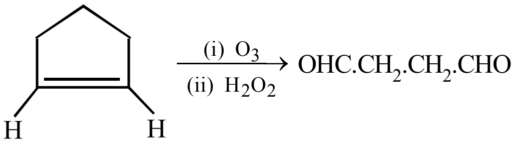
(III)

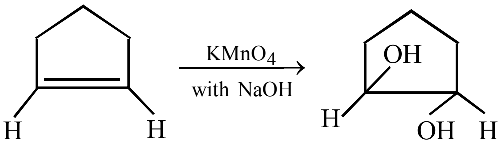
(a) I and III (b) I and II

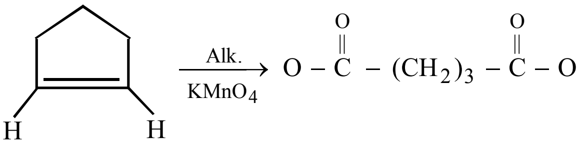
(c) II and III (d) I, II and III

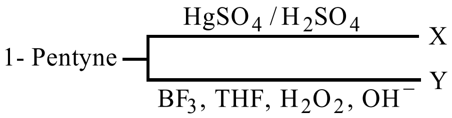
71. Which of the following is correct

(a) 

(b) 

(c) 

(d) 

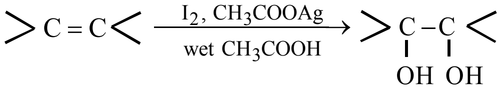
72. 

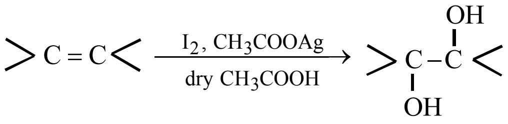
X and Y can be distinguished by

(a) silver-mirror test (b) iodoform test

(c) Both (a) and (b) (d) Neither (a) nor (b)

73. Which of the following change is correct

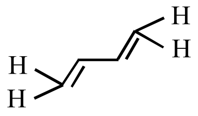
(a) 
$>C=C< \xrightarrow[\text{wet } CH_3COOH]{I_2,\ CH_3COOAg} >\underset{OH}{C}-\underset{OH}{C}<$

(b) 
$>C=C< \xrightarrow[\text{dry } CH_3COOH]{I_2,\ CH_3COOAg} >\underset{OH}{C}-\overset{OH}{C}<$

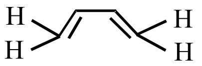
(c) Both (a) and (b) one correct

(d) Neither (a) nor (b)

74. Choose the correct among the following

(a) 

S - trans (transoid), less stable

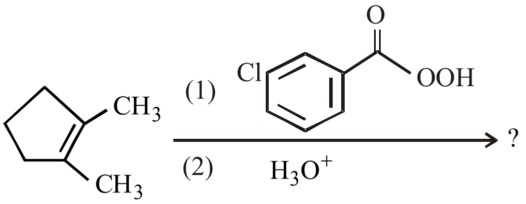
(b) 

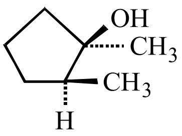
S - cis (cisoid), more stable

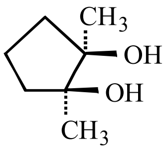
(c) S-refers to geomectrical isomerism with respect to single bond.

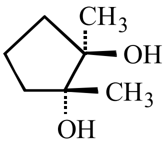
(d) All are correct

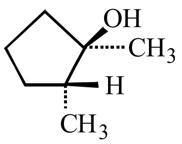
75. Choose the correct product of the following reaction



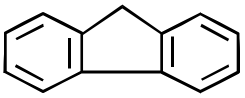
(a) 

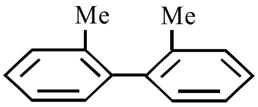
(b) 

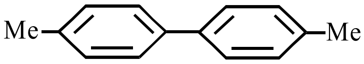
(c) 

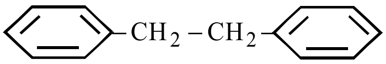
(d) 

76. $PhCH_3$ on reaction with $Cl_2/h\nu$ followed by Na/ether will give

(a) 

(b) 

(c) 

(d) 

77. In the following changes which is correct.

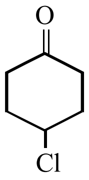
$$A \xrightarrow[R]{\text{Reagent}} B \xrightarrow{HCOOOH} \text{Erythroracemic}$$

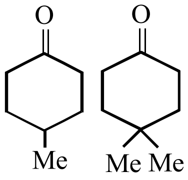
(a) A is 2-hexyne and R is Na-liquid NH_3

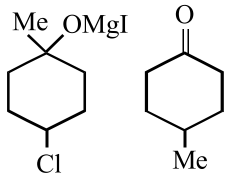
(b) A is 3-hexyne and R is H_2-Lindlar

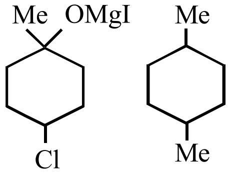
(c) B is 2-hexene and R is H_2-Lindlar

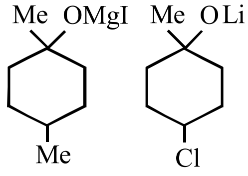
(d) A is 3-hexyne and R is H_2/Ni

78. The compound  reacts with MeMgI to give A and with Me_2CuLi to give B. What are A and B ?

(a) 

(b) 

(c) 

(d) 

Hints & Solutions

EXERCISE 1

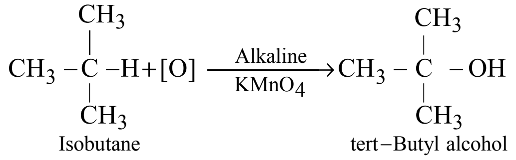
1. Liquefied petroleum gas.
2. A mixture of ethane, propane and butane is formed.
3. Acetylene, due to greater electronegativity of the sp–hybridized carbon.
4. No, because the difference of energy between these two conformations is very small.
5. because two Cl's in it have equal and opposite bond moments.
6. $CH_3-C\equiv C-CH_3 + NaNH_2 \longrightarrow$ No reaction

   $CH_3CH_2\equiv CH + NaNH_2 \longrightarrow CH_3CH_2C\equiv \overset{-}{C}\overset{+}{Na}$
7. A halogen compound used during halogenation of benzene is called halogen carrier e.g. $FeCl_3$.
8. (iii) < (iv) < (i) < (ii).

10. (i) $CH_4 + H_2O \xrightarrow[1273\,K]{Ni} CO + 3H_2$

    (ii) $CH_4 \xrightarrow[Carbon]{1500\,K} C + 2H_2$

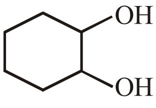
    (iii)



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-H+[O] \xrightarrow[KMnO_4]{Alkaline} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH$$

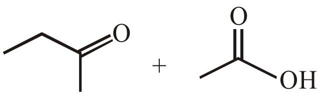
11. red phosphorus removes the iodine liberated in reaction

12. (i)



(Hydroxylation) (ii)

(iii)



Butanone Ethanoic acid

18. (d) 19. (a) 20. (d) 21. (c) 22. (a)
23. (d) 24. (a) 25. (a)

EXERCISE 2

1. (a)
2. (c)
3. (c) Vegetable oil is a mixture of triglycerides of higher fatty acids.
4. (b) Petroleum ether has lower boiling point than all the other three products
5. (d) Gasoline has the lowest boiling point, while diesel has the highest.
6. (c)
7. (d) Highly branched chain paraffins have high octane number

8. (a) 9. (a) 10. (b)

11. (d) Longer the straight chain alkane, lower is the octane number. Thus, n-hexadecane has even lower octane number than n-heptane

12. (d) 2,2,4-Trimethylpentane is the most branched hydrocarbon among the four given options

13. (b) Liquid hydrocarbons (a mixture of relatively higher hydrocarbons) is converted into gaseous hydrocarbons (a mixture of lower hydrocarbons) by strong heating, this process is known as cracking

14. (b) Since the fuel mixture contains 70% isooctane, its octane number is 70

15. (d) 16. (c) 17. (a) 18. (c)

19. (a) CH_4 has only one carbon atom, hence it can't be prepared by Wurtz reaction, which involves two molecules of alkyl halide

20. (a)

21. (d)

22. (c) Other three methods can be used for the preparation of hydrocarbons having at least 2 carbon atoms

23. (c)

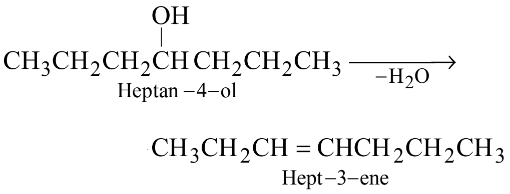
24. (c)

25. (b) Dehydrohalogenation of an alkyl halide gives an alkene

26. (a) 27. (a) 28. (a)

29. (d) The amount of alcohol absorbed depends upon the surface area of Al_2O_3

30. (b) Heptan-4-ol has similar alkyl group on both ends of the carbon atom bearing –OH group, hence dehydration of alcohol will form only one alkene, not a mixture of two alkenes



$$\underset{\text{Heptan}-4-\text{ol}}{CH_3CH_2CH_2\overset{OH}{\overset{|}{CH}}CH_2CH_2CH_3} \xrightarrow[-H_2O]{} \underset{\text{Hept}-3-\text{ene}}{CH_3CH_2CH=CHCH_2CH_2CH_3}$$

31. (b)

32. (c) $CH_3CHBrCHBrCH_3 \xrightarrow{Zn/alcohol} CH_3CH=CHCH_3$

    Since two bromine atoms are lost from different carbon atom, the reaction is known as β-elimination.

33. (a) 34. (d) 35. (d)

36. (a) $CaC_2 + 2D_2O \rightarrow C_2D_2 + Ca(OD)_2$

37. (c) $HC\equiv CNa + XR \rightarrow HC\equiv CR$

    Since the atom or group attached to two acetylenic carbon atoms are different, the alkyne formed (higher alkyne) is unsymmetrical

38. (b) 39. (a) 40. (a) 41. (a)

42. (a) Recall that first four alkanes are gaseous in nature at room temperature.

43. (a) Among isomeric alkanes, boiling point decreases with increase in branching

44. (b) n-Butane, $\overset{1}{C}H_3\overset{2}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_3$ has two different hydrogen atoms, marked by 1 and 2.

45. (c) **46. (b)** **47. (b)**

48. (a) The heat of hydrogenation of an alkene depends upon its stability. Higher the stability, lower the heat of hydrogenation. Since $CH_2{=}CH_2$ has no substituent, it is the least stable alkene and hence has the highest heat of hydrogenation

49. (a) **50. (b)** **51. (b)** **52. (b)**

53. (a) All are examples of electrophilic addition reactions and involve the formation of stable carbocation leading to the formation of addition product according to Markovnikov's rule

54. (b)

55. (c) (See Anti Markovnikov's rule)

56. (d) Markovnikov's rule is applicable only to unsymmetrical alkenes, which is option (*d*) here

57. (b) Symmetrical alkenes (option *b*) give similar products whether the addition is according to Markovnikov's rule or according to peroxide effect.

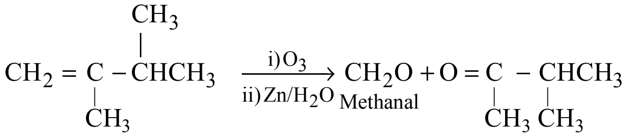
58. (d) Addition of HBr on alkenes is an electrophilic reaction, hence more the number of electron-releasing groups on the double bond easier will be the addition

59. (a) The intermediate 2° carbocation shows resonance

$$CH_2=CH-CH=CH_2 \xrightarrow{Br^+} \left[CH_2Br-\overset{+}{C}H-CH=CH_2 \leftrightarrow CH_2Br-CH=CH-\overset{+}{C}H_2\right]$$

$$\xrightarrow{Br^-} \underset{\text{1,4-Dibromo-2-butene}}{CH_2Br-CH=CH-CH_2Br}$$

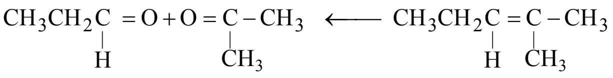
60. (c) In such questions, break the molecule at double bond by adding oxygen atom at each doubly bonded carbon



$$\underset{\text{2,3-Dimethyl-1-butene}}{CH_2=\underset{CH_3}{\overset{CH_3}{\overset{|}{C}}}-CHCH_3} \xrightarrow[\text{ii) } Zn/H_2O]{\text{i) } O_3} \underset{\text{Methanal}}{CH_2O} + \underset{\text{3-Methyl-2-butanone}}{O=\underset{CH_3}{\underset{|}{C}}-\underset{CH_3}{\underset{|}{C}}HCH_3}$$

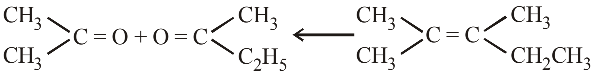
61. (c)

62. (a) In such questions follow the following points: (i) write down the structure of the given carbonyl compound(s), (ii) remove oxygen atoms of the two carbonyl compounds, (iii) join the two carbon atoms of the two carbonyl groups to each other to get the structure of the parent alkene



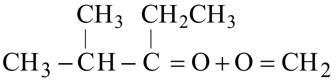
$$CH_3CH_2\underset{H}{\underset{|}{C}}=O+O=\underset{CH_3}{\underset{|}{C}}-CH_3 \longleftarrow CH_3CH_2\underset{H}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-CH_3$$

63. (d)

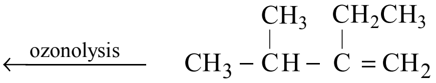


2,3-Dimethyl-2-pentene

64. (a) Since the ozonolysis product, 2-methyl-3-pentanone, contains only six carbon atoms, while the alkene has seven carbon atoms, the other ozonolysis product should be CH_2O, the only carbonyl compound having one carbon atom. Hence, the structure of the alkene C_7H_{14} can be established as below



$$\underset{\text{2-Methyl-3pentanone}}{CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{CH_2CH_3}{\overset{|}{C}}=O} + O=CH_2$$



$$\xleftarrow{\text{ozonolysis}} \underset{\text{2-Ethyl-3-methyl-1-butene}}{CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{CH_2CH_3}{\overset{|}{C}}=CH_2}$$

65. (d) **66. (b)** **67. (a)** **68. (c)**

69. (b) $CH_3C\equiv CCH_3$, being symmetrical, has the lowest dipole moment

70. (b) Reduction of alkynes with Na/liq. NH_3 gives trans-alkenes

71. (a) Reduction of alkynes with Lindlar's catalyst (Pd-$BaSO_4$) gives cis-alkenes

72. (c)

73. (d) $CH\equiv CH \xrightarrow{HBr} CH_2=CHBr$

$$\xrightarrow[\text{Markovnikov addition}]{HBr} CH_3CHBr_2$$

74. (d) **75. (c)** **76. (a)** **77 (d)**

78. (d) **79. (a)**

80. (a) 2-Butyne ($CH_3C\equiv CCH_3$), being a non-terminal alkyne, does not have acidic hydrogen atom

81. (a) Only terminal alkynes, react with bases like $NaNH_2$, CH_3MgI, ammonical $AgNO_3$ and ammonical cuprous chloride

82. (c)

83. (c) Tollen's reagent (ammonical silver nitrate) reacts with terminal alkynes

84. (d) Ammonical silver nitrate and ammonical cuprous chloride give precipitate only with terminal alkynes (propyne, $CH_3C\equiv CH$)

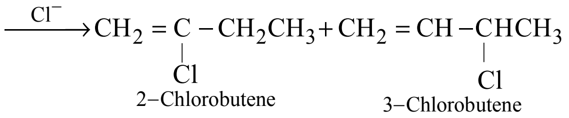
85. (d) Ammonical cuprous chloride gives precipitate (red) only with terminal alkynes, i.e. alkynes having acidic hydrogen atom, such as butyne-1 ($CH\equiv CCH_2CH_3$)

86. (c) Only alkynes, which is $CH\equiv CH$ in the present question, react with Br_2 to give bromoderivative of an alkene

$$CH\equiv CH+Br_2 \longrightarrow BrCH=CHBr$$

87. (a) $CH_2 = C = CH - CH_3 \xrightarrow{H^+}$

$$\left[CH_2 = \overset{+}{C} - CH_2CH_3 + CH_2 = CH - \overset{+}{C}HCH_3\right]$$



$$\xrightarrow{Cl^-} \underset{\text{2–Chlorobutene}}{CH_2 = \underset{Cl}{\underset{|}{C}} - CH_2CH_3} + \underset{\text{3–Chlorobutene}}{CH_2 = CH - \underset{Cl}{\underset{|}{C}}HCH_3}$$

88. (a) Conversion of C_4H_6 to $C_4H_6Br_2$ indicates that the compound is either butyne-1 or butyne-2. However, white precipitate with ammonical silver nitrate solution indicates that it is a terminal alkyne, i.e. butyne-1 and not butyne-2

89. (d) Since the hydrocarbon decolourises $KMnO_4$ solution, it must be unsaturated, i.e. alkene or alkyne. However, it does not give any precipitate with ammonical $AgNO_3$, it must be a non-terminal alkyne, i.e. butyne-2

90. (c)

91. (c)

92. (b) Mononitration occurs at about 60º C, but at 100ºC dinitration occurs. Since $–NO_2$ is m-directing, m-dinitrobenzene is formed at 100ºC

93. (b)

94. (b)

95. (c) $RCl + AlCl_3 \rightarrow \underset{\text{Electrophile}}{R^+} + AlCl_4^-$

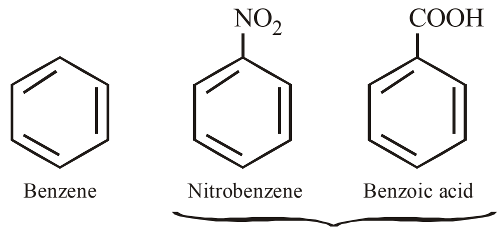
96. (d)

97. (d)

98. (a) Since the major product (>60%) is a m-isomer, the group Y must be m-directing which is –COOH

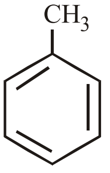
99. (b) –Cl group is o-, p-directing due to +R effect ; however it is deactivating due to strong –I effect of Cl (difference from other o-, p-directing groups which are activating). The net result is that chlorobenzene undergoes o-, p-substitution, but with difficulty

100. (d)



Benzene Nitrobenzene Benzoic acid

No group is present Deactivating group present

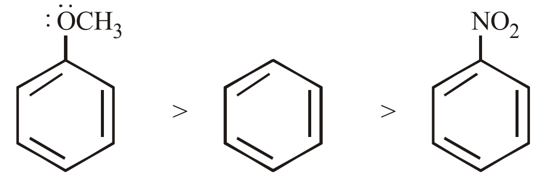


Toluene

Activating group present

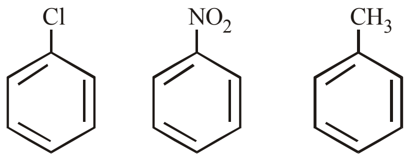
101. (c) Phenol as well as toluene have electron-releasing groups, however –OH group, in phenol, is more electron-releasing (due to +R effect) than the $–CH_3$ group in toluene, so phenol is more easily attacked by an electrophile.

102. (c)



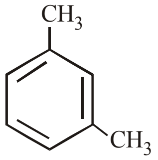
Electron-releasing group present No group is present Electron withdrawing group is present

103. (d)



(b) (c) (a)

Electron-withdrawing groups are present One electron-releasing group



(d)

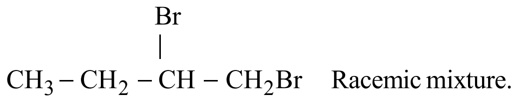
Two electron-releasing groups, hence most reactive towards sulphonation

104. (a) Mesitylene (1,3,5-trimethylbenzene) has three electron-releasing $(–CH_3)$ groups, while m-xylene, toluene and benzene have 2, 1 and 0 electron-releasing $(–CH_3)$ groups

105. (c)

106. (c)

107. (b) $CH_3 - CH_2 - CH = CH_2 + Br_2 \longrightarrow$



$$CH_3 - CH_2 - \overset{Br}{\overset{|}{C}H} - CH_2Br \quad \text{Racemic mixture.}$$

108. (b) Always remember cis 2-butene + $Br_2 \rightarrow$ Racemic 2, 3-dibromobutane \ Trans 2-butene + $Br_2 \rightarrow$ Meso 2, 3-dibromobutane.

109. (d) The given reaction is Diel's Alder reaction

110. (a) More is the stability, lower is the heat of combustion (See Baeyer's strain theory). Cyclohexane is more stable.

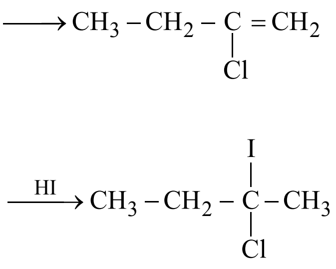
111. (b) Only 1-Alkynes form alkynides

112. (c) K salt of succinic acid or its derivatives give alkenes by Kolbe's electrolytic method.

EXERCISE 3

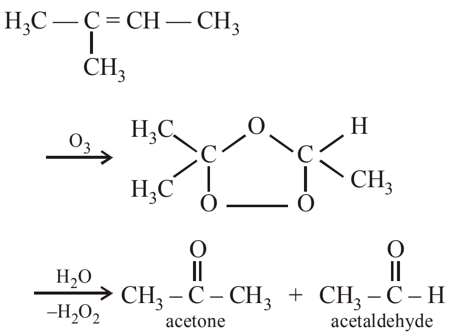
1. **(c)** This reaction occurs according to Markownikoff's rule which states that when an unsymmetrical alkene undergo hydrohalogenation, the negative part goes to that C-atom which contain lesser no. of H-atom.

$$CH_3-CH_2-C\equiv CH+HCl$$



$$\longrightarrow CH_3-CH_2-\underset{Cl}{\underset{|}{C}}=CH_2 \xrightarrow{HI} CH_3-CH_2-\overset{I}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_3$$

2. **(d)**



$$H_3C-\underset{CH_3}{\underset{|}{C}}=CH-CH_3 \xrightarrow{O_3} \text{ozonide} \xrightarrow[-H_2O_2]{H_2O} \underset{\text{acetone}}{CH_3-\overset{O}{\overset{||}{C}}-CH_3} + \underset{\text{acetaldehyde}}{CH_3-\overset{O}{\overset{||}{C}}-H}$$

3. **(c)** If both the double and triple bonds are present, the compound is regarded as derivative of alkyne. Further if double and triple bonds are at equidistance from either side, the preference is given to double bond.
4. **(b)** During cracking higher hydrocarbons (liquid) are converted to lower gaseous hydrocarbons.
5. **(d)** $C_6H_5CH_2Br+Mg \xrightarrow{ether} C_6H_5CH_2MgBr$

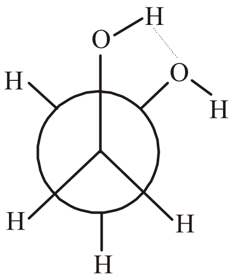
(in ether as solution)

$$\begin{array}{r|l} C_6H_5CH_2 & Mg\ Br \\ H & OH \end{array} \xrightarrow{H^+} C_6H_5CH_3+MgBr(OH)$$

6. **(c)** When both double and triple bonds are present, then triple bond is considered as the principal group.

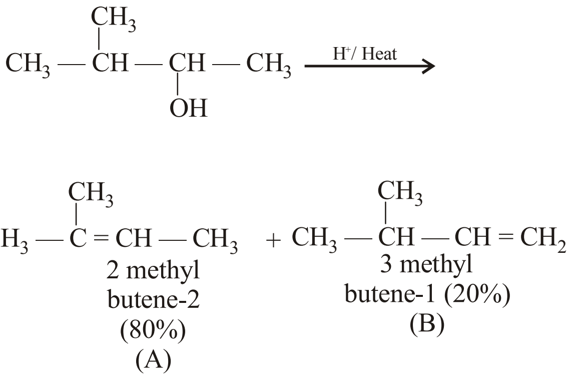
$$\underset{5}{CH_3}-\underset{4}{CH}=\underset{3}{CH}-\underset{2}{C}\equiv\underset{1}{CH}$$

7. **(b)** The bulky methyl groups are at maximum distance from each other.
8. **(a)** Due to hydrogen bonding between the two OH groups, gauche conformation of ethylene glycol (a) is the most stable conformation.



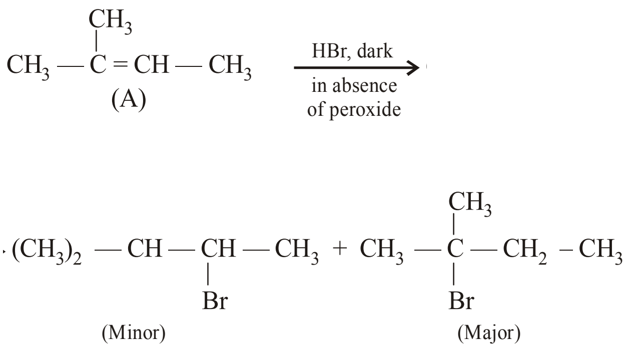
∴ **Correct choice : (a)**

9. **(b)**



$$CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{H^+/\text{ Heat}} \underset{\substack{\text{2 methyl}\\ \text{butene-2}\\ (80\%)\\ (A)}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3} + \underset{\substack{\text{3 methyl}\\ \text{butene-1 (20\%)}\\ (B)}}{CH_3-\overset{CH_3}{\overset{|}{CH}}-CH=CH_2}$$

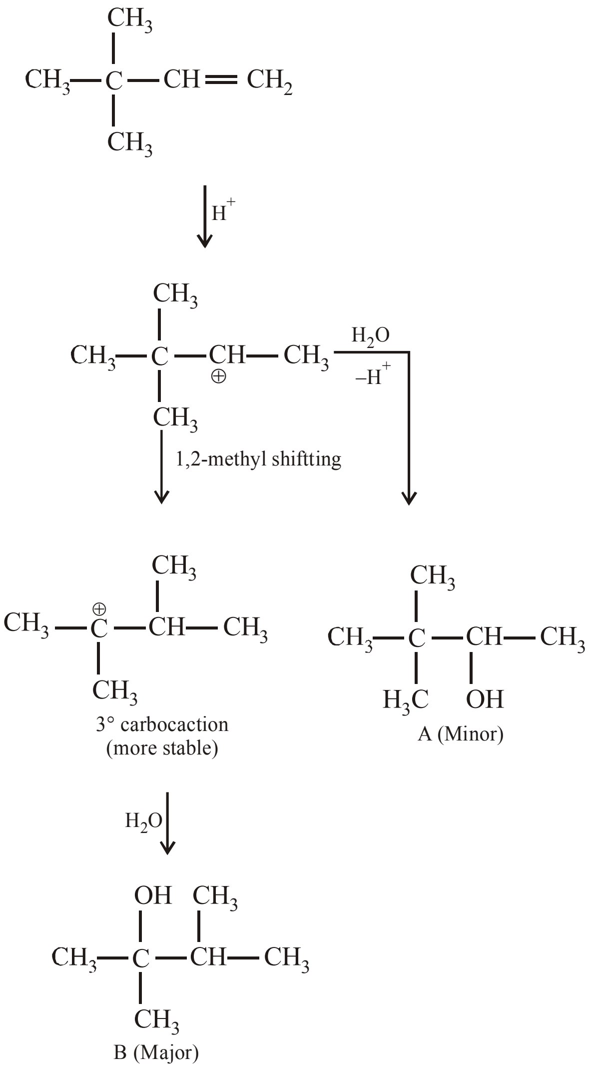
In this case dehydration is governed by Saytezeff's rule according to which hydrogen is preferentially eliminated from the carbon atom with fewer number of hydrogen atoms i.e., poor becomes poorer. Thus, 2 methyl butene-2 is the major product.



$$\underset{(A)}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3} \xrightarrow[\text{in absence of peroxide}]{\text{HBr, dark}} \underset{\text{(Minor)}}{(CH_3)_2-CH-\underset{Br}{\underset{|}{CH}}-CH_3} + \underset{\text{(Major)}}{CH_3-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_2-CH_3}$$

This reaction is governed by Markownikoff's rule according to which when an unsymmetrical reagent e.g. HBr adds to an unsymmetrical alkene, then the negative part of the reagent is added to that carbon atom of the double bond which bears the least number of hydrogen atom. Thus, in above case. 2-methyl 2-bromo butane will be the major product.

10. (a)



$$CH_3-C(CH_3)_2-CH=CH_2 \xrightarrow{H^+} CH_3-C(CH_3)_2-\overset{\oplus}{C}H-CH_3$$

11. (a) Acetylene reacts with the other three as:

$$CH\equiv CNa \xleftarrow[\text{liq. } NH_3]{Na} CH\equiv CH \xrightarrow{+HCl} \begin{matrix}CH_2\\ \|\\ CHCl\end{matrix}$$

$$\begin{matrix}CH_2\\ \|\\ CHCl\end{matrix} \xrightarrow{+HCl} \begin{matrix}CH_3\\ |\\ CHCl_2\end{matrix}$$

$$CH\equiv CH \xrightarrow{[AgNO_3+NH_4OH]} \underset{\text{white ppt.}}{AgC\equiv CAg} + NH_4NO_3$$

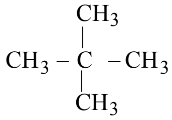
12.(c)

$$CH\equiv CH \xrightarrow{+HOCl} \begin{matrix}CHOH\\ \|\\ CHCl\end{matrix}$$

$$\xrightarrow{+HOCl} \begin{bmatrix}CH(OH)_2\\ |\\ CHCl_2\end{bmatrix} \xrightarrow{-H_2O} \begin{matrix}CHO\\ |\\ CHCl_2\end{matrix}$$

dichloroacetaldehyde

13. (c) In neopentane all the H atoms are same (1°).



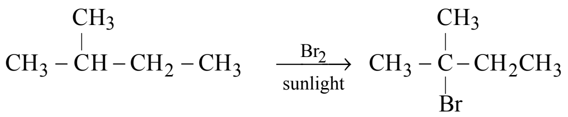
$$CH_3-C(CH_3)_2-CH_3$$

14. (c) Butene - 1 $\xrightarrow{H_2/Pd}$ Butane

15. (d) Bpt. follows the order

Alkynes > Alkenes > Alkanes (Straight chain) > Alkanes (branched chain) of comparable molecular weights.

16. (c)

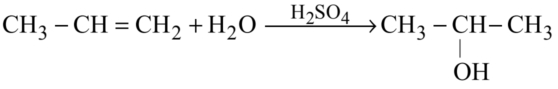


$$CH_3-CH(CH_3)-CH_2-CH_3 \xrightarrow[\text{sunlight}]{Br_2} CH_3-CBr(CH_3)-CH_2CH_3$$

2–bromo–2–methyl butane

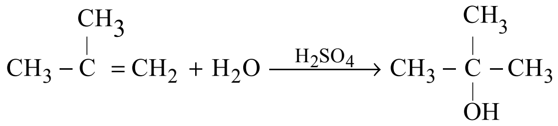
Ease of replacement of H-atom 3° > 2° > 1°.

17. (c)



$$CH_3-CH=CH_2+H_2O \xrightarrow{H_2SO_4} CH_3-CH(OH)-CH_3$$

2° alcohol

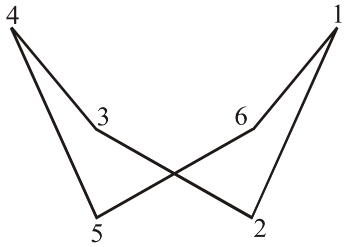


$$CH_3-C(CH_3)=CH_2+H_2O \xrightarrow{H_2SO_4} CH_3-C(CH_3)(OH)-CH_3$$

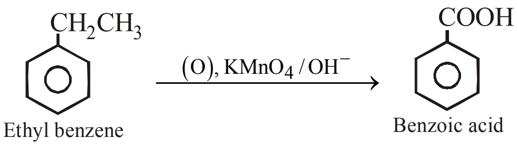
3° alcohol

Addition follows Markownikoff's rule.

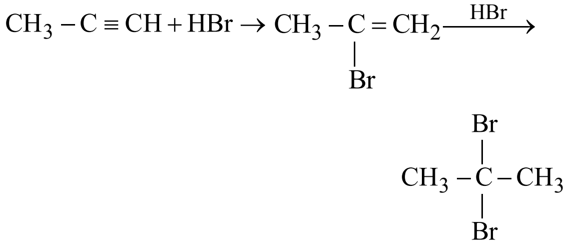
18. (b) Chiral conformation will not have plane of symmetry. Since twist boat does not have plane of symmetry it is chiral.



19. (d) When alkyl benzene are oxidised with alkaline $KMnO_4$, (strong oxidising agent) the entire alkyl group is oxidised to –COOH group regardless of length of side chain.



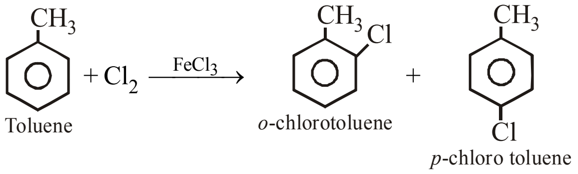
20. (b) The reaction follows Markownikov's rule which states that when unsymmetrical reagent adds across unsymmetrical double or triple bond the negative part adds to carbon atom having lesser number of hydrogen atoms.

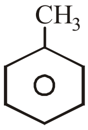


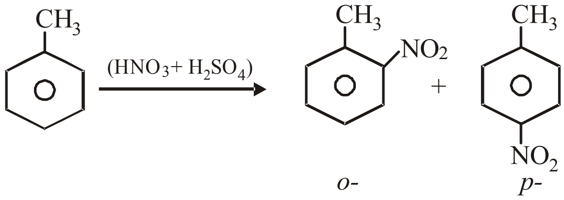
$$CH_3-C\equiv CH+HBr \rightarrow CH_3-CBr=CH_2 \xrightarrow{HBr} CH_3-CBr_2-CH_3$$

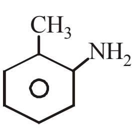
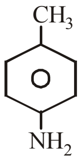
2, 2-dibromopropane

21. (d) $FeCl_3$ is Lewis acid. In presence of $FeCl_3$ *o*- and *p*-chlorotoluene is formed.



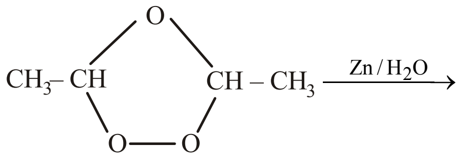
22. (a) Toluene () contains $-CH_3$ group which is *o-, p-* directing group so on nitration of toluene the $-NO_2$ group will occupy *o-, p-* positions.



on reduction with Sn/HCl they will form corresponding anilines in which $-NO_2$ group changes to $-NH_2$. The mixture now contains  and . These anilines when diazotized and then treated with CuBr forms *o-, p-* bromotoluenes.

23. (d) Completing the sequence of given reactions,

$$CH_3-CH=CH-CH_3 \xrightarrow{O_3}$$



'A'
(ozonide)

$$\underset{'B'}{2CH_3CHO} + H_2O + ZnO$$

Thus 'B' is CH_3CHO
Hence (d) is correct answer.

24. (b) Alkynes having terminal $-C \equiv H$ react with Na in liquid ammonia to yield H_2 gas. $CH_3CH_2C \equiv CH$ can react with Na in liquid NH_3 so the correct answer is (b).

$$CH_3CH_2C \equiv CH \xrightarrow[\text{liquid } NH_3]{\text{Na in}}$$

$$CH_3CH_2C \equiv C^-Na^+ + \frac{1}{2}H_2(g)$$

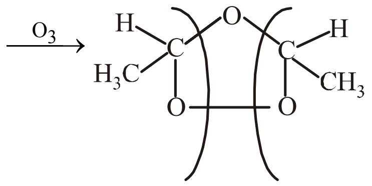
25. (d) Writing the reaction we get

$$CH_3MgX + CH_3-C \equiv C-H \longrightarrow$$
$$CH_3-C \equiv CMgX + CH_4(g)$$

So we find that CH_4 is produced in this reaction.

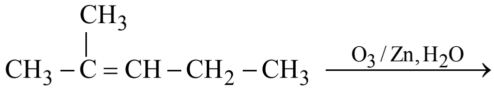
26. (c) The given molecular formula suggests that the aldehyde formed will be acetaldehyde hence the alkene will be

$$\underset{\text{2–butene}}{CH_3CH=CHCH_3}$$



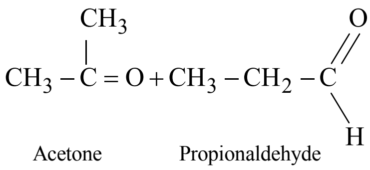
$$\xrightarrow{Zn/H_2O} 2CH_3CHO$$

27. (c) From the products formed it is clear that the compound has 5 carbon atoms with a double bond and methyl group on 2^nd^ carbon atom.



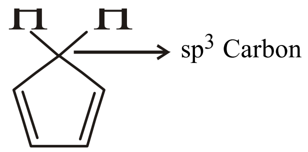
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-CH_3 \xrightarrow{O_3/Zn,H_2O}$$

(2–Methyl–2–pentene)
(A)



$$\underset{\text{Acetone}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=O} + \underset{\text{Propionaldehyde}}{CH_3-CH_2-CHO}$$

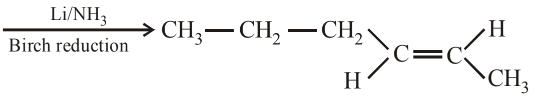
Acetone Propionaldehyde

28. (d) 

Cyclopentadiene is non aromatic, as it has sp^3 carbon in the ring.

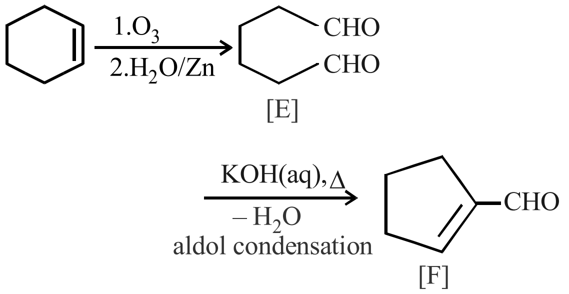
29. (b) Anti addition of hydrogen atoms to the triple bond occurs when alkynes are reduced with sodium (or lithium) metal in ammonia, ethylamine, or alcohol at low temperature. This reaction called, a dissolving metal reduction, produces an (E)- or *trans*-alkene. Sodium in liq. NH_3 is used as a source of electrons in the reduction of an alkyne to a *trans* alkene.

$$\underset{\text{2-Hexyne}}{CH_3-CH_2-CH_2-C\equiv C-CH_3}$$



Trans-2-Hexene

30. (a)



31. (d) Only (d) can form 3-Octyne

$$CH_3CH_2C\equiv CH \xrightarrow[-NH_3]{NaNH_2} CH_3CH_2C\equiv C^-Na^+$$

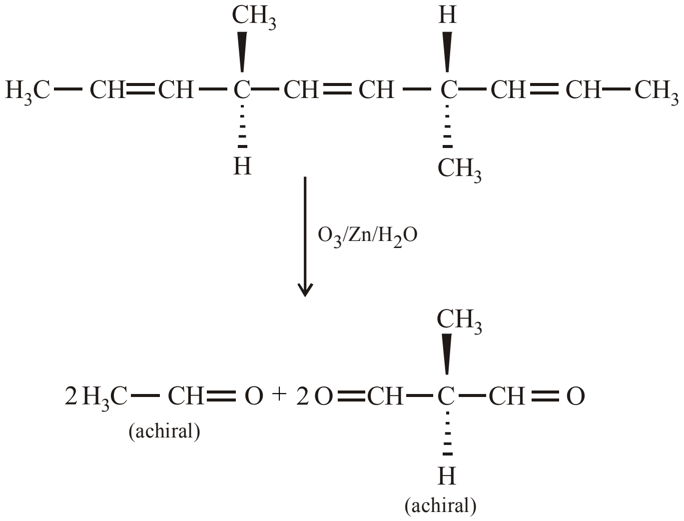
$$\xrightarrow[(S_N2)]{CH_3CH_2CH_2CH_2Br}$$

$$CH_3CH_2C\equiv CCH_2CH_2CH_2CH_3 + NaBr$$

32. (c) $C-C$ bond energy $= 348$ kJ/mol $= \frac{348}{4.2}$ kcal/mol

$= 82.85$ kcal/mol ≈ 100 kcal/mol.

33. (a)



EXERCISE 4

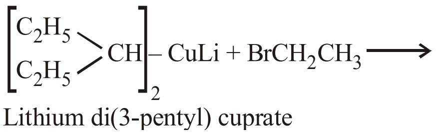
1. (c)

2. (d) $C_2H_5MgBr + DOD \rightarrow C_2H_5D + MgBr(OD)$

3. (a) $(CH_3)_3CMgCl + DOD \rightarrow (CH_3)_3CD + MgCl(OD)$

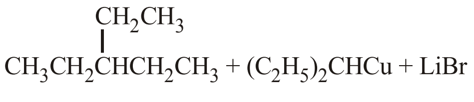
4. (c)

5. (a)



$$\left[\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!CH\right]_2\!-CuLi + BrCH_2CH_3 \longrightarrow$$

Lithium di(3-pentyl) cuprate



$$CH_3CH_2\overset{\displaystyle CH_2CH_3}{\overset{|}{C}}HCH_2CH_3 + (C_2H_5)_2CHCu + LiBr$$

3-Ethylpentane

6. (d)

7. (c)

8. (b)

9. (c) $CH_2BrCHBrCH_3 \xrightarrow[ii)\ C_2H_5Br]{i)\ xNaNH_2}$ Pentyne (No. of C atoms=5)

The reaction can be summed up as below

$$\underset{1,2-\text{Dibromopropane}}{CH_2BrCHBrCH_3} \xrightarrow{2NaNH_2} CH\equiv CCH_3 \xrightarrow{NaNH_2}$$

$$NaC\equiv CCH_3 \xrightarrow{BrCH_2CH_3} \underset{\text{Pentyne}-2}{CH_3CH_2C\equiv CCH_3}$$

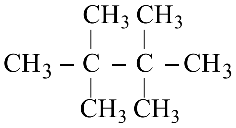
10. (b)

11. (c) Reactivity of H-atoms depends upon the stability of free radicals (3° > 2° > 1°) produced by them

12. (a) $\underset{\text{Chlorine molecule}}{Cl:Cl} \xrightarrow{hv} \underset{\text{Chlorine atoms or chlorine free radicals}}{Cl. + Cl.}$ (chain-initiation step)

13. (b) Since $Br^\bullet$ is less reactive but more selective, therefore the most stable 3° free radical will be the major product

14. (d) Since the hydrocarbon C_8H_{18} gives only one monochloroderivative, its all 18 hydrogen atoms are equivalent, which is possible only in case of 2,2,3,3-tetramethylbutane



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

15. (d) Option (d) has the lowest number of carbon atoms

16. (a)

17. (a) See the order of stability of substituted alkenes. Lesser the stability more is the reactivity.

18. (a)

19. (a) Reaction of chlorine on ethene is an electrophilic addition and involves the formation of carbocation which is $CH_2ClCH_2^+$ which may be attacked by Cl^- (from Cl_2) or Br^- (from KBr) forming $ClCH_2CH_2Cl$ and $ClCH_2CH_2Br$ respectively

20. (a) Same as above

21. (b) Peroxide effect (where free-radicals are formed) is observed only in addition of HBr ; addition of HCl is an ionic reaction and thus $CH_3{}^+CHCH_3$ (2° carbocation) is formed as an intermediate.

22. (c) The reaction of HCl with carbon radical in case of HCl, and addition of iodine radical to double bond in case of HI are endothermic steps

23. (a) Same as above

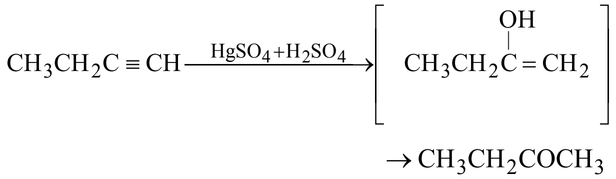
$CH_2=CH_2 < RCH=CHR < R_2C=CHR < R_2C=CR_2$

(no+ I group) (Two +I groups) (3 + I groups) (4 + I groups)

24. (d) Since O is more electronegative than Br, therefore heterolytic fission of HOBr gives HO^- & Br^+ ions

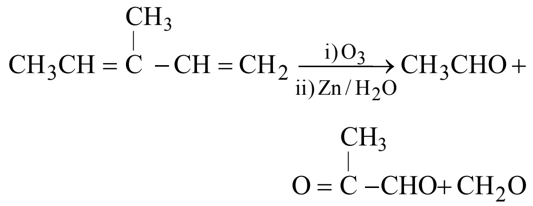
25. (b)

26. (a) Oxymercuration leads to hydration in Markovnikov's manner



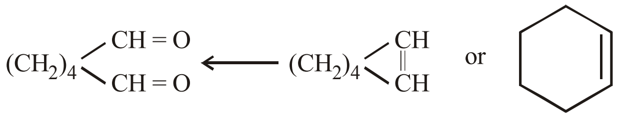
$$CH_3CH_2C\equiv CH \xrightarrow{HgSO_4+H_2SO_4} \left[CH_3CH_2\overset{OH}{\overset{|}{C}}=CH_2 \right] \rightarrow CH_3CH_2COCH_3$$

27. (c)



$$CH_3CH=\overset{CH_3}{\overset{|}{C}}-CH=CH_2 \xrightarrow[ii)\,Zn/H_2O]{i)\,O_3} CH_3CHO+ O=\overset{CH_3}{\overset{|}{C}}-CHO+CH_2O$$

28. (c) Since the alkene on ozonolysis gives a single compound, having two aldehydic groups, it must be cyclic



Cyclohexene

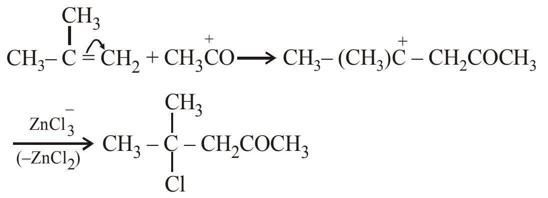
29. (a) 8g Br_2 react with 2.8g of alkene

∴ 80g Br_2 react with 28g alkene

Thus the molecular wt. of alkene is 28 which indicates C_2H_4

30. (a) **31. (d)** **32. (b)** 33. (b)

34. (c) $$CH_3COCl+ZnCl_2 \rightarrow \left[\underbrace{CH_3-\overset{+}{C}=\ddot{O} \leftrightarrow CH_3-C\equiv O^+}_{\text{Acylium ion}}\right]+ZnCl_3^-$$



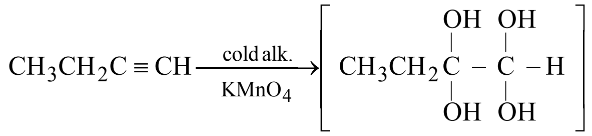
$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2+CH_3\overset{+}{C}O \longrightarrow CH_3-(CH_3)\overset{+}{C}-CH_2COCH_3 \xrightarrow[(-ZnCl_2)]{ZnCl_3^-} CH_3-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2COCH_3$$

35. (a)

36. (a) $$CH\equiv CH \xrightarrow{CH_3COOH} CH_2=CHOCOCH_3 \xrightarrow{CH_3COOH} CH_3CH(OCOCH_3)_2$$

37. (d) **38. (d)** **39. (a)**

40. (c)



$$CH_3CH_2C\equiv CH \xrightarrow[KMnO_4]{cold\ alk.} \left[CH_3CH_2\underset{OH}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-H\right]$$

$$\rightarrow CH_3CH_2COCHO \xrightarrow{oxidation} CH_3CH_2COOH+CO_2$$

41. (b) Since both gases decolourise $KMnO_4$ solution, both must be unsaturated, i.e. alkene or alkyne (option b or d). However, only one of them gives a white precipitate with ammonical $AgNO_3$ solution, it must be terminal alkyne and thus the other should be either a non-terminal alkyne or an alkene. The datas coincide with the option b

42. (c) Since the compound X(C_5H_8) reacts with ammonical $AgNO_3$ to give a white precipitate, it must be a terminal alkyne, i.e. it should have $-C\equiv CH$ grouping. Further, since X gives $(CH_3)_2CHCOOH$ on oxidation, X must have $(CH_3)_2CHC\equiv C-$ group. Thus the compound X is $(CH_3)_2CHC\equiv CH$

43. (c) Similar to that of above question

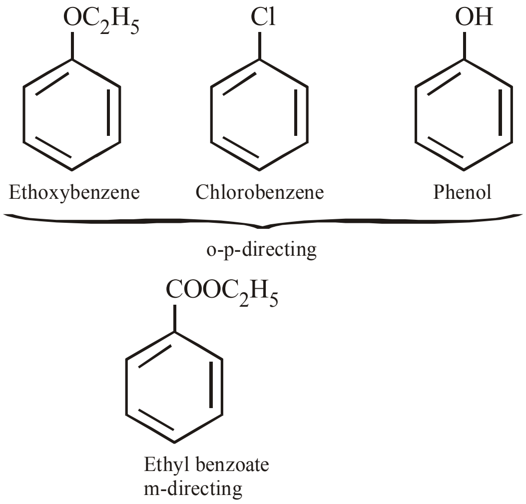
$$CO_2+(CH_3)_3C-COOH \xleftarrow[KMnO_4]{alk.} (CH_3)_3C-C\equiv CH$$

$$\xrightarrow{[Ag(NH_3)_2]^+} \underset{\text{(white ppt.)}}{(CH_3)_3C-C\equiv CAg}$$

44. (d) p-Dichlorobenzene, being symmetrical, fits closely in the crystal lattice and hence will have the highest melting point

45. (c)

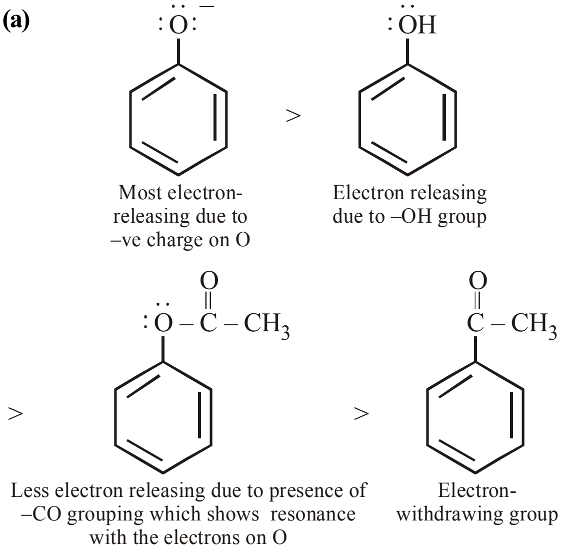
46. (c)



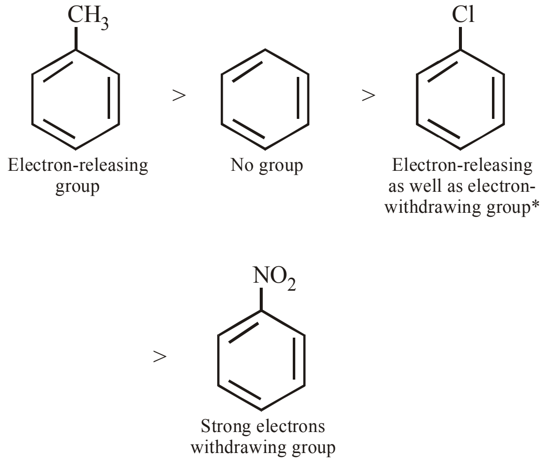
47. (c) Due to strong –R effect, –COOR is deactivating group, while all others are activating groups. Recall that all m-directing groups are deactivating groups

48. (d)

49. (a)



50. (c)



* In C_6H_5Cl, –Cl exerts electron-releasing effect due to +R effect, but simultaneously it also exerts –I effect, the result is that the molecule is deactivated due to –I effect but undergoes o, p-substitution due to powerful +R effect

51. (c)

52. (a) Determine the empirical formula of the two compounds

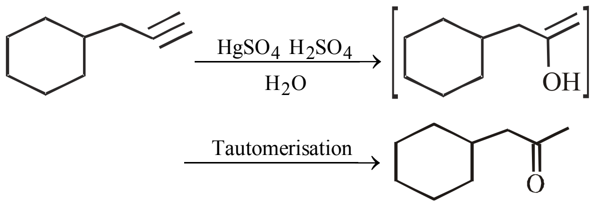
$$C : H = \left(\frac{12}{13}\times 100\right) : \left(\frac{1}{13}\times 100\right) = 92.3 : 7.7$$

$$= \frac{92.3}{12} : \frac{7.7}{1} = 7.7 : 7.7 = 1 : 1$$

∴ The empirical formula of the two compounds is CH. Thus the molecular formula of A and B will be the simple multiple of CH, i.e. C_2H_2, C_3H_3, C_4H_4, C_6H_6, etc. Thus options (c) and (d) are discarded. Further since A decolourises bromine water and B does not, A and B should be C_2H_2 (acetylene) and C_6H_6 (benzene) respectively.

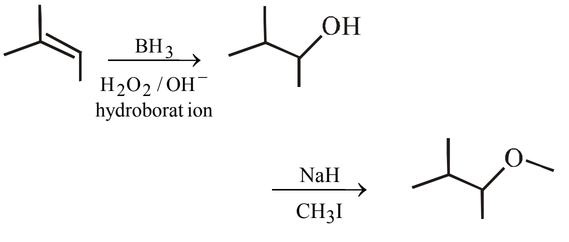
53. (d) The reaction is hydroboration which is addition of H_2O to alkene see anti to Makownikoff's's rule

54. (b)

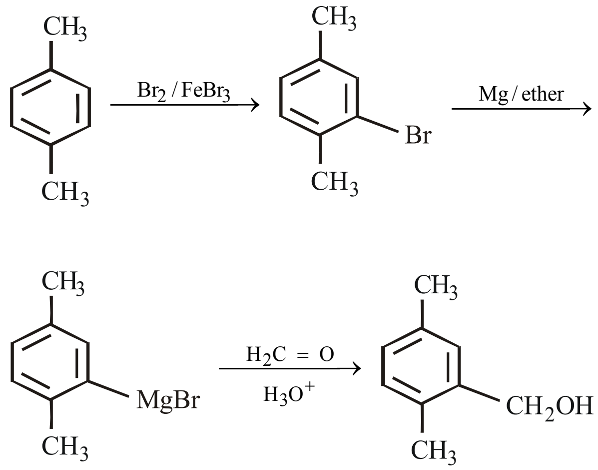


55. (a) In $H_2C = C = CH_2$ hybridisation of C atoms is sp^2 and sp. The molecule is monoplanar but H–atoms lie in different planes. See allene structure.

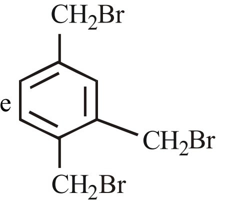
56. (d)



57. (b)



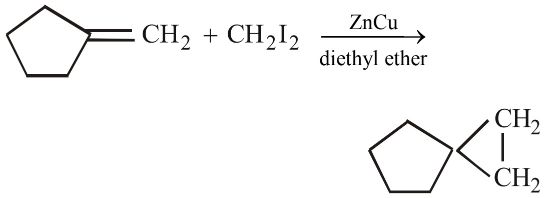
Method (1) will give



which is allylic bromination.

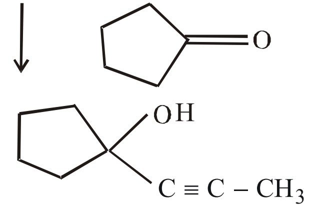
58. (a) The reaction results in the formation of one isomer, hence it is stereospecific reaction.

59. (a)

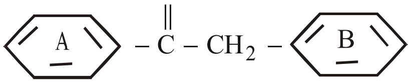


60. (d) $H_3C - C \equiv C \boxed{-H + CH_3CH_2} MgCl \longrightarrow$

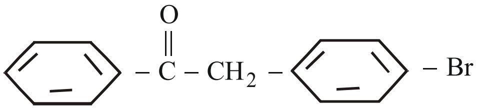
$H_3C - C \equiv C{-}MgCl + CH_3CH_3$



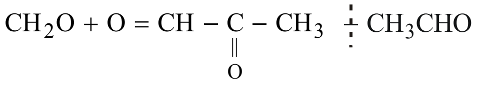
61. (a)



The ring B has o/p directing and (A) has m-directing group. Hence the product will be



62. (c) $CH_2 \vdots CH - C(CH_3) \vdots CH - CH_3 \xrightarrow[Zn/H_2O]{O_3}$



$CH_2O + O = CH - \underset{\underset{O}{\|}}{C} - CH_3 \vdots CH_3CHO$

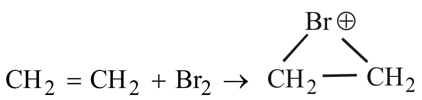
For solving such question remove the doubles bonds and join the carbons to oxygen by double bonds.

63. (c) $\overset{\bullet}{Cl} + CH_4 \rightarrow CH_3Cl + \overset{\bullet}{H}$ is not mechanistic step.

64. (a) Only Lindlar's catalyst converts alkyne to alkene (cis addition) and alkenes with Baeyer's reagent give cis glycols.

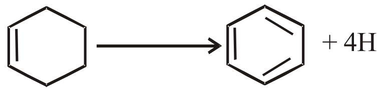
65. (b) $HC \equiv C - CH_2 - CH_2NH_2$ it contains three active hydrogen atoms (one attached to sp hybridised C-atom and two attached to N). Hence Et.MgBr will give three moles of C_2H_6 .

66. (c)



$CH_2 = CH_2 + Br_2 \rightarrow \underset{CH_2 — CH_2}{\overset{Br^{\oplus}}{/\ \backslash}}$

67. (a) Two moles of alkene is reduced thus X must be



which give 4H atoms needed for alkene.

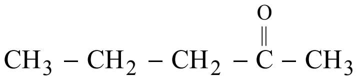
68. (a) The given reaction is Birch reduction.

69. (a) Bromination in presence of light leads to side chain substitution. For nuclear substitution we require halogen carrier.

70. (b) I and II bear mirror image relationship, hence are enantiomers.

71. (a) Peracids give epoxides (alkene oxide) with alkene. In (b), (c), and (d) the products are wrong.

72. (c) In the reactions X is



$CH_3 - CH_2 - CH_2 - \overset{\overset{O}{\|}}{C} - CH_3$

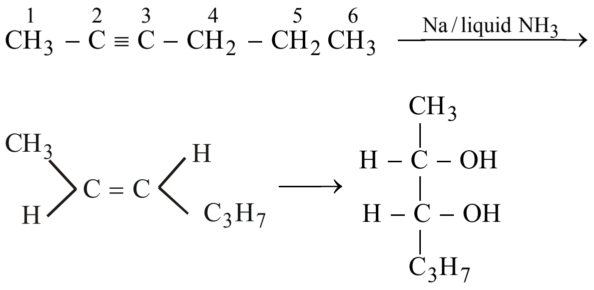
and Y is $CH_3CH_2CH_2CH_2CHO$ X will give +ve iodoform test and Y will give +ve Silver mirror test.

73. (c) Both (a) and (b) are correct. Wet CH_3COOH gives cis addition and dry CH_3COOH gives trans addition products.

74. (c) Trans is more stable, cis is less stable. Hence only (c) is correct.

75. (c) Peracids gives trans hydroxylated products with alkenes.76. (d) Side chain substitution followed by Wurtz reaction

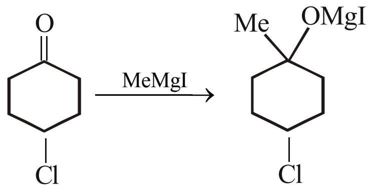
77. (a)

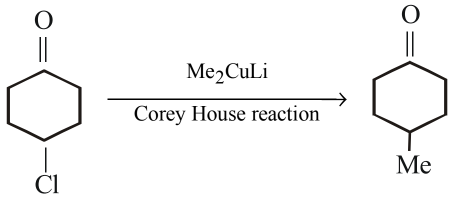


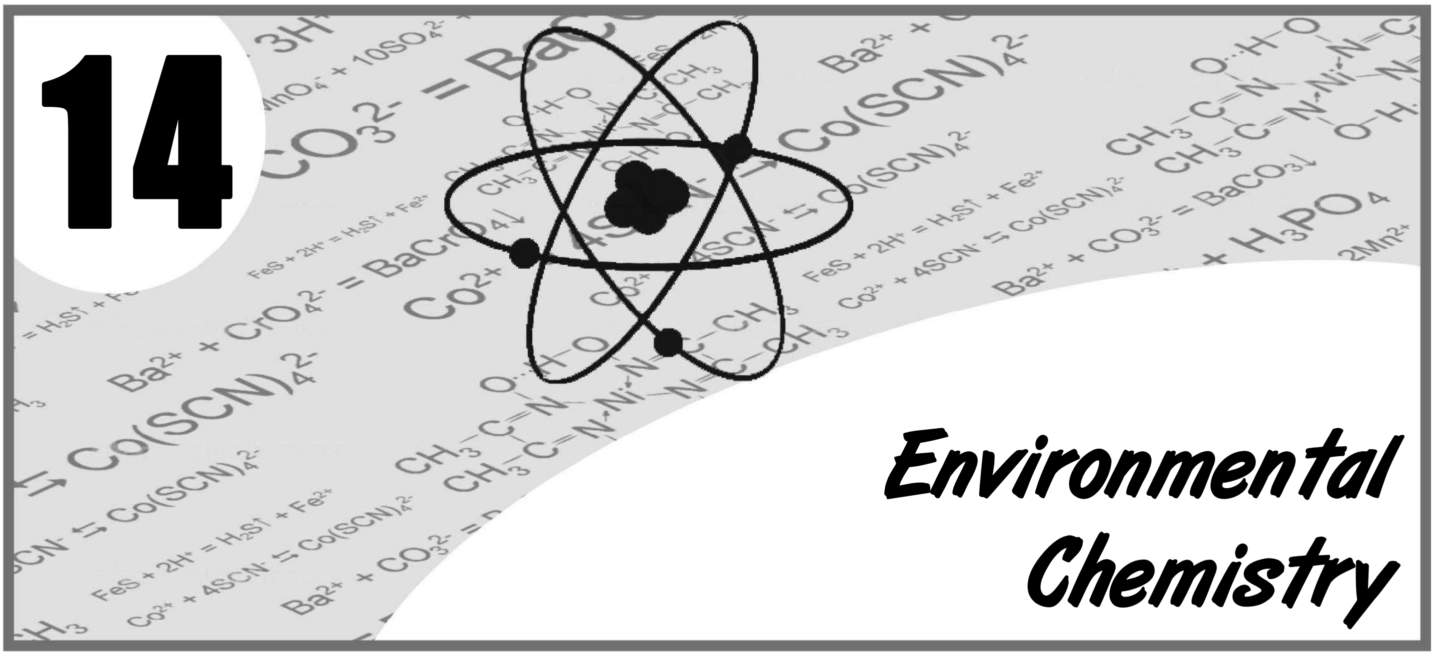
$\overset{1}{CH_3} - \overset{2}{C} \equiv \overset{3}{C} - \overset{4}{CH_2} - \overset{5}{CH_2}\,\overset{6}{CH_3} \xrightarrow{Na/liquid\ NH_3}$

Trans addition Erythroracemic

78. (b)







14

Environmental Chemistry

POLLUTION

Pollutant :- Any material affecting the life is known as pollutant and the phenomenon is known as pollution. The pollutants may be inorganic, biological or radiological in nature.

(i) Primary pollutants : These are emitted directly from the sources. eg. inorganic gases such as H_2S, SO_2, CO, NO, HF, NH_3 radioactive substancs or particulates such as smoke, ash, dust, fumes.

(ii) Secondary pollutants : These are formed in the atmosphere by chemical interactions among primary polluntants eg. SO_3, NO_2, CH_4, aldehydes, ketones, nitrates, sulphates, phenols.

(iii) Bio-degradable pollutants : These are domestic wastes which are rapidly decomposed by micro-organisms.

(iv) Non-degradable pollutants : These include chemicals, mercuric salts, lead compounds, pesticides etc.

(v) Natural pollution : It is caused by radioactive substances, volcanic eruptions, forests and mines fires, floods etc.

(vi) Artificial pollution : It is caused by industries, thermal plants, automobile exhausts, sewage etc.

ENVIRONMENT :

The conditions existing around animal or human life. It is further classified as

(a) Atmosphere :- The gaseous envelop surrounding the earth.

- **(i) Stratosphere :** The layer of the earth's atmosphere above the troposphere and below the mesosphere.
- **(ii) Troposphere :** The lowest region of the atmosphere extending from earth's surface to the lower boundary of the stratosphere. It contains water vapour and is greatly affected by air pollution.
- **(iii) Thermosphere :** The upper region of the atmosphere above the mesosphere. It is the hottest region (temp upto 1200ºC).
- **(iv) Mesosphere :** The region of the earth's atmosphere above the stratosphere and below the thermosphere. It is the coldest region (temp. –2 to –92ºC) of atmosphere.
- **(v) Exosphere :** The uppermost region of atmosphere. It contains atomic and ionic O_2, H_2 and He.

(b) Hydrosphere :- The aqueous envelop of the earth eg. oceans, lakes etc.

(c) Lithosphere :- The solid rocky portion of the earth.

(d) Biosphere :- The biological envelop which supports the life.

AIR POLLUTION :

(I) Major air pollutants: The major air pollutants are following:-

(a) *Carbon monoxide* (CO) :- It is produced by incomplete combustion of gasoline in motor vehicles, wood, coal, inceneration and forest fires.

It is treacherous and deadly poisonous gas. It induces headache, visual difficulty coma and death. It blocks the normal transport of oxygen from the lungs to other parts of the body.

(b) *Sulphur dioxide* (SO_2) :- It is produced by petrol combustion, coal combustion, petrol refining and smelting operations.

It hinders the movement of air in and out of lungs. It is particularly poisonous to trees causing chlorosis and dwarfing. In presence of air it is oxidised to SO_3 which is also irritant.

$$2SO_2 + O_2 \text{ (air)} \longrightarrow 2SO_3$$

In presence of moisture SO_3 is converted into highly corrosive sulphuric acid.

$$SO_3 + H_2O \text{ (moisture)} \longrightarrow H_2SO_4$$

It attacks marble, limestone, vegetation, paper and textiles and injurious to human beings.

(c) ***Oxides of nitrogen* :-** NO_2 and NO

(Source - combustion of coal, gasoline, natural gas, petroleum refining, chemical plants manufacturing explosives and fertilizers, tobacco smoke.

Breathing NO_2 causes chlorosis to plants and chronic lung conditions leading to death. NO_2 reacts with moisture to form acids.

$$2\,NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

$$3\,HNO_2 \longrightarrow 2\,NO + HNO_3 + H_2O$$

(d) ***Smoke, dust* :-**

Sources foundries, cement works, iron and steel works, gas works, power generating stations.

(e) ***Ammonia*** **:** Ammonia works

(f) ***Chlorine and hydrogen chloride*** **:** Chlorine works

(g) ***Chlorinated hydrocarbons*** **:** Dry cleaning works

(h) ***Mercaptans*** **:** Oil refineries, coke ovens

(i) ***Zn and Cd*** **:** Zinc industries

(j) ***Freon*** **:** Refrigeration works.

(II) **Photochemical pollutants :-** The nitrogen dioxide by absorbing sunlight in blue and U. V. region decomposes into nitric oxide and atomic oxygen followed by a series of other reactions producing O_3 formaldehyde, acrolein and peroxyacylnitrates.

Ozone causes bronchial irritation even at 1 ppm level. Ozone affects tobacco plants, spinach, tomato, potato etc. The photochemical pollutants are powerful eye irritants. The reactions are as follows

$$NO_2 + h\upsilon \longrightarrow NO + O, \qquad O + O_2 \longrightarrow O_3$$

$$RH + O \longrightarrow RO^{\bullet}, \qquad RO^{\bullet} + O_2 \longrightarrow RO_3^{\bullet}$$

$$RO_3^{\bullet} + RH \longrightarrow \text{Aldehydes} + \text{Ketones}$$

$$RO_3^{\bullet} + NO \longrightarrow RO_2^{\bullet} + NO_2$$

$$RO_2^{\bullet} + NO_2 \longrightarrow \text{Peroxyacylnitrate}$$

(III) **Smog :** It is a mixture of smoke (composed to tiny particles of carbon, ash and oil etc. from coal combustion) and fog in suspended droplet form. It is of two types :

(a) ***London smog or classical smog :*** It is coal smoke plus fog. The fog part is mainly SO_2 and SO_3. It has sulphuric acid aerosol. It causes bronchial irritation and acid rain. It is reducing in nature.

(b) ***Photochemical smog or Los Angeles smog :*** The oxidised hydrocarbons and ozone in presence of humidity cause photochemical smog.

Hydrocarbons + O_2, NO_2, NO, O, O_3 → Peroxides, formaldehyde, peroxyacetylnitrate (PAN), acrolein etc. It is oxidising in nature and causes irritation to eyes, lungs, nose, asthamatic attack and damage plants.

(IV) **Acid rain :-** The oxides of C, N and S present in the atmosphere, dissolve in water and produce acids and lower the pH of water to below 5.5.

$$H_2O + CO_2 \longrightarrow H_2CO_3 \rightleftharpoons 2\,H^+ + CO_3^{2-}$$

$$2\,H_2O + 2\,SO_2 + O_2 \rightarrow 2\,H_2SO_4$$

$$\rightleftharpoons 2\,H^+ + SO_4^{2-}$$

$$2\,H_2O + 4\,NO_2 + O_2 \rightarrow 4\,HNO_3 \rightleftharpoons 4H^+ + 4NO_3^-$$

The acids are toxic to vegetation, react with marble and damage buildings.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

Acids corrode water pipes and produce salts with heavy metals ions viz Cu, Pb, Hg and Al toxic in nature.

(V) **Green House effect :-** The retention of heat by the earth and atmosphere from the sun and its prevention to escape into the outer space is known as green house effect. Green house gases such as CO_2, ozone, methane, the chlorofluoro carbon compounds and water vapour form a thick cover around the earth which prevents the IR rays emitted by the earth to escape. It gradually leads to increase in temperature of atmosphere.

Consequences of green house effect

(i) Global warming would result in rise in sea level due to increased rate of melting of glaciers and floods.

(ii) Increase in infectious diseases like malaria, dengue etc.

(VI) **Ozone layer and its depletion :-** The ozone layer, existing between 20 to 35 km above the earth's surface, shield the earth from the harmful U. V. radiations from the sun. The U. V. radiations cause skin cancer, cataract of eye, and harmful to vegetation.

Depletion of ozone is caused by oxides of nitrogen

$$N_2O + h\upsilon \longrightarrow \underset{\text{reactive nitric oxide}}{NO} + N$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$O_3 + h\upsilon \longrightarrow O_2 + O$$

$$NO_2 + O \longrightarrow NO + O_2$$

$$2\,O_3 + h\upsilon \longrightarrow 3\,O_2 \text{ (Net reaction)}$$

The presence of oxides of nitrogen increase the decomposition of O_3. Depletion of ozone by chlorofluoro carbons.

$$CF_2Cl_2 + h\upsilon \longrightarrow CF_2Cl + Cl$$

$$CFCl_3 + h\upsilon \longrightarrow CFCl_2 + Cl$$

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$ClO + O \longrightarrow Cl + O_2$$

$$O_3 + O \longrightarrow 2\,O_2 \text{ (Net reaction)}$$

(VII) Control of air pollution :- It can be controlled by

1. Dissolving HCl, HF, SiF_4 in water and SO_2, Cl_2, H_2S in alkaline solution.
2. Adsorbing gas and liquids molecules over activated charcoal and silica gel.
3. Chemical reactions

$$2CuO + O_2 + 2\,SO_2 \longrightarrow 2\ CuSO_4$$

$$2\,CaCO_3 + O_2 + 2\,SO_2 \longrightarrow 2\,CaSO_4 + 2\ CO_2$$

$$4\,NO + 4\,NH_3 + O_2 \longrightarrow 2\,N_2 + 6\,H_2O$$

4. Use of precipitators to settle charge particles
5. Use of settling chambers under the action of gravity
6. Use of natural gas in place of diesel, petrol etc.

WATER POLLUTION

A. Water Pollution : The contamination of water by foreign substances which would constitute a health hazard and make it harmful for all purposes (domestic, industrial or agriculture etc.) is known as water pollution. The polluted water may have affensive odour, bad taste, unpleasant colour, murky oily etc.

B. Sources of water pollution :

(i) ***Domestic sewage :*** Discharges from kitchens, baths, lavatories etc.

(ii) ***Industrial waters :*** Wastes from manufacturing processes which includes acids, alkalies, pesticides, insecticides, metals like copper, Zinc, lead, mercury, fungicides etc.

(iii) ***Oil :*** from oil spills or washings of automobiles

(iv) ***Atomic explosion*** and processing of radioactive materials

(v) ***Suspended particles*** (organic or inorganic) viruses, bacterials algae protozoa etc.

(vi) ***Wastes from fertilizer*** plants such as phosphates, nitrates ammonia etc.

(vii) ***Clay :*** Ores, minerals, fine particles of soil.

C. Effects of impurities in water : Dissolved substances

(i) ***Hardness :*** Corrossive effect on boils, alkalinity, laxative effect

(ii) ***Fluorides :*** Motting of teeth enamel, nervous and skeleton disorders, above 1 mg/litre causes fluorosis.

(iii) ***Sulphates :*** Sulphates of Na, K, Mg cause **diarrihoea**

(iv) ***Sodium chloride :*** It imparts bad taste to water

(v) ***Iron and manganese :*** Stain fabrics, bad taste, modify colours

(vi) ***Lead :*** It damages kidney, liver, brain and central nervous system

(vii) ***Cadmium and Mercury :*** Cause kidney damage

(viii) ***Zn :*** Causes vomitting, dizziness and diarrhoea

(ix) ***Arsenic*** can cause cramps, paralysis and death

(x) ***Phosphates from fertilizers :*** They promote algae growth and reduce D.O. concentration of water. This process is known as *eutrophication.*

(xi) ***Anionic detergents*** (eg. alkyl benzene sulphonates, ABS) : They produce stable foam, stabilise colloidal impurities and inhibit oxidation of organic compounds like phenol. ABS is not bio-degradable.

(xii) ***Hydrogen sulphide :*** Acidic, rotten-egg odour and corrosive to metals.

(xiii) ***Polychlorinated biphenyls :*** They are resistant to oxidation and cause skin disorders and are carcinogenic.

(xiv) ***Acid polluted water ($pH < 3$) :*** H_2SO_4 produced by oxidation of Iron pyrites (FeS_2) harmful to life.

Suspended impurites :

(i) ***Parasitic worms :*** They cause infections

(ii) ***Bacterias :*** Cause dysentery, typhoid, cholera

(iii) ***Viruses :*** Cause entroviral infections

(iv) ***Algae :*** Cause foul odour, taste, turbidity

D. International standards for drinking water :

S.No.	*Characteristics (mg/l)*	*Acceptable limit*	*Rejection limit*
1.	pH value	7 - 8.5	6.5 - 9.5
2.	Total dissolved solids	500	1500
3.	Total hardness (as $CaCO_3$)	200	600
4.	Fluorides	1.0	1.5
5.	Chlorides	200	1000
6.	Sulphates	200	400
7.	Nitrates	45	45
8.	Magnesium	30	150
9.	Calcium	75	200
10.	Zinc	5.0	15.0
11.	Anionic detergents	0.2	1.0
12.	Iron	0.1	1.0
13.	Manganese / Copper	0.05	0.5
14.	Phenolic compounds	0.001	0.002
15.	Toxic Materials eg. As, Cd, Cr, CN^-, Pb, Se	0.05 - 0.001	0.05 - 0.001

AEROBIC AND ANAEROBIC OXIDATION :

The oxidation of organic compounds present in sewage in presence of good amount of dissolved or free oxygen (approx. 8.5 ml/l) by aerobic bacterials is called *aerobic oxidation*. When dissolved or free oxygen is below a certain value the sewage is called *stale* anaerobic bacterias bring out purification producing H_2S, NH_3, CH_4, $(NH_4)_2S$ etc. This type of oxidation is called *anaerobic* oxidation.

The optimum value of D.O. for good quality of water is 4-6 ppm (4-6 mg/l). The lower the concentration of D.O., the more polluted is the water.

BIOLOGICAL OXYGEN DEMAND (BOD) :

It is defined as the amount of free oxygen required for biological oxidation of the organic matter by aerobic conditions at 20°C for a period of five days. Its unit is mg/l or ppm. An average sewage has BOD of 100 to 150 mg/l.

CHEMICAL OXYGEN DEMAND (COD) :

It is a measure of all types of oxidisable impurities (biologically oxidisable and biologically inert organic matter such as cellulose) present in the sewage. COD values are higher than BOD values.

COD DETERMINATION :

A known volume of sample is refluxed with known volume of standard $K_2Cr_2O_7$ + dil. H_2SO_4 in presence of Ag_2SO_4 (catalyst) for 1½ hours. The unreacted $K_2Cr_2O_7$ is then titrated against $FeSO_4.(NH_4)_2SO_4.6H_2O$ solution. The oxygen equivalent of $K_2Cr_2O_7$ consumed is taken as a measure of COD.

1 ml. of 1 N $K_2Cr_2O_7 \equiv 0.008$ g oxygen

SOIL OR LAND POLLUTION :

The addition of substances in an indefinite proportion changing the productivity of the soil is known as soil or land pollution.

Sources of soil pollution :

- **(i)** ***Agricultural pollutants :*** Chemicals like pesticides, fertilizers, fumigants, insecticides, herbicides, fungicides.
- **(ii)** ***Domestic refuge*** and industrial wastes
- **(iii)** ***Radioactive wastes*** from research centres, and hospitals
- **(iv)** ***Soil conditioners*** containing toxic metals like Hg, Pb, As, Cd etc.
- **(v)** ***Farm wastes*** from poultries, dairies and piggery forms
- **(vi)** ***Improper disposal*** of human and animal excreta.
- **(vii)** ***Pollutants*** present in air from chemical works

CONTROL OF WATER POLLUTION :

The water pollution can be reduced by following techniques

- **(i)** **Recycling of waste water** : by aeration and use of trickling filter
- **(ii)** **Use of chemicals :** Effective filtration and chlorination
- **(iii)** **Special techniques** : Such as adsorption, ion-exchangers, reverse osomosis, electrodialysis etc.
- **(iv)** **Waste-water reclamation :** Sewage water can be directly used for irrigation and fish farms. Since it contains N, P and K.

SEWAGE TREATMENT :

The artificial treatment is called sewarage and involves the following steps :

- **(i)** **Preliminary process :** Passing sewage through screens to remove large suspended matter and then through mesh screens to remove solids, gravels, silt etc.
- **(ii)** ***Settling process (sedimentation) :*** The residual water when allowed to stand in tanks, the oils and grease float on the surface and skimmed off and solids settle down. The colloidal meterial is removed by adding alum, ferrous sulphate etc. and we get *primary sludge*.
- **(iii)** ***Secondary treatment or Biological treatment :*** It is aerobic chemical oxidation or aeration which converts carbon of the organic matter to CO_2, nitrogen into NH_3 and finally into nitrites and nitrates, dissolved bases form salts such as NH_4NO_2, NH_4NO_3 and $Ca(NO_3)_2$ etc. and *secondary* sludge is obtained.

  The primary and secondary sludge (combined) is subjected to anaerobic digestion to CO_2 and CH_4

$$2[CH_2O] \longrightarrow CO_2 + CH_4$$

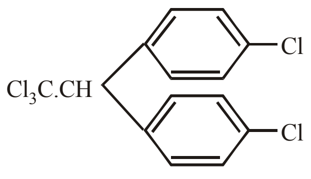
- **(iv)** ***Tertiary treatment :*** It is treatment of waste water with lime for removal of phosphate which is coagulated by adding alum and ferric chloride and removed by filtration. Water is disinfected by adding chlorine.

  Secondarty sludge forms a good fertilizer for soil as it contains nitrogen and phosphorous compounds.

PESTICIDES :

The chemical substances used to kill or stop the growth of unwanted organisms are called pesticides. They are further classified as

- **(a)** ***Insecticides :*** They are used to kill insects. The most common insecticides are

(i) 

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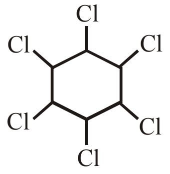
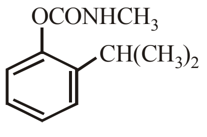
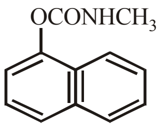
(ii) 

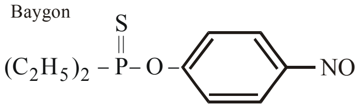
BHC, 666, gamexane

(iii) 

Baygon

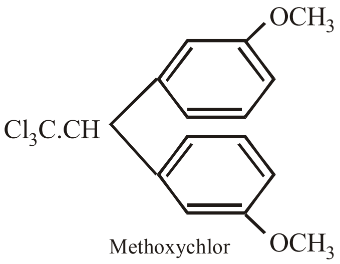
(iv) 

Sevin, Carbaryl

(v) 

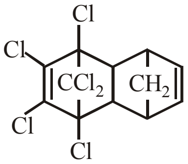
Parathion

(vi)



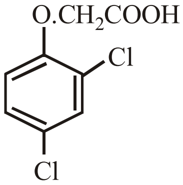
Methoxychlor

(vii) Aldrin



(b) ***Herbicides :*** They are used to kill weeds e.g.

(i)



2,4-dichlorophenory acetic acid (2,4D)

(ii) Triazines

(iii) $NaClO_3$ Sodium chlorate

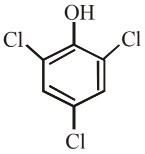
(iv) Na_3AsO_3 Sodium arsenite

The (iii) and (iv) are not used now a days.

(c)***Fungicides :*** They are used to stop or kill fungus e.g.

(i) $CuSO_4$ copper sulphate

(ii)



2,4,6-trichlorophenol

(d) ***Rodenticides :*** They are used to kill rodents e.g.

(i) Zn_3P_2 Zincphosphide

(ii) $Tl.SO_4$ Thalium sulphate

(iii) $ClCH_2COONa$ Sodium monochloroacetate

Exercise-1 | NCERT BASED QUESTIONS

Very Short/ Short Answer Questions

1. In what regions of the atmosphere, the temperature increases with altitude and in which regions it decreases?

2. What is the most important sink of CO pollutant?

3. What is marine pollution?

4. Why COD is preferred over BOD ?

5. What should be the tolerable limit of fluoride ions in drinking water? What happens if it is higher than10 ppm ?

6. Name any four methods for waste management.

7. Write the name of gas produced in Mathura refineries which can damage the great historical monument “Taj Mahal”?

8. What are 'asbestosis' and 'silicosis'?

9. (i) Why there is ozone depletion mainly over Antarctica?

(ii) In which season the depletion of ozone on Antarctica takes place and when is it replenished?

10. Depending upon the nature of pollutants, how can the pollution be classified into different types ?

11. How plant nutrients and pesticides acts as water pollutants?

12. Fish do not always grow in warm as well as in cold water, why?

13. On the basis of chemical reactions involved, explain how do chlorofluorocarbons cause thinning of ozone layer in stratosphere.

14. How can lead poisoning be cured?

Long Answer Questions

15. What is the strategy for control of Environmental pollution?

16. List industrial wastes which contaminate water.

Multiple Choice Questions

17. Dinitrogen and dioxygen are main constituents of air but these do not react with each other to form oxides of nitrogen because __________.

(a) the reaction is endothermic and requires very high temperature.

(b) the reaction can be initiated only in presence of a catalyst.

(c) oxides of nitrogen are unstable.

(d) N_2 and O_2 are unreactive

18. The pollutants which came directly in the air from sources are called primary pollutants. Primary pollutants are sometimes converted into secondary pollutants. Which of the following belongs to secondary air pollutants?

(a) CO

(b) Hydrocarbon

(c) Peroxyacetyl nitrate

(d) NO

19. Which of the following is not a consequence of greenhouse effect?

(a) Climatic conditions will be changed resulting in

(b) Plants in warmer climates with adequate rainfall would grow faster

(c) The incidence of infectious diseases is likely to increase

(d) Malaria will be controlled as the mosquitoes will not survive.

20. Which of the following statements is not true about classical smog?

(a) Its main components are produced by the action of sunlight on emissions of automobiles and factories.

(b) Produced in cold and humid climate.

(c) It contains compounds of reducing nature.

(d) It contains smoke fog and sulphur dioxide

21. Which of the following statements is wrong?

(a) Ozone is not responsible for green house effect.

(b) Ozone can oxidise sulphur dioxide present in the atmosphere to sulphur trioxide.

(c) Ozone hole is thinning of ozone layer present in stratosphere.

(d) Ozone is produced in upper stratosphere by the action of UV rays on oxygen.

22. Which of the following statements is correct?

(a) Ozone hole is a hole formed in stratosphere from which ozone oozes out.

(b) Ozone hole is a hole formed in the troposphere from which ozone oozes out.

(c) Ozone hole is thinning of ozone layer of stratosphere at some places.

(d) Ozone hole means vanishing of ozone layer around the earth completely.

23. Which among the following statements is *false*?

(a) Oil slick in sea water increases D.O. value.

(b) The main reason for river water pollution is industrial and domestic sewage discharge.

(c) Surface water contains a lot of organic matter mineral nutrients and radioactive materials.

(d) Oil spill in sea water causes heavy damage to fishery.

24. Sewage containing organic waste should not be disposed in water bodies because it causes major water pollution. Fishes in such a polluted water die because of

(a) large number of mosquitoes

(b) increase in the amount of dissolved oxygen

(c) decrease in the amount of dissolved oxygen in water

(d) clogging of gills by mud.

25. Which of the following practices will not come under green chemistry?
(a) If possible, making use of soap made of vegetable oils instead of using synthetic detergents.
(b) Using H_2O_2 for bleaching purpose instead of using chlorine based bleaching agents.
(c) Using bicycle for travelling small distances instead of using petrol/ diesel based vehicles.
(d) Using plastic cans for neatly storing substances.

26. Water is often treated with chlorine to
(a) remove hardness
(b) increase oxygen content
(c) kill germs
(d) remove suspended particles

Exercise-2 | CONCEPTUAL MCQs

1. The uppermost region of the atmosphere is called
(a) ionosphere (b) stratosphere
(c) troposphere (d) exosphere

2. Which of the following is the coldest region of atmosphere?
(a) thermosphere (b) mesosphere
(c) troposphere (d) stratosphere

3. The region which is greatly affected by air pollution is
(a) thermosphere (b) stratosphere
(c) troposphere (d) mesosphere

4. The region containing water vapour is
(a) thermosphere (b) stratosphere
(c) troposphere (d) mesosphere

5. In which of the following regions hydrogen and helium are found
(a) stratosphere (b) mesosphere
(c) exosphere (d) troposphere

6. The substance which is a primary pollutant?
(a) H_2SO_4 (b) CO
(c) PAN (d) Aldehydes

7. Which of the following is most abundant hydrocarbon pollutant?
(a) Butane (b) Ethane
(c) Methane (d) Propane

8. The aromatic compounds present as particulates are
(a) polycyclic aromatic hydrocarbons
(b) benzene
(c) toluene
(d) nitrobenzene

9. The biggest particulate matter is
(a) HNO_3 droplets (b) soot
(c) H_2SO_4 droplets (d) fly ash

10. Formation of London smog takes place in
(a) winter during day time
(b) summer during day time
(c) summer during morning time
(d) winter during morning time

11. Formation of photochemical smog takes place in
(a) winter during day time
(b) summer during morning time
(c) summer during day time
(d) winter during morning time

12. Which of the following statement is false?
(a) London smog is oxidising in nature
(b) Photochemical smog causes irritation in eyes
(c) London smog is a mixture of smoke and fog
(d) Photochemical smog results in the formation of PAN

13. The viable particulate among the following is
(a) fumes (b) algae
(c) smoke (d) mist

14. The non-viable particulate among the following is
(a) dust (b) bacteria
(c) moulds (d) fungi

15. Which of the following acts as a sink for CO?
(a) Plants
(b) Haemoglobin
(c) Microorganisms present in the soil
(d) Oceans

16. Which forms the part of hazy fumes of photochemical smog?
(a) SO_2 (b) Nitrogen dioxide
(c) PAN formation (d) Aldehydes

17. Depletion of ozone layer causes
(a) breast cancer (b) blood cancer
(c) lung cancer (d) skin cancer

18. The gas responsible for ozone depletion :
(a) NO and freons (b) SO_2
(c) CO_2 (d) CO

19. The reaction caused by U.V. radiations from sun produces
(a) ozone (b) carbon monoxide
(c) sulphur dioxide (d) fluorides

20. Which of the following chemical, harmful to ozone, is released by chlorofluoro carbon?

(a) Sulphur dioxide (b) Fluorine
(c) Chlorine (d) Nitrogen dioxide

21. Ozone hole refers to

(a) increase in concentration of ozone
(b) hole in ozone layer
(c) reduction in thickness of ozone layer in troposphere
(d) reduction in thickness of ozone layer in stratsophere

22. Ozone layer of stratosphere requires protection from indiscriminate use of

(a) baloons
(b) pesticides
(c) atomic explosions
(d) aerosols and high flying jets

23. Phosphate fertilizers when added to water leads to

(a) increased growth of decomposers
(b) reduced algal growth
(c) increased algal growth
(d) nutrient enrichment (eutrophication)

24. The type of pollution caused by spraying of DDT

(a) air and soil (b) air and water
(c) air (d) air, water and soil

25. Pollution in large cities can be checked only by

(a) shifting of factories out of the residential area
(b) less use of insecticides
(c) proper disposal of organic wastes, sewage and industrial effluents
(d) All the above

26. Sewage mostly constitutes

(a) non-biodegradable pollutants
(b) biodegradable pollutants
(c) effluents
(d) air pollutants

27. Chief source of soil and water pollution is

(a) mining (b) agro industry
(c) thermal power plant (d) All the above

28. Water pollution is caused by

(a) pesticides (b) fly ash
(c) auto exhausts (d) aeroplanes

29. Which causes death of fishes in water bodies polluted by sewage?

(a) Foul smell (b) Pathogens
(c) Clogging of gills by silt (d) Decrease in D.O.

30. Phosphate pollution is caused by

(a) sewage and agricultural fertilizers
(b) weathering of phosphate rocks only
(c) agricultural fertilizers only
(d) phosphate rocks and sewage

31. Sewage water is purified by

(a) aquatic plants (b) micro-oganisms
(c) light (d) fishes

32. Water is often treated with chlorine to

(a) remove hardness
(b) increase oxygen content
(c) kill germs
(d) remove suspended particles

33. Ozone is an important constituent of stratosphere because it

(a) destroys bacteria which are harmful to human life
(b) prevents the formation of smog over large cities
(c) removes poisonous gases of the atmosphere by reacting with them
(d) absorbs ultraviolet radiation which is harmful to human life

34. Which is the major air pollutant

(a) He (b) O_2
(c) CO_2 (d) CO

35. The ozone layer is present in

(a) stratosphere (b) troposphere
(c) thermosphere (d) mesosphere

36. The green house effect is caused by

(a) CO_2 (b) NO_2
(c) NO (d) CO

37. Surface water contains

(a) suspended impurity (b) salt + organic matter
(c) only salt (d) organic matter

Exercise-3 | PAST COMPETITION MCQs

1. The greenhouse effect is because of the **[CBSE-PMT 1996]**
   (a) presence of gases, which in general are strong infrared absorbers, in the atmosphere
   (b) presence of CO_2 only in the atmosphere
   (c) pressure of O_3 and CH_4 in the atmosphere
   (d) N_2O and chlorofluorohydrocarbons in the atmosphere

2. Which of the following is/are the hazardous pollutant(s) present in automobile exhaust gases? **[CBSE-PMT 1996]**
   (i) N_2 (ii) CO
   (iii) CH_4 (iv) Oxides of nitrogen
   (a) (ii) and (iii) (b) (i) and (ii)
   (c) (ii) and (iv) (d) (i) and (iii)

3. Green chemistry means such reactions which :
   (a) produce colour during reactions **[CBSE-PMT 2008]**
   (b) reduce the use and production of hazardous chemicals
   (c) are related to the depletion of ozone layer
   (d) study the reactions in plants

4. Which one of the following statement is **not** true ? **[CBSE-PMT 2011]**
   (a) pH of drinking water should be between 5.5 – 9.5.
   (b) Concentration of DO below 6 ppm is good for the growth of fish.
   (c) Clean water would have a BOD value of less than 5 ppm.
   (d) Oxides of sulphur, nitrogen and carbon are the most widespread air pollutant.

5. Which one of the following statements regarding photochemical smog is not correct? **[CBSE-PMT 2012]**
   (a) Carbon monoxide does not play any role in photochemical smog formation.
   (b) Photochemical smog is an oxidising agent in character.
   (c) Photochemical smog is formed through photochemical reaction involving solar energy.
   (d) Photochemical smog does not cause irritation in eyes and throat.

6. Frequent occurrence of water blooms in a lake indicates
   (a) nutrient deficiency **[AIEEE 2003]**
   (b) oxygen deficiency
   (c) excessive nutrient availability
   (d) absence of herbivores in the lake

7. When rain is accompanied by a thunderstorm, the collected rain water will have a pH value **[AIEEE 2003]**
   (a) slightly lower than that of rain water without thunderstorm
   (b) slightly higher than that when the thunderstorm is not there
   (c) uninfluenced by occurrence of thunderstorm
   (d) which depends upon the amount of dust in air

8. The smog is essentially caused by the presence of
   (a) Oxides of sulphur and nitrogen **[AIEEE 2004]**
   (b) O_2 and N_2
   (c) O_2 and O_3
   (d) O_3 and N_2

9. Identify the wrong statement in the following: **[AIEEE 2008]**
   (a) Chlorofluorocarbons are responsible for ozone layer depletion
   (b) Greenhouse effect is responsible for global warming
   (c) Ozone layer does not permit infrared radiation from the sun to reach the earth
   (d) Acid rain is mostly because of oxides of nitrogen and sulphur

10. Identify the incorrect statement from the following : **[AIEEE 2011RS]**
    (a) Ozone absorbs the intense ultraviolet radiation of the sun.
    (b) Depletion of ozone layer is because of its chemical reactions with chlorofluoro alkanes.
    (c) Ozone absorbs infrared radiation.
    (d) Oxides of nitrogen in the atmosphere can cause the depletion of ozone layer.

11. What is DDT among the following ? **[AIEEE 2012]**
    (a) Greenhouse gas
    (b) A fertilizer
    (c) Biodegradable pollutant
    (d) Non-biodegradable pollutant

12. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was : **[JEE M 2013]**
    (a) Methyl isocyanate (b) Methylamine
    (c) Ammonia (d) Phosgene

Exercise-4 | Applied MCQs

1. The substance which is not regarded as a pollutant?
(a) NO_2 (b) CO_2
(c) O_3 (d) Hydrocarbons

2. The greatest affinity for haemoglobin is shown by which of the following :
(a) NO (b) CO
(c) O_2 (d) CO_2

3. The substance having the largest concentration in acid rain?
(a) H_2CO_3 (b) HNO_3
(c) HCl (d) H_2SO_4

4. Which of the following is not involved in the formation of photochemical smog?
(a) Hydrocarbon (b) NO
(c) SO_2 (d) O_3

5. The statement which is not true
(a) NO_2 does not play any role in photochemical smog
(b) SO_3 is more harmful air polluntant than SO_2
(c) SO_2 dos not affect larynx (voice box)
(d) NO is more toxic to living tissues than NO_2

6. The false statement among the followings :
(a) The average residence time of NO is one month
(b) Limestone acts as a sink for SO_x
(c) SO_x can be removed from flue gases by passing through a solution of citrate ions
(d) Ammonia acts as a sink for NO_x

7. The statement which is not correct about control of particulate pollution
(a) In electrostatic precipitator, the particulates are made to acquire positive charge which are then attracted by the negative electrode and removed
(b) Gravity settling chamber removes larger particles from the air
(c) Cyclone collector removes fine particles in the diameter range 5-20 microns
(d) Wet scrubbers are used to wash away all types of particulates

8. Which of the following statements about polar stratosphere clouds (PSCs) is not correct?
(a) PSCs do not react with chlorine nitrate and HCl
(b) Type I clouds are formed at about –77ºC and contain solid $HNO_3 . 3H_2O$
(c) Type II clouds are formed at about –85ºC and contain some ice
(d) A tight whirlpool of wind called Polar Vortex is formed which surrounds Antarctica

9. Minamata disease is due to pollution of
(a) aresenic into the atmosphere
(b) organic waste into drinking water
(c) oil spill in water
(d) industrial waste mercury into fishing water

10. BOD is connected with
(a) microbes and organic matter
(b) organic matter
(c) microbes
(d) None of the above

11. Eutrophication causes reduction in
(a) dissolved oxygen (b) nutrients
(c) dissolved salts (d) All the above

12. Which among the following statements is *false*?
(a) Oil slick in sea water increases D.O. value
(b) The main reason for river water pollution is industrial and domestic sewage discharge
(c) Surface water contains a lot of organic matter mineral nutrients and radioactive materials
(d) Oil spill in sea water causes heavy damage to fishery

13. Presence of which of the following fuel gas in the exhaust fumes shows incomplete combustion of fuel?
(a) Sulphur dioxide
(b) Carbon monoxide and water vapour
(c) Carbon monoxide
(d) Nitrogen dioxide

14. Which one of the following statements about ozone and ozone layer is true?
(a) Ozone layer is beneficial to us because ozone cuts out the ultraviolet radiation of the sun
(b) The conversion of ozone to oxygen is an endothermic reaction
(c) Ozone has a triatomic linear molecule
(d) None of the above

Hints & Solutions

EXERCISE 1

1. Temperature increases in stratosphere and thermosphere, it decreases in troposphere and mesosphere.
2. Soil micro–organism.
3. Pollution of sea water due to discharge of wastes into it.
4. COD can be found in a few minutes whereas BOD requires at least 5 days.
5. 1 ppm or 1 mg dm^{-3}. Higher concentration is harmful to bones and teeth.
6. Recycling, burning incineration and sewage treatment.
7. Sulphur dioxide
8. The lung disease caused by particulates of asbestos is 'asbestosis' and that caused by silica is 'silicosis'.

14. By feeding the patient with an aqueous solution of calcium complex of EDTA.

17. **(a)** **18.** **(c)** **19.** **(d)** **20.** **(a)** **21.** **(a)**

22. **(c)** **23.** **(a)** **24.** **(c)** **25.** **(d)** **26.** **(c)**

EXERCISE 2

1. **(d)** The uppermost region of atmosphere is exosphere.

2. **(b)** The coldest region is mesosphere (temp. –27ºC to –92ºC)

3. **(c)** Air pollution greatly affect the troposphere.

4. **(c)** Troposphere contains water vapour.

5. **(c)** H_2, He and ionic oxygen are present in exosphere.

6. **(b)** CO is primary pollutant.

7. **(c)** Most abundant hydrocarbon pollutant is methane.

8. **(a)** PAH (Poly Aromatic Hydrocarbon)

9. **(d)** Fly ash.

10. **(d)** London smog is formed in morning during winter.

11. **(b)** Photochemical smog is formed in noon in summer.

12. **(a)** London smog is reducing in nature.

13. **(b)** Algae

14. **(a)** Dust

15. **(c)** CO is converted into CO_2 by microorganism present in soil.

16. **(b)** NO_2 forms a part of photochemical smog.

17. **(d)** Depletion of ozone layer causes skin cancer.

18. **(a)** NO and freons are responsible for ozone depletion.

19. **(a)** $O_2 \longrightarrow O + O\ ;\ O + O_2 \longrightarrow O_3$

20. **(c)** $CF_2Cl_2 \xrightarrow{h\nu} CF_2Cl + \dot{Cl}$

$$\dot{Cl} + O_3 \longrightarrow Cl\dot{O} + O_2$$

21. **(d)** Ozone hole is reduction in ozone layer in stratosphere.

22. **(d)** Aerosols use CFC an flying jets release NO. Both causes depletion of ozone layer.

23. **(d)** Addition of phosphate fertilizers to water leads to nutrient enrichment (eutrophication)

24. **(d)** DDT causes water, air and soil pollution.

25. **(d)**

26. **(c)** Domestic sewage constitute biodegradable pollutants.

27. **(d)**

28. **(a)** Pesticides cause water pollution.

29. **(d)** Decrease in D.O causes death of fish

30. **(a)** Phosphate pollution is caused by sewage and agricultural fertilizers.

31. **(b)** Sewage water is purified by micro-organisms.

32. **(c)** Water is often treated with Cl_2 to kill germs.

33. **(d)** Ozone absorbs U.V. radiations harmful to human life.

34. **(d)** CO is major air pollutant.

35. **(a)** Ozone layer is present in stratosphere.

36. **(a)** CO_2 causes green house effect.

37. **(b)** Surface water contains salts + organic matter.

EXERCISE 3

1. **(a)** Green house gases such as CO_2, ozone, methane, the chlorofluorocarbon compounds and water vapour form a thick cover around the earth which prevents the IR rays emitted by the earth to escape. It gradually leads to increase in temperature of atmosphere.

2. **(c)** CO and oxides of Nitrogen are poisnous gases present in automobile exhaust gases.

3. **(b)** Green chemistry may be defined as the programme of developing new chemical products and chemical processes or making improvements in the already existing compounds and processes so as to make less harmful to human health and environment. This means the same as to reduce the use and production of hazardous chemicals.

i.e. correct answer is option (b).

4. **(b)** The ideal value of D.O for growth of fishes is 8 mg/ℓ. 7mg $/\ell$ is desirable range, below this value fishes get susceptible to disease. A value of 2 mg/ℓ or below is lethal for fishes.

5. **(d)** The oxidised hydrocarbons and ozone in presence of humidity cause photochemical smog.

Hydrocarbons + O_2, NO_2, NO, O, O_3 → Peroxides, formaldehyde, peroxyacetylnitrate (PAN), acrolein etc.

It is oxidising in nature and causes irritation to eyes, lungs, nose, asthamatic attack and damage plants.

6. **(b)**

7. **(a)** Normal rain water has pH 5.6 Thunderstorm results in the formation NO and HNO_3 which lowers the pH.

8. **(a)** Smog is caused by oxides of sulphur and nitrogen.

9. **(c)** Ozone layer acts as a shield and does not allow ultraviolet radiation from sun to reach earth. It does not prevent infra-red radiation from sun to reach earth.

Thus option (c) is wrong statement and so it is the correct answer.

10. **(c)** The ozone layer, existing between 20 to 35 km above the earth's surface, shield the earth from the harmful U. V. radiations from the sun.

Depletion of ozone is caused by oxides of nitrogen

$$N_2O + h\upsilon \longrightarrow \underset{\text{reactive nitric oxide}}{NO} + N$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$O_3 + h\upsilon \longrightarrow O_2 + O$$

$$NO_2 + O \longrightarrow NO + O_2$$

$$2O_3 + h\upsilon \longrightarrow 3O_2 \text{ (Net reaction)}$$

The presence of oxides of nitrogen increase the decomposition of O_3.

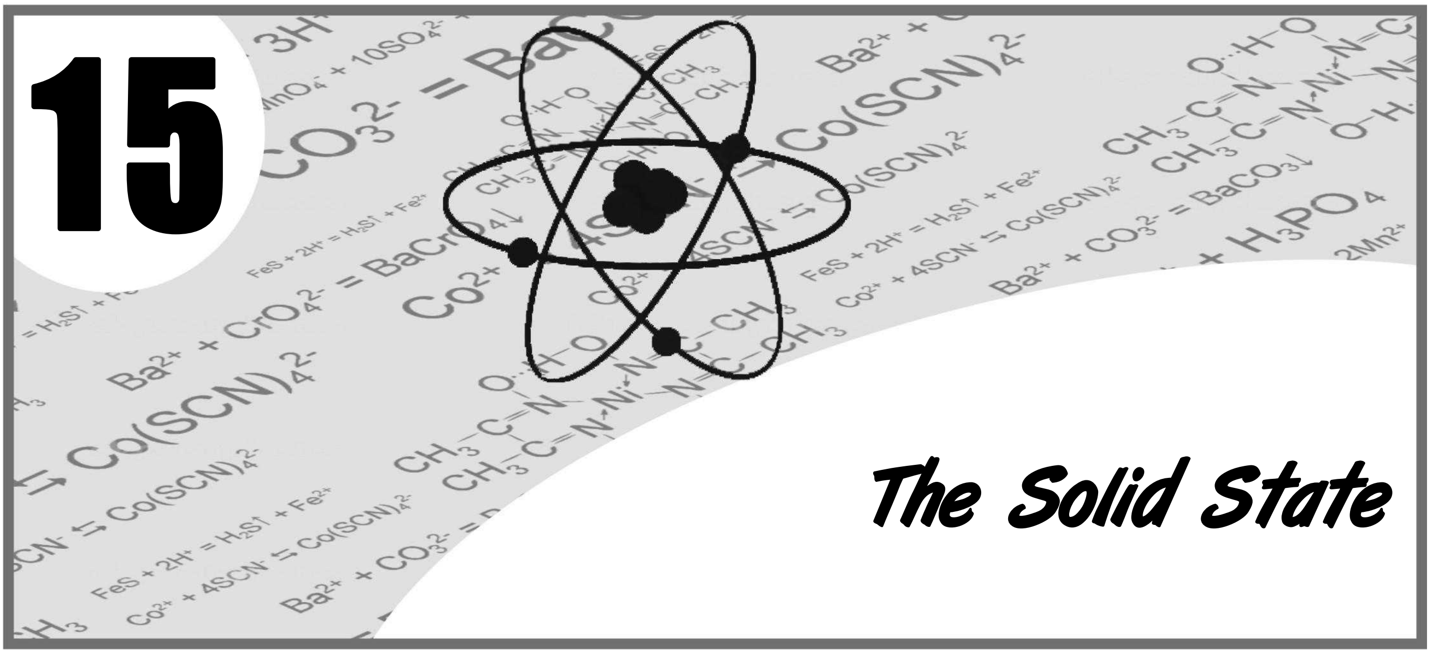
11. **(d)** DDT is a non-biodegradable pollutant.

12. **(a)** Methyl isocyanate, $CH_3 - N = C = O$

EXERCISE 4

1. **(b)** CO_2 is generally not regarded as an pollutant.
2. **(a)** Haemoglobin has great affinity for NO.
3. **(d)** Acid rain contains $H_2SO_4 > HNO_3 > HCl$.
4. **(c)** Photochemical smog does not involve SO_2.
5. **(b)** SO_3 is more harmful pollutant than SO_2.
6. **(a)** The average residence time of NO is 4 days.
7. **(a)** Particulates acquire negative charge and are attracted by the positive electrode.
8. **(a)** PSCs react with chlorine nitrate and HCl to give HOCl and Cl_2.
9. **(d)** Minamata is caused by Hg poisoning.
10. **(a)** BOD is connected with microbes and organic matter
11. **(a)** Eutrophication causes reduction in D.O
12. **(a)** Oil slick in sea water decreases D.O value.
13. **(c)** Presence of CO in the exhaust fumes shows incomplete combustion.
14. **(a)** Statement (a) is correct.

❑❑❑



15

The Solid State

SOLIDS :

Solid substances are characterised by ***definite shape, volume, rigidity, high density, low compressibility, mechanical strength, slow diffusion*** and ***hard*** *nature.* The constituent particles (atoms, molecules or ions) are **closely packed** and held together by **strong forces.**

CRYSTALLINE SOLIDS :

The constituent particles are arranged in definite geometrical pattern i.e. they have **lattice structure**.

AMORPHOUS SOLIDS :

They have random arrangement of the constituent particles (amorphous - means without any form).

DIFFERENCES BETWEEN CRYSTALLINE AND AMORPHOUS SOLIDS ARE :

Crystalline	*Amorphous*
• Have lattice structure	• Do not have lattice structure
• Have sharp melting point	• No sharp mpt
• They are **anisotropic** i.e. their physical properties are different along different directions	• They are **isotropic** i.e. their physical properties are the same along all directions
• They are symmetrical	• They are non symmetrical. They are supercooled liquids
• Show clean cleavage	• No clean cleavage
Examples: Diamond, NaCl, etc.	*Examples:* Glass, Rubber, Plastic

TYPES OF CRYSTALLINE SOLIDS :

Character	*Ionic*	*Covalent*	*Molecular*	*Metallic*
Constituent particles	Positive and negative ions	Atoms	Molecules	Positive ions
Binding forces	Electrostatic attraction	Shared electrons	Vander Waals' Dipole-dipole	Electrostatic between +ve ions and negative electrons
Properties	High melting points	Very high mpt	Low mpt	Moderate to high mpt.
	Hard & brittle	Very hard	Very soft	Hard & Soft
	Semi Conductors	Non Conductors	Insulators Conductors	good
Examples	NaCl, CaF_2	Diamond, Silica	H_2O, CO_2	Cu, Fe

CRYSTAL LATTICE :

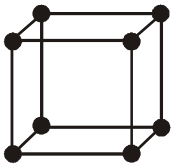
The three dimensional orderly arrangement of constituent particles of a crystalline solid is known as Crystal lattice.

UNIT CELL :

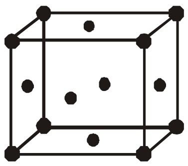
The smallest geometrical portion of the crystal lattice which can be used as repetitive unit to build up the whole crystal is called unit cell.

TYPES OF UNIT CELL :

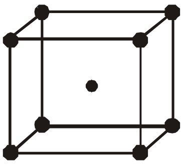
(i) **Simple or primitive :** Unit cell in which the particles are present at the corners only



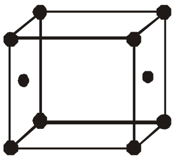
(ii) Face centred : In which the particles are present at the corners & at the centre of each of six faces.



(iii) Body centred : In which the particles are present at the corners and in the centre.



(iv) End face centred : In which the particles are present at the corners and at the centre of two opposite faces.



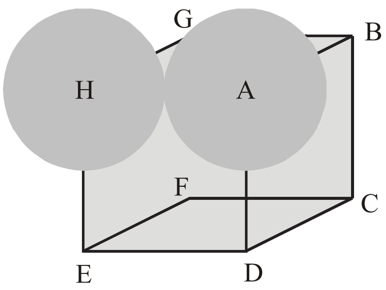
NUMBER OF PARTICLES PER UNIT CELL :

	Unit Cell	*No. of particles and their contribution*			*Total*
		Corner	*Face*	*Centre*	
1.	Simple Cubic	$8 \times \frac{1}{8}$	–	–	1
2.	Face Centred	$8 \times \frac{1}{8}$	$6 \times \frac{1}{2}$	–	4
3.	Body Centred	$8 \times \frac{1}{8}$	–	1	2
4.	End face Centred	$8 \times \frac{1}{8}$	$2 \times \frac{1}{2}$	–	2

PACKING FRACTION :

It is defined as the ratio of the volume of the unit cell that is occupied by the spheres to the volume of the unit cell.

(i) Primitive cubic unit cell : Number of atoms per unit cell = 1

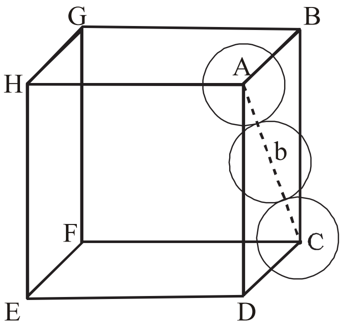


Atoms touch each other along edges. Hence $r = \frac{a}{2}$

(r = radius of atom and a = edge length)

$$\text{Therefore P.F.} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = 0.52$$

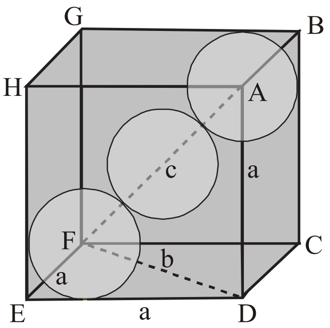
(ii) Face centred cubic unit cell : Number of atoms per unit cell = 4



Atoms touch each other along the face diagonal. Hence r = $\frac{\sqrt{2}\,a}{4}$ (length of face diagonal = $\sqrt{2}a$)

$$\text{Therefore P.F.} = \frac{4 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} = 0.74$$

(iii) Body centred cubic unit cell : Number of atoms per unit cell = 2.

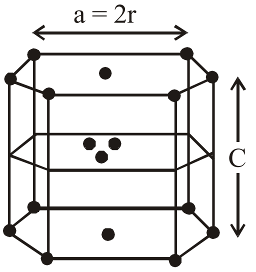


Atoms touch each other along the body diagonal. Hence $r = \frac{\sqrt{3}\,a}{4}$ (length of body diagonal = $\sqrt{3}$ a)

$$\text{Therefore P.F.} = \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = 0.68$$

(iv) Hexagonal primitive unit cell : Each corner atom is being shared by 6 other unit cells therefore their contribution to one unit cell would be $\frac{1}{6}$.

Total number of atoms per unit cell $\frac{1}{6}\times 12 + 3 + \frac{1}{2}\times 2 = 6$



Height of unit cell C = $4r\sqrt{\frac{2}{3}}$

Length of unit cell a = 2r

Area of base = area of six equilateral triangles

$$= 6\times\left(\frac{\sqrt{3}}{4}\right)(2r)^2$$

Volume of unit cell = $6\times\left(\frac{\sqrt{3}}{4}(2r)^2\right)\times 4r\sqrt{\frac{2}{3}}$

$$PF = \frac{6\times\frac{4}{3}\pi r^3}{6\times\frac{\sqrt{3}}{4}(2r)^2\times 4r\sqrt{\frac{2}{3}}} = 0.74$$

SIZE AND SHAPE OF CRYSTALS :

The slower the rate of formation of crystal, the bigger is the size of crystal and vice versa.

MICRO CRYSTALLINE :

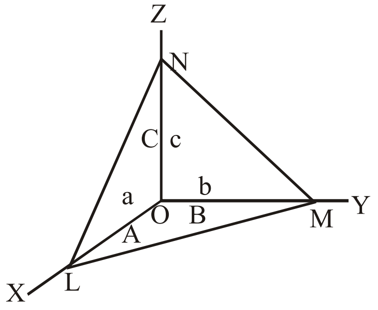
Crystals can be seen only under powerful microscope.

INTERFACIAL ANGLES :

The angle between any two faces is called an interfacial angle. Interfacial angle remains the same in the same substance although the size of faces or even shape of crystal may vary.

LAW OF RATIONALITY OF INDICES OR INTERCEPTS:

The ratio between intercepts on crystallographic axes for the different faces of a crystal can always be expressed by rational numbers.



The plane LMN has intercepts OL, OM and ON along X, Y and Z axes of lengths 2a, 4b and 3c respectively. When OA = a, OB = b and OC = c are taken as unit distances, the intercepts are in the ratio 2a : 4b : 3c and coefficients of a, b and c are known as **WEISS INDICES**.

Weiss indices may have any values integers, fractional or infinity.

MILLER INDICES :

Reciprocals of Weiss indices and multiplying throughout by smallest number to make integers are known Miller indices and represented by h, k and l and the plane as (hkl). For example, in (112) plane h = 1, k = 1 and l = 2.

The distance between the parallel planes in a crystal is designated as d_{hkl}. For different cubic lattices the interplanar distances are given by $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$

where a = length of cube side and h, k and l are Miller indices.

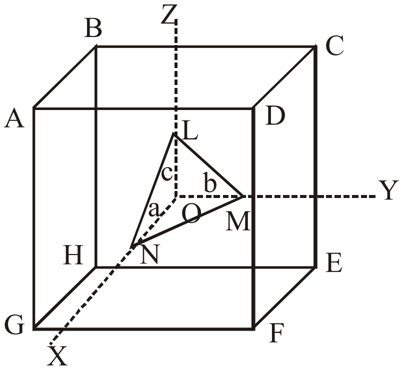
CRYSTALLOGRAPHIC AXES :

The three mutually perpendicular lines meeting at a common point are called crystallographic axes. The angles between the axes opposite to the intercepts a, b, c on crystallographic axes are represented by α, β and γ. If axes coincide with or are parallel to the edges of crystal faces, then α, β, γ will be the same as interfacial angles.

MORE ABOUT THE LAW OF RATIONAL INDICES :

Consider a cubic unit cell, crystallographic axes, the intercepts, the faces represented as follows :

X, Y and Z are crystallographic axes meeting at O. Let LMN be a unit plane having intercepts a, b and c on X, Y and Z axis.



(1) Intercepts of axis X :

  (i) On face ADFG will be multiple of a

  (ii) On face BCEH will be multiple of 'a' with negative sign since it is in opposite direction (negative value is represented by putting a bar over it)

  (iii) On the faces ABHG and DCEF will be ∞ since X-axis can never cut these faces.

(2) Intercepts of axis Y :

  (i) On face DCEF will be multiple of b

  (ii) On face ABHG will be multiple of b with negative sign since in opposite direction

  (iii) On faces ABCD and EFGH will be ∞ since Y can never cut these faces

(3) **Intercepts of axis Z :**

  (i) On face ABCD will be multiple of C.

  (ii) On face EFGH will be multiple of C with negative sign since in opposie direction.

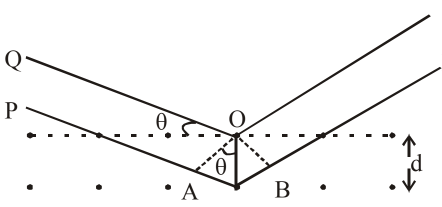
  (iii) On faces ABHG and DCEF will ∞ since Z axis can never cut these faces.

CRYSTALLOGRAPHY AND X-RAY DIFFRACTION (BRAGG'S EQUATION) :

When X-rays strike the parallel planes of the crystal at an angle θ, they are reflected from different planes. The resulting reflected beam will be strong if all reflected rays are in phase. Now as

$$\text{Phase difference} = \frac{2\pi}{\lambda} \times \text{path difference}$$

If path difference is an integral multiple (say n) of wavelength, then phase difference becomes an integral multiple of 2π or 360° and hence the reflected rays will be in same phase



X-ray reflection from crystals

Now from figure the path difference between waves reflected from upper planes = AO + OB

From simple trignometry, if d is the distance between successive layers then $\sin\theta = \frac{OA}{d}$

$OA = d \sin\theta$

Similarly $OB = d \sin\theta$

Thus net path difference = $OA + OB = 2d \sin\theta$

Now for maximum reflection condition (defined above)

path difference = n × wavelength

$2d \,.\, \sin\theta = n\lambda$

This is ***Bragg's equation.***

SYMMETRY IN CRYSTAL SYSTEMS :

(i) **Plane of symmetry :** Which divides a crystal in two parts in such a way that one part is the mirror image of the other.

(ii) **Axis of symmetry :** It is a line about which the crystal may be rotated such that it presents the same appearance more than once during complete revolution.

(iii) **Centre of symmetry :** It is a point such that any line drawn through it intersects the surface of the crystal at equal distances in both directions.

ELEMENTS OF SYMMETRY :

Total number of planes, axes and centre of symmetries present in a crystal are termed as elements of symmetry. A cubic crystal of NaCl possesses 23 elements of symmetry.

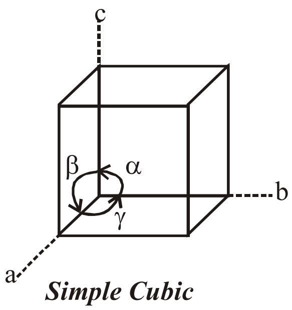
- Planes of symmetry = 3 + 6 = 9
- Axes of symmetry = 3 + 4 + 6 = 13
- Centre of symmetry = 1
- Total number of symmetry elements = 23

SEVEN CRYSTAL SYSTEMS :

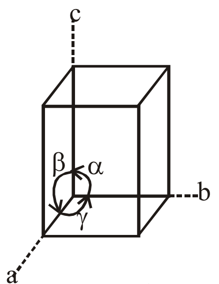
There are about 230 crystal forms, which have been grouped into 14 types of space lattices called ***BRAVAIS LATTICES*** on the basis of their symmetry and 7 different crystal systems on the basis of interfacial angles and axes.

	Crystal System	*Parameters of unit Cell* *Intercepts/axes*	*angles*	*Bravais Lattices*
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	3 Primitive, Face Centred, Body centred
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	2 Primitive, Body centred
3.	Rhombohedral	$a = b = c$	$\alpha = \beta = 90°\ \ \gamma \neq 90°$	1 Primitive
4.	Ortho Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	4 Primitive, Face centred, Body centred, End centred
5.	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90°,\ \gamma \neq 90°$	2 Primitive, End Centred
6.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	1 Primitive
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°,\ \gamma = 120°$	1 Primitive

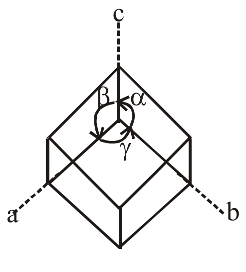
TYPES OF UNIT CELLS OCCURING IN CRYSTALS :



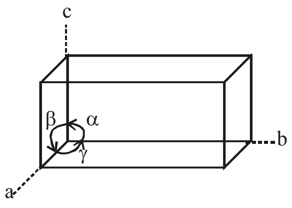
Simple Cubic



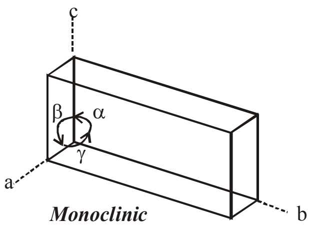
Tetragonal



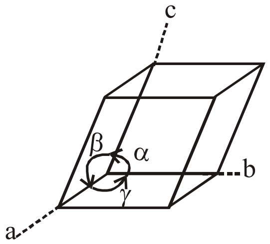
Rhombohedral



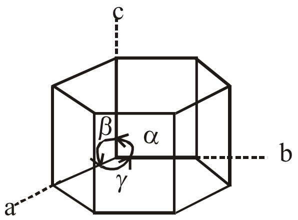
Orthorhombic



Monoclinic



Triclinic



Hexagonal

Bravais showed from geometrical considerations that there are only seven **shapes** in which unit cells can exist.

These are

(i) Cubic
(ii) Orthorhombic
(iii) Rhombohedral
(iv) Hexagonal
(v) Tetragonal
(vi) Monoclinic
(vii) Triclinic

On the basis of presence of particles there are four types of unit cells

(i) Primitive or simple
(ii) Face centred
(iii) Body centred
(iv) End centred

He also showed that out of possible twenty eight unit cells. (Seven shapes × four types in each shape = 28) only fourteen actually exist. These are called BRAVAIS LATTICES.

CO-ORDINATION NUMBER :

It is defined as the number of particles immediately adjacent to each particle in the crystal lattice.

In simple cubic lattice C.N. is 6
In body centred lattice C.N. is 8 and
In face centred cubic lattice C.N. is 12.

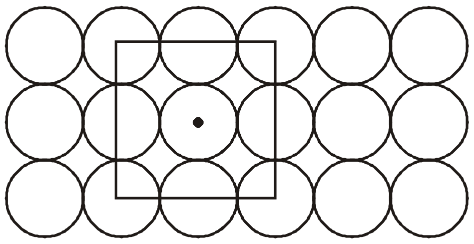
High pressure increases C.N. and high temperature decreases the C.N.

PACKING OF CONSTITUENT PARTICLES IN CRYSTALS :

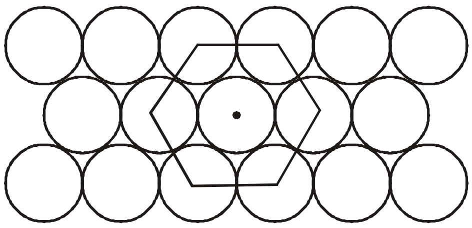
Generally the particles of larger size do the packing and particles of smaller size occupy interstitial places

(i) **Close packing in two dimensions :** It is of two types

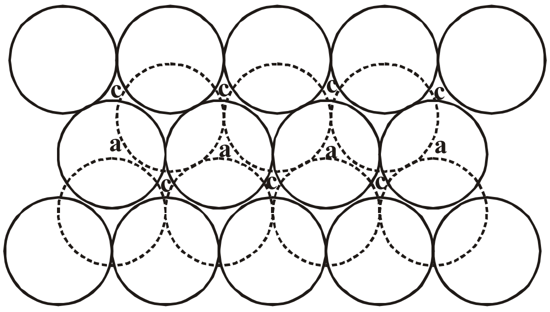
(a) ***Square close packing :*** Space occupied by spheres is 52.4%



(b) ***Hexagonal close packing :*** Space occupied by spheres is 60.4%. Hence it is more efficient.



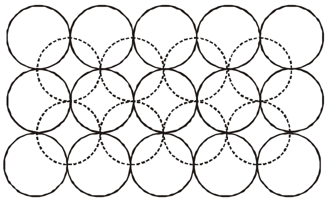
(ii) **Close packing in three dimensions :** Following the hexagonal close packing here, we have two layers.



For third layer there are two types of voids, marked **a** tetrahedral voids and marked **c** octahedral voids. If spheres are placed over **a**, first layer is repeated and we have AB- AB arrangement. This is known as **hexagonal close packing** (hcp). If spheres for third layer are placed over **c**, a different layer is formed and we have ABC-ABC arrangement. This is knwon as **cubic close packing** (ccp).

Both hcp and ccp are equally efficient and space occupied by spheres is **74.0%.** The cubic close packing has face centered cubic (fcc) unit cell.

Following the square close packing in three dimensions, we have AB, AB arrangement of spheres.



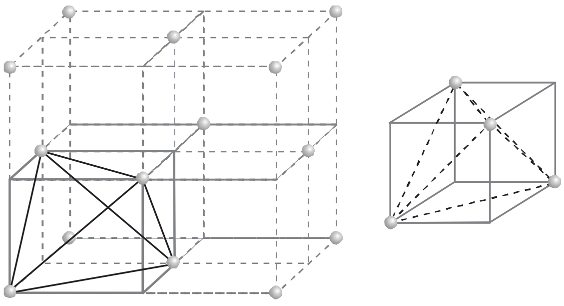
The resulting structure in this arrangement is referred to as body-centred cube (bcc). In this arrangement only **68%** of the available space is occupied by spheres and occur in many solids.

INTERSTITIAL VOIDS :

The space left after hcp and ccp (74.0% in each case) is known as interstitial voids. They are of two types:

(i) **Tetrahedral voids :** The vacant space touching four spheres is called tetrahedral void. The radius ratio is

$$\frac{r_{void}}{r_{sphere}} = 0.225$$



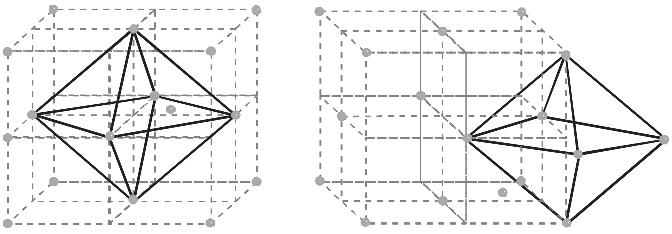
(a) (b)

(a) Eight tetrahedral voids per unit cell of ccp structure
(b) one tetrahedral void showing the geometry.

The number of tetrahedral voids is twice the number of spheres (atoms).

(ii) Octahedral voids : The vacant space touching six spheres is called octahedral void. The radius ratio is

$$\frac{r_{void}}{r_{sphere}} = 0.414$$



(a) (b)

Location of octahedral voids per unit cell of ccp or fcc lattice
(a) at the body centre of the cube and
(b) at the centre of each edge (only one such void is shown).

The number of octahedral voids is equal to the number of spheres (atoms).

LIMITING RADIUS RATIO :

Cations tend to get surrounded by the largest number of anions therefore the larger the $\frac{r_{void}}{r_{sphere}}$ ratio, the larger is the coordination number.

Limiting radius ratio(r^+/r^-)	*Shape*	*Coordination number*	*Example*
0.155 – 0.225	Planar triangle	3	B_2O_3
0.225 – 0.414	Tetrahedral	4	ZnS
0.414 – 0.732	Square planar	4	
0.414 – 0.732	Octahedral	6	NaCl
0.732 – 1.000	Body Centred Cubic	8	CsCl

STRUCTURE OF SOME SIMPLE IONIC COMPOUNDS :

It can be summarised in the following table, for cubic ionic solids.

S. No.	*Crystal Structure*	*Packing*	*C.No.*	*No. of formula Units per unit cell*	*Examples*
1.	Rock Salt (NaCl)	Cl^- in ccp Na^+ in octahedral voids	6	4	Halides of Li, Na K, Rb, AgCl, AgBr, NH_4Cl
2.	Zinc blends (ZnS)	S^{--} in ccp Zn^{++} alternate tetrahedral voids	4	4	CuX (Cl, Br, I), AgI, BeS
3.	Wurtzite (ZnS)	Zn^{++} hcp S^{--}alternate tetrathedral voids	4	4	
4.	CsCl	Cs^+ in Cubic Voids Cl^- at the corners of a cube or *vice versa*	8	1	CsBr, CsI, CsCl, TlCl, TlBr, TlI, TlCN
5.	Fluorite CaF_2	Ca^{++} in ccp, F^- tetrahedral voids	Ca^{++} F^- (8:4)	4	SrF_2, BaF_2, $BaCl_2$, CaF_2, CdF_2, PbF_2
6.	Antifluorite Li_2S	S^{--} in ccp, Li^+ tetrahedral voids	Li^+S^{2-} (4:8)	4	Na_2O, Li_2O, K_2O, Na_2O, K_2S

PRESENCE OF CATIONS AND ANIONS IN UNIT CELL :

S.No.	*Crystal Structure*	*Anion*	*Cation*
1.	NaCl	8 at corners 6 at faces	12 at edges, 1 in body
2.	ZnS	8 at corners 6 at faces	4 in body
3.	CsCl	8at corners	1 in body
4.	CaF_2	8 in body	8 at corners, 6 at faces

Lattices of some elements :

(i) ***Cubic close packed lattice :*** Cu, Ag, Au, Fe, Ni, Al

(ii) ***Hexagonal close packed lattice :*** Zn, Cd, Hg, Be, Mg, Ti

In both the above structures each atom is surrounded by twelve nearest touching neighbours hence coordination number is 12.

(iii) ***Body centred cubic lattice :*** Li, Na, K, Rb, Cs, W, Cr

This packing is not so tight as the first two are, each atom is surrounded by eight nearest touching neighbours, hence coordination number is 8.

RELATION BETWEEN EDGE OF UNIT CELL AND RADIUS OF CATION AND ANION IN FCC STRUCTURE :

$$\sqrt{2}r^+ + \sqrt{2}r^- = a$$

$$\therefore r^+ + r^- = \frac{a}{\sqrt{2}} \text{ or } r = \frac{a}{2\sqrt{2}} = \frac{\sqrt{2}}{4}a$$

In NaCl structure, distance between cation and anion

$$= \frac{a}{2}\left(r^+ + r^-\right)$$

BODY DIAGONAL :

In CsCl ions touch along body diagonal :

$$2r^+ + 2r^- = \sqrt{3}.a \text{ (length of body diagonal)}$$

$$\therefore r^+ + r^- = \frac{\sqrt{3}.a}{2} \quad \text{or} \quad r = \frac{\sqrt{3}}{4}a$$

FACE DIAGONAL :

If there is cube of edge length a then face diagonal is $\sqrt{2}a$, Body diagonal is $\sqrt{3}.a$.

COORDINATION NUMBER OF AN ATOM IN :

(i) Primitive Cubic unit cell = 6

(ii) Body centred cubic unit cell = 8

(iii) Face centred cubic unit cell = 12

NORMAL SPINEL STRUCTURE :

The mineral $MgAl_2O_3$ is known as spinel. The oxide ions are arranged in ccp, Mg^{++} ions occupy tetrahedral voids and Al^{+++} ions occupy the octahedral voids. Ferrite $ZnFe_2O_4$ has spinel structure. Being magnetic these are used in telephones and memory loops in computers.

INVERSE SPINEL STRUCTURE :

Divalent ions occupy octahedral voids and trivalent ions are equally distributed in tetrahedral and octahedral voids. e.g. Fe_3O_4 or FeO. Fe_2O_3.

DENSITY OF UNIT CELL :

It is given by

$$d = \frac{Z \times M}{N_A \times a^3 \times 10^{-30}} \text{ g/cm}^3$$

where Z = Number of formula units present in unit cell. It is also known as rank or unit cell content.

M = Molecular weight, N_A = Avogadro number

a = edge length of unit cell in pm

IMPERFECTIONS IN SOLIDS :

They are of two types.

(i) Electronic imperfections : In Crystals of pure Silicon or Germanium some electrons are released from covalent bonds at temperatures above 0K which are now free to move in the crystal. The electron deficient bonds produced are known as holes. Electrons (e) and holes (h) in solids are considered to be electronic imperfections. Concentrations of electrons (e) and holes (h) is represented by n and p.

(ii) Atomic imperfections : Further they may be divided as

(a) ***Point imperfections :*** The periodic arrangement of constituent particles is disturbed.

(b) ***Lattice imperfections :*** The deviations from periodic arrangement extend over microscopic regions of the crystal.

(c) ***Line defects / dislocations :*** The lattice imperfections extend along lines.

(d) ***Plane defects :*** The lattice imperfections extend along surfaces of crystals.

STOICHIOMETRIC POINT DEFECTS :

They include

(i) Schottky defect : It is due to missing of ion pairs (one cation and one anion) from their lattice sites. It maintains the electrical neutrality. Density of crystal decrease. It is more common in compounds with high coordination number and when size of positive and negative ions is almost equal. Example NaCl, KCl, CsCl and KBr etc.

(ii) Frenkel defect : It is due to dislocation of ion from its usual site to interstitial position. Density remains the same. It is common in compounds having low coordination number and large difference in size of +ve and –ve ions. Examples ZnS, AgCl, AgBr and AgI.

AgBr shows both of the above defects.

NON STOICHIOMETRIC POINT DEFECTS :

They include

(i) Metal excess (due to anion vacancy) : It is due to absence of anion from lattice site leaving a hole which is occupied by electron to maintain electrical neutrality

$A^+ \; B^- \qquad A^+ \qquad B^-$

$B^- \; A^+ \qquad e^- \qquad A^+$

F-Centres - Holes occupied by electrons are called F-Centres (Colour centres). The greater the number of F-centres the greater is the intensity of colour of solid and solids are paramagnetic in nature. Due to F-centres

NaCl is yellow
KCl is violet
LiCl is pink.

Crystals showing schottky defect also show this defect.

(ii) Metal excess due to interstitial cations : It is due to extra positive ion and an electron occupying an interstitial position

A^+ B^- A^+ B^-
A^+ e^-
B^- A^+ B^- A^+

Crystals exhibiting Frenkel defect show this defect eg ZnO.

(iii) Metal deficiency due to cation vacancy : It is due to absence of a metal ion from its lattice site and charge is balanced by ion having higher positive charge.

A^+ B^- O B^-
B^- A^{++} B^- A^+

Transition metals exhibits this defect due to metal deficiency, the compound obtained are non stoichiometric. e.g. it is difficult to prepare ferrous oxide with the ideal composition FeO. What we actually obtain is $Fe_{0.95}O$ or Fe_xO with x=0.93 to 0.96

(iv) **Metal deficiency due to interstitial negative ion :** It is due to presence of negative ion in interstitial position and presence of metal ion with extra charge.

A^+ B^- A^+ B^-
B^-
B^- A^+ B^- A^{++}

This defect is not common

NON STOICHIOMETRIC DEFECT DUE TO PRESENCE OF FOREIGN ATOMS :

In AgCl crystals two Ag^+ ions may be missing while one Cd^{++} occupies one of the vacant sites.

Ag^+ Cl^- Ag^+ Cl^-
Cl^- Cd^{++} Cl^- □

FOOL'S GOLD :

Some samples of Iron pyrites shine like gold due to exchange of electrons between Fe^{2+} and $Fe^{3+,}$ which leads to metallic lustre. Such samples are known as fool's gold.

SEMI CONDUCTORS :

Electronic conductors having electrical conductivity in the range of $10^4 - 10^{-7}$ ohm^{-1} cm^{-1} are known as semi-conductors. Examples Si, Ge, Sn (grey) Cu_2O, SiC and GaAs.

INTRINSIC SEMI CONDUCTORS :

Pure substances those are semi-conductors known as intrinsic semi conductors e.g. Si, Ge.

EXTRINSIC SEMI CONDUCTORS :

Their conductivity is due to the presence of impurities. They are formed by doping e.g. Si doped with P.

DOPING :

It is defined as addition of impurities to a semiconductor to increase the conductivity. Doping of Si or Ge is carried out with P, As, Sb, B, Al or Ga.

DONORS :

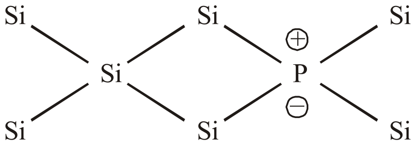
Impurities capable of donating electrons are known as donors e.g. P, As, Sb.

ACCEPTORS :

Impurities capable of accepting electrons are known as acceptors e.g. B, Al, Ga.

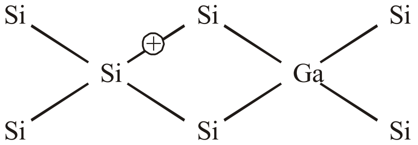
n-TYPE SEMI CONDUCTORS :

Silicon doped with phosphorous is called n-type semi conductor. The conductivity is due to presence of negative charge (electrons).



p-TYPE SEMI CONDUCTORS :

Silicon doped with gallium is called p-type semi conductor. The conductivity is due to the presence of positive holes.



Some typical 13-15 comounds are InSb, AlP and GaAs and some typical 12-16 compounds are ZnS, CdS, CdSe and HgTe.
These exhibit electrical and optical properties of great use in electronic industry.

PIEZOELECTRIC EFFECT AND PIEZOELECTRICITY :

The charge developed on the crystal due to mechanical stress is called piezoelectric effect and the current thus produced is called piezo electricity.

PYROELECTRICITY :

The electric current produced by heating on the faces of a crystal is called pyroelectricity.

FERROELECTRIC EFFECT :

The reversal of direction of permanently lined up dipoles of piezo electric crystal by applying electric field is called ferro electric effect.
Examples Rochelle Salt, KH_2PO_4 and Barium titanate $BaTiO_3$.

ANTIFERRO ELECTRIC SOLID :

When the dipoles in alternate lattices point are in opposite direction and net dipole moment is zero, the crystals are referred to as antiferro electric. Example is lead Zirconate $PbZrO_3$.

DIAMAGNETIC :

The substances which are weakly repelled by magnetic fields e.g. KCl, NaCl and TiO_2. It is independent of temperature.

PARAMAGNETIC :

The substances which are attracted by magnetic field and loss magnetism in the absence of a magnetic field e.g. O_2, Cu^{++}, Fe^{+++}, Na, K etc.

FERROMAGNETIC :

The substances which are strongly attracted by magnetic field and retain magnetism even when the magnetic field is removed e.g. CrO_2, Fe, Co & Ni show ferro magnetism at room temperature. The alignment of magnetic moments is spontaneous in such substances $\uparrow \uparrow \uparrow \uparrow \uparrow$.

ANTIFERRO MAGNETISM :

It is due to compensatory alignment of moments $\uparrow\downarrow \ \uparrow\downarrow \ \uparrow\downarrow$.

The net moment is zero e.g. MnO, MnSe and $KMnFe_3$.

FERRIMAGNETISM :

The alignment of moments are parallel and anti-parallel unequal in number, there is net moment e.g. Fe_3O_4, ferrites of formula $M^{2+}Fe_2O_4$ (M = Mg, Cu, Zn)

CLASSIFICATION OF SOLIDS ON THE BASIS OF ELECTRICAL CONDUCTIVITY :

(i) Metals : 10^8 ohm^{-1} cm^{-1}

(ii) Insulators : 10^{-12} ohm^{-1} cm^{-1}

(iii) Semiconductors : $10^4 - 10^{-7}$ ohm^{-1} cm^{-1}

BERTHOLLIDES :

Non Stoichiometric compounds are called Berthollides. The common are sulphides and oxides e.g. FeO, CuO.

LIQUID CRYSTALS (MESOMORPHIC OR PARA CRYSTALLINE) :

The substances having the properties of crystalline solids and flow properties of liquids. Examples : Para-azoxy anisole and Normal Octyl-para azoxy cinnamate. Such solids undergo two sharp phase transformations on fusion, first yielding turbid liquid and at higher temperature a clear liquid. The turbid liquids are called liquid crystals and are anisotopic in nature (a property of crystalline solid).

TRANSITION POINT :

It is the temperature at which a substance changes sharply into the state of liquid crystals.

POLYMORPHISM :

Existence of a substance in more than one crystalline form is known as polymorphism e.g. Carbon, Sulphur, Tin etc.

ALLOTROPY :

The polymorphism in elements is known as allotropy.

ENANTIOTROPIC SUBSTANCE :

Polymorphic form of a substance whose transition temperature is lower than the fusion temperature is known enantiotropic substance and phenomenon is called enantiotropy.

MONOTROPY :

When fusion temperature of both the forms is below the transition temperature the phenomenon is known as monotropy.

ISOMORPHISM :

Two or more substances having the same crystalline form are known as isomorphous and the phenomenon is called isomorphism $K_2SO_4.Cr_2(SO_4)_3.24H_2O$ and $K_2SO_4.Al_2(SO_4)_3.24H_2O$ are isomorphous.

MITSCHERLICH'S LAW :

It states that isomorphous substances possess an equal number of atoms united in a similar way.

ISOPOLYMORPHISM :

When each form of a polymorphic substance is isomorphous with a form of another polymorphic substance the phenomenon is known as Isopolymorphism e.g. antimony trioxide and arsenious oxide both exist in rhombic and octahedral form. The rhombic forms of two oxides are isomorphous and octahedral forms of the oxides are also isomorphous.

SILICATES :

Silicates are metal derivatives of silicic acid H_4SiO_4 obtained by fusing metal oxides or metal carbonates with sand.

$$Na_2CO_3 \xrightarrow[1770K]{\text{Fuse } SiO_2} Na_4SiO_4(Na_2SiO_3)_n$$

CLASSIFICATION OF SILICATES :

ORTHO SILICATES :

They contain discrete SiO_4^{4-} units.
Examples : Phenacite Be_2SiO_4, willemite Zn_2SiO_4. Metal cations are tetrahedrally surrounded by four O atoms.

PYRO SILICATES :

Two tetrahedral units are joined by one oxygen atom and contain $Si_2O_7^{6-}$ unit.
Examples : Thortiveitite $Se_2(Si_2O_7)$
Hemimorphite $Zn_3(Si_2O_7) . Zn(OH)_2 . H_2O$.

CHAIN SILICATES :

(i) $(SiO_3^{2-})_n$ Two oxygen atoms per SiO_4 tetrahedron are shared giving polymeric anion chains.
Example : Spodumene $LiAl(SiO_3)_2$, Diposide $CaMg(SiO_3)_2$.

(ii) $(Si_4O_{11}^{6-})_n$ contain double chain.
Example : Tremolite $Ca_2Mg_5(Si_4O_{11})(OH)_2$.

CYCLIC SILICATES :

Two oxygens per SiO_4 tetrahedron are shared containing $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$ units.
Example : Benyl : $Be_3Al_2Si_6O_{18}$

SHEET SILICATES :

Here three oxygens of each SiO_4 tetrahedron are shared. Containing $(Si_2O_5^{2-})_n$
Example : Clay.

FRAME WORK SILICATES :

All oxygen atoms of each SiO_4 tetrahedron are shared. They contain three dimensional net work.
Examaple : Quartz, zeolite.

Miscellaneous Solved Examples

1. Sodium metal crystallises in a body centred cubic lattice with the cell edge a = 4.29 Å. What is the radius of sodium atom.

Sol. In bcc the atoms touch along body diagonal

$$\therefore 2r + 2r = \sqrt{3}\ .\ a\ ;\ \ r = \frac{\sqrt{3} \times 4.29}{4} = 1.857\,\text{Å}$$

2. Chromium metal crystallizes with a body centred cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/cm^3.

Sol. In bcc lattice $r = \frac{\sqrt{3}.a}{4} = \frac{\sqrt{3} \times 287}{4} = 124.24$ pm

$$\text{Density} = \frac{Z \times M}{N_A \times a^3}$$

$$\rho = \frac{2 \times 51.99}{6.023 \times 10^{23} (287 \times 10^{-10})^3} = 7.30\ \text{g/ml}$$

3. Gold has closed packed structure which can be viewed as spheres occupying 0.74 of the total volume. If the density of gold is 19.3 g/ml. Calculate the approximate radius of gold ion in the solid (gold = 197 amu).

Sol. Packing fraction = 0.74. It has fcc type cell.
So number of gold ions per cell = 4

$$\rho = \frac{Z \times M}{N_A \times a^3} = \frac{4 \times 197}{a^3 \times 6.023 \times 10^{23}} = 19.3\ ;$$

$$\therefore a = 4.07 \times 10^{-8}\ \text{cm}$$

For fcc cell,

$$r = \frac{\sqrt{2}\ .\ a}{4} = \frac{\sqrt{2} \times 4.07 \times 10^{-8}}{4} = 1.439 \times 10^{-8}\ \text{cm}$$

4. A metal crystallizes into two cubic phases. (fcc and bcc) whose unit cell lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of fcc and bcc.

Sol. $\rho = \frac{Z \times M}{N_A \times a^3}$

For fcc, $\rho_1 = \frac{4 \times M}{N_A\ (3.5 \times 10^{-8})^3}$; For bcc, $\rho_2 = \frac{2 \times M}{N_A\ (3.0 \times 10^{-8})^3}$

$$\frac{\rho_1}{\rho_2} = \frac{4}{2}\frac{(3.0 \times 10^{-8})^3}{(3.8 \times 10^{-8})^3} = 1.259$$

5. A solid has a structure in which X atoms are located at the cube corners of the unit cell. O atoms are located at the centre of cube edges and Na atom at the cube centre. What type of lattice is represented by this compound. Also suggest a molecular formula for the compound.

Sol. The arrangement of atoms shows a simple cubic cell.

Number of X atoms = $\frac{1}{8} \times 8 = 1$ (at corners)

Number of O atoms = $\frac{1}{4} \times 12 = 3$ (at edges)

Number of Na atoms = 1 (at centre)

Hence formula $NaXO_3$

6. A solid $\overset{+}{A}\overset{-}{B}$ has NaCl type close packed structure. If the anion has a radius of 250 pm; What should be the ideal radius for the Cation? Can a cation C^+ having radius 180 pm be slipped into the tetrahedral void of the crystal $\overset{+}{A}\overset{-}{B}$? Give reasons for your answer.

Sol. Since $\overset{+}{A}\overset{-}{B}$ has NaCl type close packed structure it must belong to a crystal system having coordination number 6. Hence limiting radius ratio

$$\frac{r^+}{r^-} = 0.414 - 0.732$$

$r^- = 250$ pm ; $r^+ \geq 0.414 \times 250 = 103.5$ pm

Ideal radius for cation.

(II) Cation C^+ having radius 180 pm cannot be slipped into the tetrahedral site of crystal $\overset{+}{A}\overset{-}{B}$ because $\frac{r^+}{r^-}$ should be 0.225 – 0.414. In the given case $\frac{r^+}{r^-} = \frac{180}{250} = 0.72$.

7. In an ionic crystalline solid AB, r^+ = 0.74 Å and r^- = 1.84Å. The atomic weights of A and B are 70 and 40 amu respectively. Find (a) Coordination number of A & B (b) Density in g/cc of solid.

Sol. Given $\frac{r^+}{r^-} = \frac{0.74}{1.84} = 0.402 < 0.414$ therefore coordination number = 4 (tetrahedral)

$2r^+ + 2r^- = a$

$$\therefore a = 2(0.74 + 1.84) = 5.16\text{Å}$$

$$\rho = \frac{4 \times 110}{6.023 \times 10^{23} (5.16 \times 10^{-8})^3} = 5.33\ \text{g/cc}$$

8. What is the concentration of cation vacancies when NaCl is doped with 10^{-3} mole % of $SrCl_2$.

Sol. The number of cation vacancies created in the lattice of NaCl is equal to the number of divalent Sr^{2+} ion added

Concentration of Sr^{2+} ions = 10^{-3} mole per cent

$$= 10^{-3} \div 100 = 10^{-5} \text{ mol}$$

1 mole of Sr^{2+} contains 6.023×10^{23} Sr^{2+} ions

10^{-5} mole of Sr^{2+} ions contains $6.023 \times 10^{23} \times 10^{-5}$ ions.

Therefore the number of cation vacancies in NaCl crystal is 6.023×10^{18}.

9. In $Fe_{0.93}O$, find the % of Fe^{+++} ions.

Sol. Iron 93% and O is 100%.

Let Fe^{+++} be x% then Fe^{++} (93 – x)% then

Positive charge = Negative charge

$$2(93 - x) + 3x = 2 \times 100$$

$$\therefore x = 14$$

$$\therefore \% \text{ of } Fe^{+++} = \frac{14}{93} \times 100 = 15.2\%.$$

10. X-rays of wavelength 1.54Å strike a crystal and are observed to be deflected at an angle of 22.5°. Assuming that n = 1. Calculate the placing between the planes of atoms that are responsible for the reflection.

Sol. Bragg's equation is $n\lambda = 2d\sin\theta$

$$\therefore d = \frac{1.54 \times 1}{2\sin 22.5^\circ} = 2.01\text{Å}$$

11. At what glancing angle would be first order diffraction from (110) plane of KCl observed using X-ray of wavelength of 154 pm. The dimensions of the unit cell is 315 pm.

Sol. For the first order diffraction; $\lambda = 2d\sin\theta$

$$\lambda = 154 \text{ pm} ; d = 315 \text{ pm}$$

$$154 = 2 \times 315 \sin\theta ; \quad \therefore \theta = 14.1^\circ$$

12. The planes in a crystalline solid intersect the crystal axes at (2a, b, c) (–a, b, c) (a, 2b, 3c), (3a, b, c), (–a, b, ∞). Calculate the miller indices for these planes.

Sol.

Intercepts	2a, b, c	–a, b, c	a, 2b, 3c	3a, b, c	–a, b, ∞
Weiss indices	211	–111	123	311	–11 ∞
Reciprocal of weiss indices					
	$\frac{1}{2}\frac{1}{1}\frac{1}{1}$	$\frac{1}{-1}\frac{1}{1}\frac{1}{1}$	$\frac{1}{1}\frac{1}{2}\frac{1}{3}$	$\frac{1}{3}\frac{1}{1}\frac{1}{1}$	$\frac{1}{-1}\frac{1}{1}\frac{1}{\infty}$
Clear fractions	122	–111	632	133	–110
Miller indices	122	111	632	133	110

13. Determine the interplanar spacing between the (220) planes of a cubic lattice of length 450 pm.

Sol. $$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{450}{\sqrt{2^2 + 2^2 + 0^2}} = \frac{450}{\sqrt{8}} = 159 \text{ pm}$$

14. First order X-ray reflection (λ = 154) maximum from a set of (200) planes of a body centred cubic lattice was observed at 16°6'. Calculate the length of the edge of unit cell.

Sol. For first order reflection n = 1.

$$\therefore \lambda = 2d\sin\theta$$

$$d_{200} = \frac{\lambda}{2\sin\theta} = \frac{154}{2\sin 16^\circ 6'} = 280 \text{ pm}$$

$$d_{200} = \frac{a}{\sqrt{2^2 + 0^2 + 0^2}}$$

$$\therefore a = 2 \times 280 = 560 \text{ pm}$$

15. A solid $\overset{+}{A}\,\overset{-}{B}$ has an NaCl type closest packed structure. If the radius of the anion is 250 pm. What is the radius of the cation?

Sol. For NaCl type structure, $\frac{r_c}{r_a} = 0.414$

$$\therefore \quad r_c = (0.414)\, r_a = 0.414 \times 250 \text{ pm} = 103.5 \text{ pm}$$

16. KF has NaCl structure. What is the distance between K^+ and F^- in KF, if the density of KF is 2.48 g cm^{-3}.

[At. wt. of K = 39 and F = 19]

Sol. For NaCl type structure the rank of unit cell = 4

$$a^3 = \frac{Z \times M}{\rho \times N_A} = \frac{4 \times 58}{2.48 \times 10^{-30} \times 6.023 \times 10^{23}}$$

Edge length a = 538 pm

So the distance between K^+ and F^- ion $= \frac{a}{2} = 269.0$ pm

17. The unit cell of an element of atomic mass 96 and density 10.3 g cm^{-3} is a cube with edge length of 314 pm. Find the structure of the crystal lattice.

Sol. $$Z = \frac{\rho \times N_A \times a^3}{M} = \frac{10.3 \times 6.023 \times 10^{23} \times (314 \times 10^{-10})^3}{96} = 2$$

The number of atoms per unit cell is two. Hence the crystal lattice has bcc unit cell.

18. KCl crystallises in the same type of lattice as does NaCl.

Given that, $\frac{r_{Na^+}}{r_{Cl^-}} = 0.5$ and $\frac{r_{Na^+}}{r_{K^+}} = 0.7$

Calculate (a) the ratio of the side of the unit cell for KCl to that for NaCl and (b) the ratio of density of NaCl to that of KCl.

Sol. NaCl crystallises in the fcc unit cell such that

$$\left(r_{Na^+} + r_{Cl^-}\right) = \frac{a}{2}$$

Where a is the edge of length of unit cell. Since

$$\frac{r_{Na^+}}{r_{Cl^-}} = 0.5 \text{ and } \frac{r_{Na^+}}{r_{K^+}} = 0.7$$

We have, $$\frac{r_{Na^+} + r_{Cl^-}}{r_{Cl^-}} = 1.5 \quad ....(i)$$

and $$\frac{r_{K^+}}{r_{Cl^-}} = \frac{r_{K^+}}{r_{Na^+}/0.5} = \frac{0.5}{r_{Na^+}/r_{K^+}} = \frac{0.5}{0.7}$$

Adding 1 on both sides

$$\frac{r_{K^+}+r_{Cl^-}}{r_{Cl^-}}=\frac{1.2}{0.7} \qquad ...(ii)$$

Dividing (ii) by (i)

$$\frac{r_{K^+}+r_{Cl^-}}{r_{Na^+}+r_{Cl^-}}=\frac{1.2}{0.7}\times\frac{1}{1.5}$$

or $\frac{a_{KCl}/2}{a_{NaCl}/2}=\frac{1.2}{0.7\times1.5}$ or $\frac{a_{KCl}}{a_{NaCl}}=\frac{1.2}{1.05}$

Now since $\rho=\frac{Z\times M}{N_A\times a^3}$

We will have $\frac{\rho_{NaCl}}{\rho_{KCl}}=\left(\frac{a_{KCl}}{a_{NaCl}}\right)^3\left(\frac{M_{NaCl}}{M_{KCl}}\right)$

$$=\left(\frac{1.2}{1.05}\right)^3\times\left(\frac{58.5}{74.5}\right)=1.172$$

19. The density of CsBr which has bcc structure is 4.4 g cm^{-3}. The unit cell has edge length a pm. Calculate the inter ionic distance in crystals of CsBr (Atomic mass Cs = 133, Br = 80)

Sol. $a^3=\frac{2\times213}{4.4\times6.023\times10^{23}}$ $\left[\text{Formula } \rho=\frac{Z\times M}{N_A\times a^3}\right]$

$a=5.438\times10^{-8}$ cm

For bcc lattice the interionic distance

$$r^+ + r^- = \frac{\sqrt{3}}{2}\times a=\frac{1.732\times5.438\times10^{-8}}{2}=470.9\text{ pm}$$

20. If the radius of Cs^+ is 169 pm and that of Cl^- is 181 pm. Predict the structure of CsCl. What is the coordination number of Cs^+ ion?

Sol. $\frac{r_c}{r_a}=\frac{169}{181}=0.94$

Since the value is greater than 0.732, the structure of CsCl is bcc. Its coordination number is 8.

21. The nearest neighbour Ag atoms in the silver crystal are 2.5×10^{-8} cm. Presuming fcc structure of the crystal, what will be the density of the silver? [At. wt. of Ag = 108 mol^{-1}]

Sol. We know that the nearest neighbour distance between the silver atoms is half of the face diagonal which is related to the edge length a by $\frac{\sqrt{2}.a}{2}$

$\frac{\sqrt{2}.a}{2}=2.5\times10^{-8}$ cm or $a=3.53\times10^{-8}$ cm

Hence density $\rho=\frac{Z\times M}{N_A\times a^3}=\frac{4\times108}{6.023\times10^{23}(3.53\times10^{-8})^3}$

$=16.3$ g cm^{-3}

22. LiI occurs as a cubical closest packing. If the edge length of the unit cell is 624 pm, determine the ionic radii of Li^+ and I^- ions

Sol. The cubical closest packing has fcc unit cell. I^- ions occupy the corner and the face centers. These ions touch each other along the face diagonal of the cube. Hence

$$4r_{I^-}=\sqrt{2}.a$$

or $r_{I^-}=\frac{a}{2\sqrt{2}}=\frac{624\text{pm}}{2(1.414)}=220.65$ pm

Along the edge we have I^- Li^+ I^- arrangement where I^- are at the corners and Li^+ at the centre of the edge (Octahedral void)

$\therefore$ $2r_{I^-}+2r_{Li^+}=a$

$r_{Li^+}=\frac{a}{2}-r_{I^-}=\left(\frac{624}{2}-220.65\right)$pm $=91.35$ pm

23. Calculate the packing fraction for Ca unit cell, given that Ca crystallises in face centred cube unit cell

Sol. The rank of fcc unit cell = 4

The atomic radius $r=\frac{\sqrt{2}.a}{4}$

(The atoms touch along face diagonal)

Volume of 4 atoms

$$=4\times\frac{4}{3}\pi r^3=4\times\frac{4}{3}\pi\left(\frac{\sqrt{2}.a}{4}\right)^3=\frac{\sqrt{2}\,\pi a^3}{6}$$

Packing fraction $=\frac{\sqrt{2}\,\pi a^3}{6}\Big/a^3=0.74$

24. The first order reflection of a beam of X-rays of wavelength 1.54Å from the (100) plane of a crystal of the simple cubic type occurs at an angle of 11.29. Calculate the length of the unit cell (sin 11.29° = 0.1991)

Sol. $n\lambda=2d\sin\theta$

$1\times1.54\times10^{-8}$ cm $=2\times d\times\sin11.29$

$d=3.68\times10^{-8}$ cm

Further

$d=\frac{a}{\sqrt{h^2+k^2+\ell^2}}$ or $3.68\times10^{-8}=\frac{a}{\sqrt{1^2+0^2+0^2}}$

or $a=3.68\times10^{-8}$ cm

Exercise-1 | NCERT Based Questions

Very Short/Short Answer Questions

1. How can you convert NaCl structure into CsCl structure and vice versa?
2. What are coordination number of each ion present in the cubic close packed structure of Na_2O at ordinary temperature and pressure?
3. AgI crystallises in cubic close packed ZnS structure. What fraction of tetrahedral sites are occupied by Ag^+ ions?
4. How does the electrical conductivity of superconductors vary with temperature?
5. What makes the crystal of KCl appear sometimes violet?
6. Pure silicon is an insulator. Silicon doped with phosphorus is a semiconductor. Silicon doped with gallium is also a semiconductor. What is the difference between the two doped silicon semiconductors?
7. Account for following:
   (*a*) Silicon is an insulator but silicon doped with phosphorous acts as a semiconductor.
   (*b*) Some of glass objects recovered from ancient monuments look milky instead of being transparent.
8. Copper crystallises in fcc lattice and has density of $8{\cdot}930\ g\ cm^{-3}$ at 293 K. Calculate the radius of copper atom. Atomic mass of Cu = 63·55 amu, Avogadro's constant, $N_A = 6{\cdot}02 \times 10^{23}$.
9. A compound is formed by two elements M and N. The element N forms ccp and atoms of M occupy 1/3 rd of tetrahedral voids. What is the formula of the compound?
10. Which of these two $CdCl_2$ and NaCl will produce schottky defect, if added to a AgCl crystal?
11. Why is Fe_3O_4 ferrimagnetic at room temperature but becomes paramagnetic at 850 K?
12. Why does LiCl acquire pink colour when heated in Li vapours?
13. Which stoichiometric defect in crystals increases the density of a solid?
14. How many atoms constitute one unit cell of a face-centered cubic crystal?
15. (a) What type of semiconductor is obtained when silicon is doped with boron?
    (b) What type of magnetism is shown in the following alignment of magnetic moments?
    ↑↑↑↑↑↑
    (c) What type of point defect is produced when Ag*Cl* is doped with CdCl_2?
16. The unit cell of an element of atomic mass 108 u and density $10.5\ g\ cm^{-3}$ is a cube with edge length, 409 pm. Find the type of unit cell of the crystal.
    [Given: Avogadro's constant = $6.023 \times 10^{23}\ mol^{-1}$]
17. The radius of Na^+ ion is 94 pm and that of Cl^- ion is 181 pm. Predict whether the coordination number of Na^+ ion is 6 or 4.

Multiple Choice Questions

18. How many Cl^- ions are there around Na^+ ion in NaCl crystal?
    (a) 3
    (b) 4
    (c) 6
    (d) 8
19. Which of the following is the incorrect statement?
    (a) NaCl has 6 : 6 coordination and CsCl has 8 : 8 coordination.
    (b) In Na_2O each oxide ion is coordinated by $8Na^+$ ions and each Na^+ ion by 4 oxide ions
    (c) NaCl structure transform to CsCl structure on heating
    (d) In CaF_2 structure each F^- ion is coordinated by 4 Ca^{2+} and vice-versa.
20. Which of the following is a correct statement ?
    (a) Bonding in metallic crystals is directional
    (b) Diamond has two dimensional crystal lattice
    (c) Co-ordination number of bcc lattice is 12
    (d) A ccp structure has 8 tetrahedral and 4 Octahedral interstices.
21. The r_+ / r_- ratio of ZnS is 0.402. Pick out the false statements of the following
    (a) ZnS is 4 : 4 coordination compound.
    (b) ZnS does not crystallize in rock salt type lattice because r_+ / r_- is too small to avoid overlapping of S^{2-} ions.
    (c) Zn^{2+} ion is too small to fit precisely into the octahedral voids of S^{2-} ions.
    (d) Zn^{2+} ion is too large to fit into the octahedral voids of S^{2-} ions.
22. The unit cell dimensions of a cubic lattice (edges a, b, c and the angles between them, α, β and γ) are
    (a) $a = b = c, \alpha = \beta = \gamma = 90^0$
    (b) $a = b \neq c, \alpha = \beta = \gamma = 90^0$
    (c) $a = b = c, \alpha = \gamma = 90^0, \beta \neq 90^0$
    (d) $a \neq b \neq c, \alpha = \beta = 90^0, \gamma \neq 90^0$
23. A NaCl crystal is changed into CsCl type structure by:
    (a) increasing temperature and decreasing pressure.
    (b) increasing pressure and decreasing temperature.
    (c) increasing both temperature and pressure
    (d) None of these.
24. M_2X has anti fluorite structure. In such structure
    (a) X^{--} ions occupy all the 8 octahedral voids
    (b) Each X^{--} is surrounded by 4 M^+ in tetrahedral arrangement
    (c) Larger cations occupy the position of F^- ions and smaller anions that of C^{++} ions
    (d) Smaller cations occupy the position of F^- ions and larger anions that of C^{++} ions

25. For two ionic solids CaO and KI, identify the wrong statement amongst the following :

(a) The lattice energy of CaO is much large than that of KI

(b) KI is more soluble in water

(c) KI has higher melting point

(d) CaO has higher melting point

26. For a covalent solid, the units which occupy lattice points are:

(a) atoms (b) ions

(c) molecules (d) electrons

27. Graphite is a

(a) molecular solid (b) covalent solid

(c) ionic solid (d) metallic solid

Exercise-2 | CONCEPTUAL MCQs

1. Which of the following is not a crystalline solid?

(a) KCl (b) CsCl

(c) Glass (d) Rhombic S

2. Among solids, the highest melting point is exhibited by

(a) Covalent solids (b) Ionic solids

(c) Pseudo solids (d) Molecular solids

3. The major binding force of diamond, silicon and quartz is

(a) electrostatic force

(b) electrical attraction

(c) covalent bond force

(d) non-covalent bond force

4. The maximum proportion of available volume that can be filled by hard spheres in diamond is

(a) 0.52 (b) 0.34

(c) 0.32 (d) 0.68

5. The packing fraction for a body-centred cubic is

(a) 0.42 (b) 0.53

(c) 0.68 (d) 0.82

6. In a solid AB having the NaCl type structure, 'A' atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is

(a) AB_2 (b) A_2B

(c) A_4B_3 (d) A_3B_4

7. A substance A_xB_y crystallizes in a face centred cubic (fcc) lattice in which atoms 'A' occupy each corner of the cube and atoms 'B' occupy the centres of each face of the cube. Identify the correct composition of the substance A_xB_y

(a) AB_3

(b) A_4B_3

(c) A_3B

(d) Composition can't be specified

8. Crystals can be classified into basic crystal habits, equal to

(a) 7 (b) 4

(c) 14 (d) 2

9. Tetragonal crystal system has the following unit cell dimensions

(a) $a = b = c, \alpha = \beta = \gamma = 90°$

(b) $a = b \neq c, \alpha = \beta = \gamma = 90°$

(c) $a \neq b \neq c, \alpha = \beta = \gamma = 90°$

(d) $a = b \neq c, \alpha = \beta = 90° \ \gamma = 120°$

10. A match box exhibits

(a) cubic geometry

(b) monoclinic geometry

(c) tetragonal geometry

(d) orthorhombic geometry.

11. When molten zinc is cooled to solid state, it assumes hcp structure. Then the number of nearest neighbours of zinc atom will be

(a) 4 (b) 6

(c) 8 (d) 12

12. Co-ordination number of Na^+ in NaCl is

(a) 4 (b) 3

(c) 6 (d) 5

13. A crystal lattice with alternate +ve and –ve ions has radius ratio 0.524. Its co-ordination number is

(a) 4 (b) 3

(c) 6 (d) 12

14. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00 g?

[Atomic masses : Na = 23, Cl = 35.5]

(a) 2.57×10^{21} unit cells (b) 5.14×10^{21} unit cells

(c) 1.28×10^{21} unit cells (d) 1.71×10^{21} unit cells

15. Which of the following is example of body centred cube ?

(a) Mg (b) Zinc

(c) Copper (d) Sodium

16. Which of the following describes the hexagonal close packed arrangement of spheres?

(a) ABCABA (b) ABCABC

(c) ABABA (d) ABBABB

17. A metallic crystal crystallizes into a lattice containing a sequence of layers AB AB AB......Any packing of spheres leaves out voids in the lattice. What percentage of volume of this lattice is empty space?

(a) 74% (b) 26%

(c) 50% (d) none of these.

18. In crystal structure of sodium chloride, the arrangement of Cl^- ions is

(a) fcc (b) bcc

(c) Both fcc and bcc (d) None of these.

19. The intermetallic compound LiAg crystallizes in cubic lattice in which both lithium and silver have co-ordination number of eight. The crystal class is
(a) simple cubic (b) body centred cubic
(c) face-centred cubic (d) None of these

20. In the crystals of which of the following ionic compounds would you expect maximum distance between the centres of the cations and anions?
(a) LiF (b) CsF
(c) CsI (d) LiI

21. Potassium crystallizes with a
(a) body-centred cubic lattice
(b) face-centred cubic lattice
(c) simple cubic lattice
(d) orthorhombic lattice

22. The range of radius ratio (cationic to anionic) for an octahedral arrangement of ions in an ionic solid is
(a) 0 – 0.155 (b) 0.155 – 0.225
(c) 0.225 – 0.414 (d) 0.414 – 0.732

23. The interionic distance for cesium chloride crystal will be
(a) a (b) $\frac{a}{2}$
(c) $\frac{\sqrt{3}a}{2}$ (d) $\frac{2a}{\sqrt{3}}$

24. Which of the following has hcp crystal stucture?
(a) NaCl (b) CaCl
(c) Zn (d) RbCl

35. In the fluorite structure, the coordination number of Ca^{2+} ion is :
(a) 4 (b) 6
(c) 8 (d) 3

26. For an ionic crystal of the general formula AX and co-ordination number 6, the radius ratio value will be
(a) greater than 0.73 (b) between 0.73 and 0.41
(c) between 0.41 & 0.22 (d) Less than 0.22

27. In CsCl, if coordination number of Cs^+ is 8, then coordination number of Cl^- ion is :
(a) 4 (b) 6
(c) 8 (d) 12

28. The number of unit cells in 58.8 g of NaCl is nearly
(a) 6×10^{20} (b) 3×10^{22}
(c) 1.5×10^{23} (d) 0.5×10^{24}

29. An element has bcc structure having unit cells 12.08×10^{23}. The number of atoms in these cells is
(a) 12.08×10^{23} (b) 24.16×10^{23}
(c) 48.38×10^{23} (d) 12.08×10^{22}

30. An element (atomic mass = 100 g / mol) having bcc structure has unit cell edge 400 pm. Then, density of the element is
(a) $10.376\ g/cm^3$ (b) $5.188\ g/cm^3$
(c) $7.289\ g/cm^3$ (d) $2.144\ g/cm^{36}$

31. The edge length of face centred unit cubic cell is 508 pm. If the radius of the cation is 110 pm, the radius of one anion is
(a) 144 pm (b) 288 pm
(c) 618 pm (d) 398 pm

32. When electrons are trapped into the crystal in anion vacancy, the defect is known as :
(a) Schottky defect (b) Frenkel defect
(c) Stoichiometric defect (d) F-centres

33. In the laboratory, sodium chloride is made by burning sodium in the atmosphere of chlorine. The salt obtained is yellow in colour. The cause of yellow colour is
(a) Presence of Na^+ ions in the crystal lattice
(b) Presence of Cl^- ions in the crystal lattice
(c) Presence of electrons in the crystal lattice
(d) Presence of face centred cubic crystal lattice.

34. Schottky defect in crystals is observed when
(a) unequal number of cations and anions are missing from the lattice
(b) equal number of cations and anions are missing from the lattice
(c) an ion leaves its normal site and occupies an interstitial site
(d) density of the crystal is increased

35. Which of the following has Frenkel defects?
(a) Sodium chloride (b) Graphite
(c) Silver bromide (d) Diamond

36. Which of the following crystals does not exhibit Frenkel defect?
(a) AgBr (b) AgCl
(c) KBr (d) ZnS

37. Due to Frenkel defect, the density of ionic solids
(a) decreases (b) increases
(c) neither (a) nor (b) (d) does not change

38. A solid with high electrical and thermal conductivity from the following is
(a) Si (b) Li
(c) NaCl (d) Ice

39. If we mix a pentavalent impurity in a crystal lattice of germanium, what type of semiconductor formation will occur?
(a) p-type (b) n-type
(c) both (a) and (b) (d) None of the two.

40. The addition of arsenic to germanium makes the latter a
(a) metallic conductor (b) intrinsic semiconductor
(c) mixed conductor (d) extrinsic semiconductor

41. A semiconductor of Ge can be made p-type by adding
(a) trivalent impurity (b) tetravalent impurity
(c) pentavalent impurity (d) divalent impurity

42. On doping Ge metal with a little of Ga, one gets
(a) p-type semi conductor (b) n-type semi conductor
(c) insulator (d) rectifier

43. The pure crystalline substance on being heated gradually first forms a turbid liquid at constant temperature and still at higher temperature turbidity completely disappears. The behaviour is a characteristic of substance forming.
(a) Allotropic crystals (b) Liquid crystals
(c) Isomeric crystals (d) Isomorphous crystals.

44. If one end of a piece of a metal is heated the other end becomes hot after some time. This is due to
(a) Energised electrons moving to the other part of the metal
(b) resistance of the metal
(c) mobility of atoms, in the metal
(d) minor perturbation in the energy of atoms.

45. Which of the following is ferroelectric compound?
(a) $BaTlO_3$ (b) $K_4[Fe(CN)_6]$
(c) Pb_2O_3 (d) None of these

46. Which of the folliowing metal oxides is anti-ferromagnetic in nature?
(a) MnO_2 (b) TiO_2
(c) VO_2 (d) CrO_2

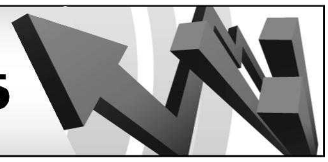
47. Among the following which compound will show the highest lattice energy?
(a) KF (b) NaF
(c) CsF (d) RbF

48. The existence of a substance in more than one solid modifications is known as
(a) Isomorphism
(b) Polymorphism
(c) Amorphism
(d) Allotropy

49. The second order Bragg diffraction of X-rays with $\lambda = 1.0Å$ from a set of parallel planes in a metal occurs at an angle of 60°. The distance between the scattering planes in the crystal is
(a) 0.575Å (b) 1.00Å
(c) 2.00Å (d) 1.15Å

50. Superconductors are derived from compounds of
(a) p-block elements (b) lanthanides
(c) actinides (d) transition elements

Exercise-3 | PAST COMPETITION MCQs



1. If NaCl is doped with 10^{-4} mol % of $SrCl_2$, the concentration of cation vacancies will be $(N_A = 6.02 \times 10^{23}\ mol^{-1})$ **[CBSE-PMT 2007]**
(a) $6.02 \times 10^{16}\ mol^{-1}$ (b) $6.02 \times 10^{17}\ mol^{-1}$
(c) $6.02 \times 10^{14}\ mol^{-1}$ (d) $6.02 \times 10^{15}\ mol^{-1}$

2. The fraction of total volume occupied by the atoms present in a simple cube is **[CBSE-PMT 2007]**
(a) $\frac{\pi}{3\sqrt{2}}$ (b) $\frac{\pi}{4\sqrt{2}}$ (c) $\frac{\pi}{4}$ (d) $\frac{\pi}{6}$

3. If '*a*' stands for the edge length of the cubic systems : simple cubic, body centred cubic and face centred cubic, then the ratio of radii of the spheres in these systems will be respectively, **[CBSE-PMT 2008]**
(a) $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$ (b) $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$
(c) $\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{3}}{2}a$ (d) $1a : \sqrt{3}a : \sqrt{2}a$

4. With which one of the following elements silicon should be doped so as to give *p*-type of semiconductor ? **[CBSE-PMT 2008]**
(a) Germanium (b) Arsenic (c) Selenium (d) Boron

5. AB; crystallizes in a body centred cubic lattice with edge length '*a*' equal to 387 pm. The distance between two oppositely charged ions in the lattice is : **[CBSE-PMT 2010]**
(a) 335 pm (b) 250 pm (c) 200 pm (d) 300 pm

6. Among the following which one has the highest cation to anion size ratio? **[CBSE-PMT 2010]**
(a) NaF (b) CsI (c) CsF (d) LiF

7. A solid compound XY has NaCl structure. If the radius of the cation is 100 pm, the radius of the anion (Y^-) will be : **[CBSE-PMT 2011 M]**
(a) 275.1 pm (b) 322.5 pm (c) 241.5 pm (d) 165.7 pm

8. A metal crystallizes with a face-centered cubic lattice. The edge length of the unit cell is 408 pm. The diameter of the metal atom is : **[CBSE-PMT 2012]**
(a) 288 pm (b) 408 pm
(c) 144 pm (d) 204 pm

9. A metal has a *fcc* lattice. The edge length of the unit cell is 404 pm. The density of the metal is 2.72 g cm^{-3}. The molar mass of the metal is : (N_A Avogadro's constant = $6.02 \times 10^{23}\ mol^{-1}$) **[NEET 2013]**
(a) 30 g mol^{-1} (b) 27 g mol^{-1}
(c) 20 g mol^{-1} (d) 40 g mol^{-1}

10. Which of the following statements about the interstitial compounds is incorrect ? **[NEET 2013]**
(a) They are chemically reactive.
(b) They are much harder then the pure metal.
(c) They have higher melting points than the pure metal.
(d) They retain metallic conductivity.

11. The number of carbon atoms per unit cell of diamond unit cell is : **[NEET 2013]**
(a) 8 (b) 6
(c) 1 (d) 4

12. Na and Mg crystallize in bcc and fcc type crystals respectively, then the number of atoms of Na and Mg present in the unit cell of their respective crystal is **[AIEEE 2002]**
(a) 4 and 2 (b) 9 and 14
(c) 14 and 9 (d) 2 and 4.

13. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00 g ?

[Atomic masses : Na = 23, Cl = 35.5] **[AIEEE 2003]**

(a) 5.14×10^{21} unit cells (b) 1.28×10^{21} unit cells

(c) 1.71×10^{21} unit cells (d) 2.57×10^{21} unit cells

14. What type of crystal defect is indicated in the diagram below? **[AIEEE 2004]**

$Na^+Cl^-Na^+Cl^-Na^+Cl^-$
Cl^- □ Cl^-Na^+ □ Na^+
Na^+Cl^- □ $Cl^-Na^+Cl^-$
$Cl^-Na^+Cl^-Na^+$ □ Na^+

(a) Interstitial defect

(b) Schottky defect

(c) Frenkel defect

(d) Frenkel & Schottky defects

15. An ionic compound has a unit cell consisting of A ions at the corners of a cube and B ions on the centres of the faces of the cube. The empirical formula for this compound would be **[AIEEE 2005]**

(a) A_3B (b) AB_3

(c) A_2B (d) AB

16. Total volume of atoms present in a face-centred cubic unit cell of a metal is (r is atomic radius) **[AIEEE 2006]**

(a) $\frac{12}{3}\pi r^3$ (b) $\frac{16}{3}\pi r^3$

(c) $\frac{20}{3}\pi r^3$ (d) $\frac{24}{3}\pi r^3$

17. In a compound, atoms of element Y form *ccp* lattice and those of element X occupy 2/3rd of tetrahedral voids. The formula of the compound will be **[AIEEE 2008]**

(a) X_4Y_3 (b) X_2Y_3 (c) X_2Y (d) X_3Y_4

18. Copper crystallises in *fcc* with a unit cell length of 361 pm. What is the radius of copper atom? **[AIEEE 2009]**

(a) 127 pm (b) 157 pm

(c) 181 pm (d) 108 pm

19. The edge length of a face centered cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is **[AIEEE 2010]**

(a) 288 pm (b) 398 pm (c) 618 pm (d) 144 pm

20. Percentages of free space in cubic close packed structure and in body centered packed structure are respectively **[AIEEE 2010]**

(a) 30% and 26% (b) 26% and 32%

(c) 32% and 48% (d) 48% and 26%

21. Lithium forms body centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be : **[AIEEE 2012]**

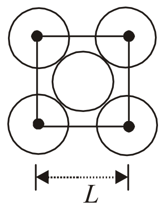
(a) 75 pm (b) 300 pm (c) 240 pm (d) 152 pm

22. Which of the following exists as covalent crystals in the solid state ? **[JEE M 2013]**

(a) Iodine (b) Silicon

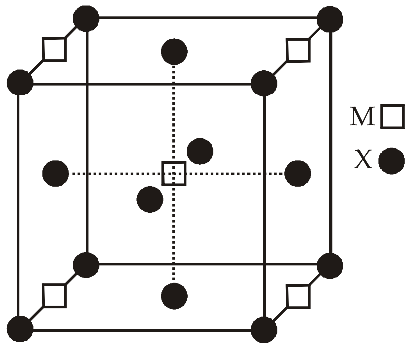
(c) Sulphur (d) Phosphorus

23. The packing efficiency of the two-dimensional square unit cell shown below is : **[IIT-JEE 2010]**



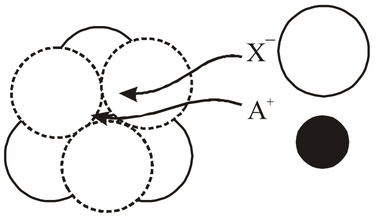
(a) 39.27% (b) 68.02% (c) 74.05% (d) 78.54%

24. A compound M_pX_q has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is **[IIT-JEE 2012]**



(a) MX (b) MX_2 (c) M_2X (d) M_5X_{14}

25. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is **[JEE Advanced 2013]**



(a) 104 pm (c) 183 pm (b) 125 pm (d) 57 pm

Exercise-4 | Applied MCQs

1. The radius of Li^+ ion is 60pm and that of F^- is 136 pm. Structure of LiF and coordination number is

(a) Like NaCl, C.No. = 6 (b) Like CsCl, C.No. = 8

(c) Anti fluoride, C.No. = 8 (d) None of these

2. Atoms A are arranged in ccp array. Atoms B occupy all octahedral voids and half of the tetrahedral voids. The formula of compound AB is

(a) AB_2 (b) A_2B

(c) AB (d) Al_2B_3

3. If Germanium crystallises in the same way as diamond, then which of the following statement is not correct?

(a) Every atom in the structure is tetrahedrally bonded to 4 atoms.

(b) Unit cell consists of 8 Ge atoms and co-ordination number is 4.

(c) All the octahedral voids are occupied.

(d) All the octahedral voids and 50% tetrahedral voids remain unoccupied.

4. Amorphous solid may be classified as

(a) Isotropic and superheated solid

(b) Isoenthalpic and superheated liquid

(c) Isotropic and supercooled liquids

(d) Anisotropic and supercooled liquids

5. In a solid lattice the cation has left a lattice site and is located at an interstitial position, the lattice defect is :

(a) Interstitial defect (b) Valency defect

(c) Frenkel defect (d) Schottky defect

6. Which of the following will not adopt CsCl structure ?

(a) CsF (b) CsBr

(c) CsS (d) CsCN

7. Sodium metal crystallises in bcc lattice with the cell edge, a = 4.29 Å. What is the radius of sodium atom?

(a) 1.79 Å (b) 1.89Å

(c) 4Å (d) 3.2Å

8. Which of the following statements is wrong ?

(a) The coordination number of each type of ion in CsCl crystal is 8.

(b) A metal that crystallizes in bcc structure has a coordination number of 12.

(c) A unit cell of an ionic crystal shares some of its ions with other unit cells.

(d) The length of the unit cell in NaCl is 552 pm. (r_{Na+} = 95 pm; r_{Cl^-}=181 pm).

9. Argon crystallizes in a structure in which the atoms are located at the postions (0, 0, 0)

$\left(0,\frac{1}{2},\frac{1}{2}\right),\left(\frac{1}{2},0,\frac{1}{2}\right)and\left(\frac{1}{2},\frac{1}{2},0\right)$. The unit cell is

(a) simple cubic

(b) body-centred cubic

(c) face-centred cubic

(d) hexagonal close packed

10. In NaCl, the centre-to-centre nearest-neighbour distance of ions is

(a) $\frac{1}{4}a$ (b) $\frac{\sqrt{3}}{2}a$

(c) $\frac{1}{2}a\sqrt{2}$ (d) $\frac{1}{2}a$

11. Consider the radii 0.095 nm (Na^+), 0.181 nm (Cl^-), 0.074 nm (Zn^{2+}), 0.184 nm (S^{2-}), 0.068 nm (Ti^{4+}), 0.140 nm (O^{2-}), 0.169 nm (Cs^+). Choose the correct option from among the following. (Use radius ratio rules)

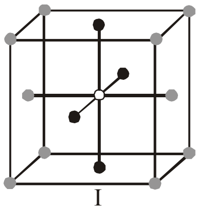
(a) Na^+ ions are packed in octahedral holes between the planes of close-packed Cl^- ions.

(b) Zn^{2+} ions are packed in tetrahedral holes

(c) Cs^+ ions are packed in a simple cubic array of Cl^- ions

(d) All of these

12. Consider the following fcc unit cells choose the correct option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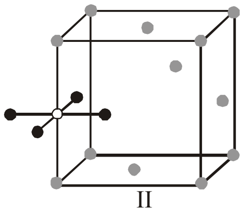
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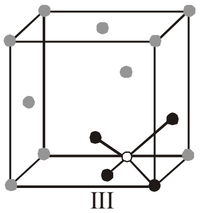
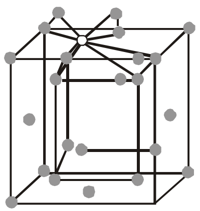

III


IV

(a) I and II represent tetrahedral holes

(b) II, III and IV represent tetrahedral holes

(c) I and II represent octahedral holes

(d) I, II and IV represent octahedral holes

13. Which of the following is the incorrect statement

(a) NaCl has 6 : 6 coordination and CsCl has 8 : 8 coordination.

(b) In Na_2O each oxide ion is coordinated by $8Na^+$ ions and each Na^+ ion by 4 oxide ions

(c) NaCl structure transform to CsCl structure on heating

(d) In CaF_2 structure each F^- ion is coordinated by 4 Ca^{2+} and vice versa.

14. The compound having the lowest lattice energy

(a) NaF (b) CsF

(c) KF (d) RbF

15. In the unit cell of KCl, Cl^- ions constitute ccp and K^+ ions fall into the octahedral holes. These holes are

(a) one at the centre and 12 are at the centres of the edges.

(b) one at the centre and 6 at the centres of the faces.

(c) 8 at the corners of 8 small cubes forming the unit cell

(d) None is correct

16. The non stoichiometric compound $Fe_{0.94}O$ is formed when x % of Fe^{2+} ions are replaced by as many $\frac{2}{3}Fe^{3+}$ ions, x is

(a) 18 (b) 12

(c) 15 (d) 6

17. The incorrect statement for the sulphur atom of ZnS is

(a) As S^{2-} is larger than Zn^{2+} only 4 rather than 6 or 8 S^{2-} can be packed around Zn^{2+}

(b) Its structure is similar to diamond except that alternate atoms are Zn and S

(c) As S^{2-} is larger than Zn^{2+} only 6 rather than 8 or 4 sulphide ions can be placed around Zn^{2+} ions

(d) ZnS is a covalent compound

18. In KBr crystal structure, the second nearest neighbour of K^+ ion will be............. and its number is

(a) K^+, 12 (b) K^+, 6

(c) Br^-, 12 (d) Br^-, 6

19. Which of the following expression is correct for CsCl unit cell with lattice parameter a

(a) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$ (b) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}a}{2}$

(c) $r_{Cs^+} + r_{Cl^-} = \frac{a}{\sqrt{2}}$ (d) $r_{Cs^+} + r_{Cl^-} = 2a$

20. For a cubic crystal, the lattice parameter, a is 300 pm. The spacing (d) for (111) plane will be

(a) 212.1 pm (b) 259.8 pm

(c) 173.2 pm (d) 300 pm

21. Which of the following is a correct statement ?

(a) Bonding in metallic crystals is directional

(b) Diamond has two dimensional crystal lattice

(c) Co-ordination number of bcc lattice is 12

(d) A ccp structure has 8 tetrahedral and 4 Octahedral voids.

22. M_2X has anti fluorite structure. In such structure

(a) X^{--} ions occupy all the 8 octahedral voids

(b) each X^{--} is surrounded by 4 M^+ in tetrahedral arrangement

(c) larger cations occupy the position of F^- ions and smaller anions that of C^{++} ions

(d) smaller cations occupy the position of F^- ions and larger anions that of C^{++} ions

23. The coordination number X (........) of each ion in KBr is changed to Y (..........) by............

(a) X = 6 to Y = 8 applying higher temperature

(b) X = 8 to Y = 6 applying high pressure

(c) X = 6 to Y = 8 applying high pressure

(d) None of these

24. The unit cell of diamond is made up of

(a) 6 C atoms, 4 atoms constitute ccp and 2 atoms occupy the half of octahedral voids

(b) 12 C atoms, 4 atoms form fcc lattice and 8 atoms occupy all tetrahedral holes

(c) 8 C atoms, 4 atoms constitute ccp and 4 atoms occupy all the octahedral voids

(d) 8 C atoms, 4 atoms form fcc lattice and 4 atoms occupy half of the tetrahedral voids alternately

25. CaO and NaCl have the same crystal structure and nearly the same ionic radii. If x is the lattice energy of NaCl, the lattice energy of CaO is very nearly

(a) x (b) 2x

(c) $\frac{x}{2}$ (d) 4x

26. Doping of AgCl crystals with $CdCl_2$ results in

(a) Frenkel defect

(b) Schottky defect

(c) Substitutional cation vacancy

(d) Formation of F - centres

27. NaCl is doped with 2×10^{-3} mole % of $SrCl_2$. The concentration of cation vacancies is

(a) 12.04×10^{20} per mol

(b) 3.01×10^{18} per mol

(c) 6.02×10^{18} per mol

(d) 12.04×10^{18} per mol

28. NH_4Cl crystallises in a bcc lattice with edge length of unit cell equal to 387 pm. If the radius of the Cl^- ion is 181 pm, the radius of $\overset{+}{N}H_4$ ions is

(a) 366.3 pm (b) 154.1 pm

(c) 92.6 pm (d) None of these

29. A metal crystallizes in 2 cubic phases fcc and bcc whose unit cell lengths are 3.5 Å and 3.0Å respectively. The ratio of their densities is

(a) 0.72 (b) 2.04

(c) 1.46 (d) 3.12

30. In a cubic closed packed structure of mixed oxides, the lattice is made up of oxide ion, 20% of tetrahedral voids are occupied by divalent X^{2+} ions and 50% of the octahedral voids are occupied by trivalent Y^{3+} ions. The formula of the oxide is

(a) $X.Y_2O_4$ (b) $X_4Y_5O_{10}$

(c) $X_5Y_4O_{10}$ (d) X_2YO_4

31. The ranks of atoms in face centred cubic and hexagonal unit cells respectively are

(a) 6, 4 (b) 4, 6

(c) 1, 6 (d) 2, 6

32. Al (at. wt 27) crystallizes in the cubic system with a cell edge of 4.05 Å. Its density is 2.7 g per cm^3. Determine the unit cell type calculate the radius of the Al atom

(a) fcc, 2.432 Å (b) bcc, 2.432 Å

(c) bcc, 1.432 Å (d) fcc, 1.432 Å

33. The ratio of inner planar distancess of three types of planes $(d_{100}, d_{110}, d_{111})$ for simple cubic lattice are

(a) $1:\frac{1}{\sqrt{2}}:\frac{1}{\sqrt{3}}$ (b) $\frac{1}{\sqrt{3}}:\frac{1}{\sqrt{2}}:1$

(c) $\sqrt{3}:\sqrt{2}:1$ (d) $1:\sqrt{2}:\sqrt{3}$

34. In mineral MX_2, M^{2+} does ccp and X^- occupy the tetrahedral voids. The number of cations and anions per unit cell, the coordination number of cation and percent of tetrahedral voids occupied are

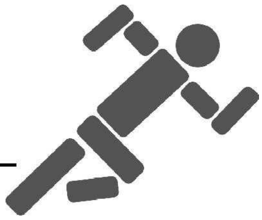
(a) 8, 4, 8, 100 % (b) 8, 4, 8, 50%

(c) 4, 8, 8, 50% (d) 4, 8, 8, 100%

35. Iron crystallizes in several modifications. At about 911°C, the bcc 'α' form undergoes a trasition to fcc 'γ' form. If the distance between the two nearest neighbours is the same in the two forms at the transition temperature, the ratio of the density of iron in fcc form (ρ_2) to that of iron of bcc form (ρ_1) at the transition temperature

(a) $\frac{\rho_1}{\rho_2} = 0.918$ (b) $\frac{\rho_1}{\rho_2} = 0.718$

(c) $\frac{\rho_1}{\rho_2} = 0.518$ (d) $\frac{\rho_1}{\rho_2} = 0.318$



Hints & Solutions

EXERCISE 1

1. $\underset{(CN\ 6:6)}{\text{NaCl structure}} \underset{\text{Heat to 760K}}{\overset{\text{High Pressure}}{\rightleftharpoons}} \underset{(CN8:8)}{\text{CsCl structure}}$

3. In the face-centred unit cell, there are eight tetrahedral voids. Of these, half are occupied by silver cations.

4. Electrical conductivity increases with decrease of temperature.

8. 128 pm.

9. The formula of the compound will be = N_3M_2 or M_2N_3.

18. (c) 19. (c) 20. (d) 21. (d) 22. (a)
23. (b) 24. (d) 25. (c) 26. (a) 27. (b)

EXERCISE 2

1. **(c)** Glass is amorphous solid.
2. **(a)** Covalent as in case of diamond.
3. **(c)** Covalent bond force (see text).
4. **(b)** The volume to be filled by hard spheres in diamond is 0.34.
5. **(c)** The p.f. for body centred cube = 0.68 (see text).
6. **(d)** In NaCl structure we have particles at (8 corners + 6 faces) one type. (12 edges + 1 in body) other type.
A atoms are at eight corners. Removal of atoms along one axis from face means removal of two A atoms.

$$\therefore \text{Number of A atoms} = \frac{1}{8}\times 8+\frac{1}{2}\times 4 = 3$$

$$\text{Number of B atoms} = \frac{1}{4}\times 12+1 = 4. \qquad \therefore A_3B_4.$$

7. **(a)** Number of A atoms $= \frac{1}{8}\times 8 = 1$

$$\text{Number of B atoms} = \frac{1}{2}\times 6 = 3$$

$\therefore$ Formula AB_3

8. **(a)** Seven crystal systems.
9. **(b)** For tetragonal $a = b \neq c$, $\alpha=\beta=\gamma=90°$
10. **(d)** Match box is orthorhombic $a \neq b \neq c;\ \alpha=\beta=\gamma=90°$
11. **(d)** Number of nearest neighbours means coordination number = 12.
12. **(c)** Coordination number 6. (See Text)
13. **(c)** $\frac{r^+}{r^-} = 0.524$. It is in between 0.414 – 0.732.
Hence C. No. = 6.
14. **(a)** Number of unit cells $= \frac{N_A\times \text{Weight of substance}}{\text{M. Wt.}\times Z}$

$$= \frac{6.023\times 10^{23}\times 1}{58.5\times 4} = 2.57\times 10^{21}\ \text{unit cells}.$$

15. **(d)** Na has Body centred cubic lattice.
16. **(c)** ABAB is hexagonal close packing.
17. **(b)** In AB AB packing spheres occupy 74%. 26% is empty.
18. **(a)** Arrangement of Cl^- ions is fcc in NaCl
19. **(b)** In bcc each atom has C. No. = 8.
20. **(c)** In CsI since Cs^+ and I^- have largest size.
21. **(a)** Potassium crystallises in BCC lattice.
22. **(d)** For octahedral $r^+/r^- = 0.414 - 0.732$.
23. **(c)** CsCl is body centred. Therefore $2r^+ + 2r^- = \sqrt{3}.a$ body diagonal.

$$\therefore r^+ + r^- = \frac{\sqrt{3}\,a}{2}.$$

24. **(c)** Zn has hcp lattice.
25. **(c)** In fluorite structure the C.No. of Ca^{++} is 8. See structure of simple ionic compounds.
26. **(b)** Since C.No. is 6 it is octahedral and $\frac{r^+}{r^-} = 0.414 - 0.73$.
27. **(c)** It is bcc hence, C. No. of each ion is 8.
28. **(c)** Number of unit cells $= \frac{N_A\times \text{Wt. of substance}}{\text{M. Wt.}\times Z}$

$$= \frac{6.023\times 10^{23}\times 58.8}{58.8\times 4} = 1.5\times 10^{23}$$

29. **(b)** Number of unit cells $= \frac{\text{Total number of molecules}}{(Z)}$

$\therefore$ Number of atoms $= 12.08\times 10^{23}\times 2 = 24.16\times 10^{23}$ (for bcc Z = 2)

30. **(b)** $\rho = \frac{Z\times M}{N_A\times a^3} = \frac{2\times 100}{6.023\times 10^{23}\times (400\times 10^{-10})^3}$

$$= 5.188\ g/cm^3$$

31. **(a)** $2r^+ + 2r^- = a$; (edge length)

$$\therefore 2\times 110+2r^- = 508 \quad \therefore r^- = 144\ \text{pm}$$

32. **(d)** F-centres (see text.)
33. **(c)** Due to presence of F-centres.
34. **(b)** It is stoichiometric defect and it is observed when equal number of cations and anions are missing from the lattice site.

35. **(c)** AgBr exhibit Frenkel defect.

36. **(c)** KBr does not exhibit Frenkel defect.

37. **(d)** No change in density (see text).

38. **(b)** From the given substances Li has high thermal & Electrical conductivity (due to metallic bond).

39. **(b)** n-type, since electron is set free.

40. **(d)** Extrinsic semiconductor (see text).

41. **(a)** p-type semiconductors are formed by doping 14 group elements with 13 group elements (valency 3).

42. **(a)** p-type semi-conductor.

43. **(b)** It is the property of liquid crystal.

44. **(a)** It is due to movement of energised electrons (KE $\propto$ T).

45. **(a)** $BaTlO_3$ (see text.)

46. **(a)** MnO_2 (see text).

47. **(b)** The smaller the size of cation and anion the more is lattice energy Na^+ has smaller size than others.

48. **(b)** Polymorphisms (see text).

49. **(d)** $n\lambda = 2d\sin\theta$;

$$2\times 1\text{Å} = 2\times d\sin 60 \Rightarrow d = 1.15\text{Å}\left(\sin 60 = \frac{\sqrt{3}}{2}\right)$$

50. **(a)** Superconductors are derived from compound of p block elements.

EXERCISE 3

1. **(b)** Since each Sr^{++} ion provides one cation vacancy, hence Concentration of cation vacancies = mole % of $SrCl_2$ added

$= 10^{-4}$ mole %

$$= \frac{10^{-4}}{100}\times 6.023\times 10^{23} = 6.023\times 10^{17}\ \text{mol}^{-1}$$

2. **(d)** Number of atoms per unit cell = 1

Atoms touch each other along edges. Hence $r = \frac{a}{2}$

(r = radius of atom and a = edge length)

$$\text{Therefore \% fraction} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$$

3. **(a)** Following generalization can be easily derived for various types of lattice arrangements in cubic cells between the edge length (a) of the cell and r the radius of the sphere.

For simple cubic : $a = 2r$ or $r = \frac{a}{2}$

For body centred cubic :

$$a = \frac{4}{\sqrt{3}}r \text{ or } r = \frac{\sqrt{3}}{4}a$$

For face centred cubic :

$$a = 2\sqrt{2}r \text{ or } r = \frac{1}{2\sqrt{2}}\,a$$

Thus the ratio of radii of spheres for these will be simple : bcc : fcc

$= \frac{a}{2} : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}\,a$ i.e. option (a) is correct answer.

4. **(d)** The semiconductors formed by the introduction of impurity atoms containing one elecron less than the parent atoms of insulators are termed as *p*-type semiconductors. Therefore silicon containing 14 electrons is to be doped with boron containing 13 electrons to give a *p*-type semi-conductor.

5. **(a)** For *bcc* lattice body diagonal = $a\sqrt{3}$.

The distance between the two oppositely charged ions

$$= \frac{a}{2}\sqrt{3}$$

$$= \frac{387\times 1.732}{2} = 335\text{pm}$$

6. **(c)** $\frac{M^+}{X^-}$ is highest in CsF

$\therefore$ correct choice : (c)

7. **(c)** Radius ratio of NaCl like crystal

$$= \frac{r^+}{r^-} = 0.414$$

$$r^- = \frac{100}{0.414} = 241.5\,\text{pm}$$

8. **(a)** For *ccp* $\sqrt{2}a = 4r$

$$\frac{\sqrt{2}\times 408}{2} = 2r \qquad (2r = \text{Diameter})$$

Diameter = 288.5

9. **(b)** Density is given by

$d = \frac{Z\times M}{N_A a^3}$; where Z = number of formula units present in unit cell, which is 4 for *fcc*

a = edge length of unit cell. M = Molecular mass

$$2.72 = \frac{4\times M}{6.02\times 10^{23}\times\left(404\times 10^{-10}\right)^3}$$

$(\because\ 1\text{pm} = 10^{-10}\text{cm})$

$$M = \frac{2.72\times 6.02\times (404)^3}{4\times 10^7} = 26.99$$

$= 27$ gm mole^{-1}

10. **(a)** In interstitial compounds small atoms like H, B & C enter into the void sites between the packed atoms of crystalline metal. They retain metallic conductivity and are chemically inert.

11. **(a)** Diamond is like ZnS. In diamond cubic unit cell, there are eight corner atoms, six face centered atoms and four more atoms inside the structure.

Number of atoms present in a diamond cubic cell

$$= 8\times\frac{1}{8} + 6\times\frac{1}{2} + 4 = 8$$

(corners) (face centered) (inside body)

12. **(d)** bcc - points are at corners & one in centre of the unit cell.

Number of atoms per unit cell = $8\times\frac{1}{8}+1=2$.

fcc - points are at the corners and also centre of the six faces of each cell.

Number of atoms per unit cell $=8\times\frac{1}{8}+6\times\frac{1}{2}=4$.

13. **(d)** Number of formulas in cube shaped crystals $=\frac{1.0}{58.5}\times 6.02\times 10^{23}$ since in NaCl type of structure 4 formula units form 'a' cell

$\therefore$ units cells $=\frac{1.0\times 6.02\times 10^{23}}{58.5\times 4}=2.57\times 10^{21}$ unit cells.

14. **(c)**

15. **(b)** Each corners is shared by 8 cubes and each face is shared by 2 faces

Number of A ions in the unit cell. $=\frac{1}{8}\times 8=1$

Number of B ions in the unit cell $=\frac{1}{2}\times 6=3$

Hence empirical formula of the compound $=AB_3$

16. **(b)** The face centered cubic unit cell contains 4 atom

$\therefore$ Total volume of atoms $=4\times\frac{4}{3}\pi r^3=\frac{16}{3}\pi r^3$

17. **(a)** From the given data, we have
Number of Y atoms in a unit cell = 4

Number of X atoms in a unit cell $=8\times\frac{2}{3}=\frac{16}{3}$

From the above we get the formula of the compound as $X_{16/3}Y_4$ or X_4Y_3

18. **(a)** For *fcc* unit cell, $4r=\sqrt{2}\,a$

$r=\frac{\sqrt{2}\times 361}{4}=127$ pm

19. **(d)** For an *fcc* crystal

$r_{\text{cation}}+r_{\text{anion}}=\frac{\text{edge length}}{2}$

$110+r_{\text{anion}}=\frac{508}{2}$

$r_{anion}=254-110=144$ pm

20. **(b)** Packing fraction is defined as the ratio of the volume of the unit cell that is occupied by the spheres to the total volume of the unit cell.
P.F. for *ccp* and *bcc* are 0.74 and 0.68 respectively.
So, the free space in *ccp* and bcc are 26% & 32% respectively.

21. **(d)** For *bcc* structure $\sqrt{3}\,a=4r$

$r=\frac{\sqrt{3}}{4}a=\frac{\sqrt{3}}{4}\times 351=152\,\text{pm}.$

22. **(b)** Among the given crystals, only silicon exists as a covalent solid. It has diamond like structure.

23. **(d)** Packing efficiency

$=\frac{\text{Area occupied by circles within the square}}{\text{Area of square}}$

$=\frac{2\pi r^2}{L^2}\times 100=\frac{2\pi r^2}{2(\sqrt{2}r)^2}\times 100=\frac{\pi}{4}\times 100=78.54\%$

24. **(b)** No. of M atoms $=\frac{1}{4}\times 4+1=1+1=2$

No. of X atoms $=\frac{1}{2}\times 6+\frac{1}{8}\times 8=3+1=4$

So, formula $=M_2X_4=MX_2$

25. **(a)** The arrangement given shows octahedral void arrangement-limiting radius ratio for octahedral void is

$\frac{r_{A^+}}{r_{X^-}}=0.414$

$r_{A^+}=0.414\times r_{X^-}=0.414\times 250=103.5\approx 104\,\text{pm}.$

EXERCISE 4

1. **(a)** $\frac{r+}{r-}$ ratio is $\frac{60}{136}=0.441$, Hence LiF has NaCl structure with CN = 6.

2. **(a)** **3.** **(c)**

4. **(c)** Amorphous solids are isotropic and supercooled liquids.

5. **(c)** Frenkel defect is due to dislocation of ion from its usual lattice site to interstitial position.

6. **(a)** CsF will not adopt CsCl structure due to small size of F^-.

7. **(b)** For bcc lattice we have $2r^+ + 2r^- = \sqrt{3}\,a$. In question we have $4r=\sqrt{3}.a$

$\therefore\ r=\frac{\sqrt{3}\times 4.29}{4}=1.89\text{Å}$.

8. **(b)** The crystals of CsCl has body - centred cubic unit cell. Hence, each ion in this structure has coordination number of eight. In case of crystals of NaCl two interpenetrating face-centred cubic lattices are present out of these one composed entirely of Na^+ ions and the other of Cl^- ions. Each Na^+ ion is located half way between two Cl^- ions and vice versa. A unit cell of NaCl crystal has Cl^- ions at the corners as well as at the face centres and Na^+ ions are located in octahedral voids. On each edge of cubic unit cell, there are two Cl^- ions and one Na^+ ions. Hence $a=2\left(r_{Na^+}+r_{Cl^-}\right)$

$=2\,(95\,\text{pm}+181\,\text{pm})=552\,\text{pm}$

9. **(c)** The planes indicate, the unit cell is fcc.

10. **(d)** In NaCl the Cl^- and Na^+ touch along edge of cube the distance between ions is $\frac{a}{2}$

11. (d) Calculate the $\frac{r+}{r-}$ ratio to get the limiting ratio value and consult the table. All are correct.

12. (c) Examine the nearest number of neighbours in (I) and (II). The number is six which is octahedral.

13. (c) CsCl (8 : 8 coordination) transform to NaCl (6 : 6 coordination) on heating but reverse is not possible.

14. (b) The coulombic attractions between Cs^+ and F^- ions is lowest due to larger size of Cs^+.

15. (a) One octahedral void is present at the body centre of the cube and 12 octahedral voids are present on the centres of the cube.

16. (a) The number of Fe^{3+} ions replacing x Fe^{2+} ions $= \frac{2x}{3}$

vacancies of cations $= x - \frac{2x}{3} = x/3$

But $x/3 = 1 - 0.94 = 0.06$, $x = 0.06 \times 3 = 0.18 = 18\%$

17. (a) Statement (a) is correct.

18. (a) The first nearest neighbour of K^+ ion will be 6 Br^- ions at a distance of a/2 and the second nearest neighbours will be 12 K^+ ions at a distance of $\frac{a\sqrt{2}}{2}$.

19. (b) CsCl has a bcc structure ions touching along body diagonal

20. (c) $d_{111} = \frac{a}{(1^2+1^2+1^2)^{1/2}} = \frac{a\sqrt{3}}{3} = \frac{300\sqrt{3}}{3} = 173.2$ pm

21. (d) The statement (d) is correct.

22. (d) The statement (d) is correct.

23. (c) The increase in pressure results in decrease in size of ions (more in case of anion than cation), the r^+/r^- increases and the coordination number also increase.

24. (d) The statement (d) is correct.

25. (d) Lattice energy $= \frac{\text{Product of charges}}{\text{Interionic distance}}$

In NaCl the product of charges = 1 × 1 = 1 and

In CaO it is 2 × 2 = 4

The interionic distance is almost same.

26. (c) The statement (c) is correct.

27. (d) The addition of one Sr^{2+} replaces $2Na^+$ and one cationic vacancy is created.

No. of cationic vacancy $= 2 \times 10^{-3}$ mole % of NaCl

$= \frac{2 \times 10^{-3}}{100} \text{mol}^{-1}$ of NaCl

$= 2 \times 10^{-5} \times 6.02 \times 10^{23} \text{mol}^{-1}$

$= 12.04 \times 10^{18} \text{mol}^{-1}$ of NaCl

28. (b) For bcc lattice

$2r^+ + 2\bar{r} = a\sqrt{3}$

$\therefore r_{NH_4^+} + r_{Cl^-} = \frac{a\sqrt{3}}{2} = \frac{387 \times 1.732}{2} = 335.1$

or, $r_{Cl^-} = 335.1 - 101.0 = 154.1$ pm

29. (c) $\frac{d_1}{d_2} = \frac{(a_2)^3}{(a_1)^3} \times \frac{z_1}{z_2} = \left(\frac{3}{3.5}\right)^3 \times \frac{4}{2} = 1.46$

30. (b)

Sphere	Tetrahedral void	Octahedral void
O^{2-}	X^{2+}	Y^{3+}
O	OO	O
1	$\frac{2 \times 20}{100}$	$\frac{50}{100}$
1	0.4	0.5
10	4	5

Hence formula $X_4Y_5O_{10}$

31. (b) No. of particles in face centered cubic unit cell

$= \frac{1}{8} \times 8$ (corners) $+ \frac{1}{2} \times 6$ (faces) $= 4$

No. of particles in hexagonal unit cell

$= \frac{1}{6} \times 12$ (corners) $+ \frac{1}{2} \times 2$(faces) + 3 (in the body) = 6

32. (d) $\rho = \frac{Z \times M}{N_o \times a^3}$,

$2.7 = \frac{Z \times 27}{6.02 \times 10^{23} \times (4.05)^3 \times 10^{-24}} \quad \therefore Z = 4$

Hence it is face centred cubic unit lattice.

Again $4r = a\sqrt{2} = 5.727$ Å

$\therefore r = 1.432$ Å

33. (a) $d_{hkl} = \frac{a}{(h^2+k^2+l^2)^{1/2}}$

Hence $d_{100} = a$, $d_{110} = \frac{1}{\sqrt{2}}$, $d_{111} = \frac{1}{\sqrt{3}}$

34. (d) The number of formula units in ccp (rank) = 4

$\therefore$ $4MX_2$

Hence number of cations $(M^{2+}) = 4$,

Anions $(X^-) = 8$

C. N. of cation = 8; All tetrahedral voids are occupied.

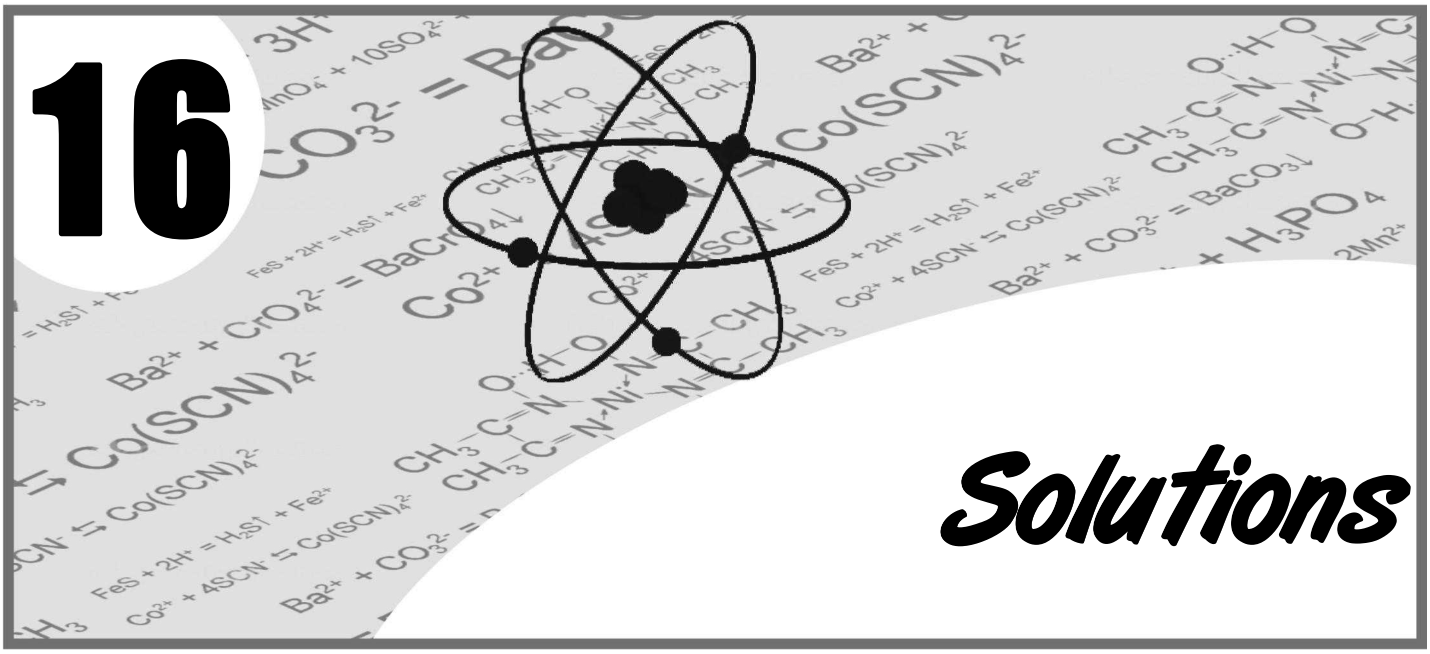
35. (a) In α – from distance between nearest neighbour atom is $\frac{\sqrt{3}a_1}{2}$.

In γ form distance between nearest neighbour atom is $\frac{a_2}{\sqrt{2}}$.

$\therefore \frac{\sqrt{3}a_1}{2} = \frac{a_2}{\sqrt{2}}$ (given)

or $\frac{a_2}{a_1} = \sqrt{\frac{3}{2}}$

$$\frac{\rho_1}{\rho_2} = \frac{z_1}{z_2}\left(\frac{a_2}{a_1}\right)^3 = \frac{1}{2}\left(\sqrt{\frac{3}{2}}\right)^3 = 0.918$$



16

Solutions

SOLUTION :

Homogeneous mixture of two or more non reacting components whose composition can be varied within certain limits is known as solution.

SOLUTE :

The component which is present relatively in smaller proportion in the solution is called solute.

SOLVENT :

The component which is present in larger proportion in solution is called solvent.

BINARY SOLUTION :

Containing two components only.

TYPES OF SOLUTIONS :

Depending upon the physical state of solute and solvent, the solutions may be of the following types.

S.No.	*Solute*	*Solvent*	*Example*
1.	Gas	Gas	gases in air
2.	Gas	Liquid	Aerated Water
3.	Gas	Solid	Occluded hydrogen
4.	Liquid	Gas	Moist air
5.	Liquid	Liquid	Alcohol in water, Toluene + Benzene
6.	Liquid	Solid	Mercury in Zinc amalgam
7.	Solid	Gas	Smog
8.	Solid	Liquid	Salt solution, Sugar solution
9.	Solid	Solid	Alloys

SOLUTIONS OF SOLIDS IN LIQUIDS :

(Solute = Solid and Solvent = Liquid)

(i) **Saturated solution :** A solution which remains in contact with excess of the solute is said to be saturated.

(ii) **Solubility :** The amount of solute dissolved in 100 g of a solvent to form a saturated solution at a given temperature is termed as the solubility of solute.

Soluble substances : Have solubility greater than 1g per 100 ml

Insoluble substances : Have solubility less than 0.001 g per 100 ml

Sparingly soluble substances : Have solubility less than 1g and more than 0.001 g per 100 ml.

(iii) **Factors influencing solubility :**

(a) **Temperature :** If the dissolution is endothermic the solubility increases with temperature e.g. $NaNO_2$, KNO_3, NaCl.

If the dissolution is exothermic the solubility decreases with temperature e.g. Li_2CO_3, Na_2CO_3, Na_2SO_4, $CeSO_4$

(b) **Nature of solute/solvent.**

SOLUBILITIES OF IONIC SOLIDS :

The smaller the value of **lattice energy** and more the value of **heat of hydration more** is the solubility of ionic compounds. Lattice energy depends upon force of attraction (F) between oppositely charged ions and is given by $F = \frac{qq'}{r^2D}$.

q, q' are charges, r distance between charges, D is the dielectric constant of medium. Dielectric constant of water is 80, methanol 33.5, Benzene 2.3

Ionic solids dissolve more in a solvent having high dielectric constant.

SOLUBILITIES OF MOLECULAR SOLIDS (NON IONIC SOLIDS) :

Molecular solids containing polar groups (e.g. OH) are soluble in polar solvents like water, methanol etc. Others are soluble in non polar solvents.

SOLUBILITY OF GASES :

It is generally expressed in terms of **absorption coefficient** which is defined as the volume of gas, reduced to NTP, dissolved by unit volume of solvent at particular temperature and 1 atmospheric pressure of the gas.

Absorption co-efficients of some gases at 20°C.

Solvent	*Hydrogen*	*Nitrogen*	*Oxygen*	*Carbon dioxide*
Water	0.017	0.015	0.028	0.88
Ethanol	0.080	0.130	0.143	3.00
Benzene	0.060	0.104	0.165	

FACTORS INFLUENCING THE SOLUBILITY OF A GAS :

(i) Nature of the gas : Easily liquifiable gases are more soluble. e.g. CO_2 is more soluble than O_2 and H_2

(ii) Nature of solvent : Gases capable of forming ions in aqueous solution are more soluble in water than in other solvents. eg. HCl, NH_3 etc.

(iii) Temperature : Solubility decreases with rise of temperature at constant pressure.

(iv) Pressure of the gas (Henry's Law)

Henry's law : The mass of a gas dissolved per unit volume of solvent is proportional to the pressure of the gas at constant temperature.

$$\mathbf{m \propto P} \text{ or}$$

$m = k.P$ where k is Henry's constant.

Henry's Law in terms of volume : The volume of a gas dissolved in a solvent at a given temperature is independent of the pressure.

Most gases obey Henry's law :

(a) when pressure is not very high

(b) temperature is not very low

(c) gas is not highly soluble

(d) gas does not form any compound with solvent

(e) gas does not undergo dissociation.

EXPRESSION OF THE CONCENTRATION OF A SOLUTION :

(i) Percentage :

(a) **By weight** - weight of solute per 100 g of solution.

(b) **By volume** - weight of solute per 100 ml of solution. Volume of solute per 100 ml of solution.

(ii) Strength : Number of grams of solute dissolved per litre of solution. (g/litre)

Strength = Equivalent weight × Normality

(iii) Normality (N) : Number of gram equivalents of the solute dissolved per litre of the solution.

$$\text{Normality (N)} = \frac{\text{wt. of solute} \times 1000}{\text{E. wt of solute} \times \text{volume in mL}}$$

(iv) Molarity (M) : Number of moles of the solute dissolved in one litre of solution.

$$\text{Molarity (M)} = \frac{\text{wt. of solute} \times 1000}{\text{M. wt of solute} \times \text{volume in mL}}$$

(v) Molality (m) : Number of moles of solute dissolved in 1000 g of the solvent.

Molality (m)

$$= \frac{\text{wt. of solute} \times 1000}{\text{M. wt of solute} \times \text{wt. of solvent in grams}}$$

(vi) Mole fraction : The ratio of the number of moles of one component to the total number of moles of solution. For components A & B.

$$x_A = \frac{n_A}{n_A + n_B}\ ;\ x_B = \frac{n_B}{n_A + n_B};\ x_A + x_B = 1 \text{ always.}$$

(vii) Mass fraction :

$$\text{Mass fraction of A} = \frac{\text{Mass of A}}{\text{Total mass of solution}};$$

$$\text{Mass fraction of B} = \frac{\text{Mass of B}}{\text{Total mass of solution}}$$

(viii) ppm (parts per million) : It is the mass of the solute present in million (10^6) parts by mass of the solution.

$$ppm_A = \frac{\text{Mass of A} \times 10^6}{\text{Mass of solution}}$$

Molality, mole fraction and mass fraction do not change with temperature.

(ix) Demal (D) : When one mole of solute is present in one litre of the solution at 0°C, it is known as one demal.

(x) Formality (f) : Number of formula mass in grams present in one litre of solution.

SOME IMPORTANT RELATIONS :

(i) $$M = \frac{md}{1 + m\dfrac{M_2}{1000}} \quad \text{or} \quad d = M\left(\frac{1}{m} + \frac{M_2}{100}\right)$$

(ii) $$m = \frac{1000x_2}{x_1M_1}$$

(iii) $$M = \frac{1000\ dx_2}{x_1M_1 + x_2M_2}$$

(iv) $$\text{Mole fraction } (x_2) = \frac{m}{m + \dfrac{1000}{M_1}}$$

M = molarity

m = molality

d = density of solution

x_1 = mole fraction of solvent

x_2 = mole fraction of solute

M_1 = molecular mass of solvent

M_2 = molecular mass of solute

Normality = n × Molarity

$$\text{where } n = \frac{\text{Molecular Mass}}{\text{Equivalent mass}}$$

VAPOUR PRESSURE :

It is defined as the pressure of the vapour in equilibrium with the liquid at that temperature

(i) Vapour pressure of a liquid increases with rise in temperature.

(ii) When intermolecular forces are weak, the liquid is more volatile and has more vapour pressure.

VARIATION OF VAPOUR PRESSURE WITH TEMPERATURE :

It is given by Clapeyron-Clausius Equation

$$\log\frac{P_2}{P_1}=\frac{\Delta H_v}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

ΔH_v = Enthalpy of vapourisation of liquid; R = gas constant; P_2 = vapour pressure at T_2 and P_1= vapour pressure at T_1.

VAPOUR PRESSURE OF SOLUTION :

The vapour pressure of a solution is the sum of the partial vapour pressures of the components of the solution. (**Dalton's law**)

$$P = p_A + p_B + p_C \text{ .... etc}.$$

In general, the vapour pressure of a component in solution is less than that of pure solvent.

RAOULT'S LAW :

(i) The partial pressure of a volatile component of a solution is directly proportional to its mole fraction in solution at any temperature.

$p_A \propto x_A$ and $p_B \propto x_B$ and

$p_A = p_A^o.x_A\ ,\ p_B = p_B^o.x_B$

where p_A = partial pressure of component A,

p_A^o = vapour pressure of component A in pure form,

x_A = mole fraction of component A in solution.

Also remember, $p_A = p\times\gamma_A$, where p = Total pressure

and γ_A = Mole fraction of component A in vapour phase

(ii) **Raoult's law for solution containing non-volatile solute :** The relative lowering of vapour pressure of a solution containing non volatile solute is equal to the mole fraction of

non volatile solute $\dfrac{p_A^o-p_A}{p_A^o}=x_B=\dfrac{n}{n+N}$.

For very dilute solution :

Alternate formula $\dfrac{p_A^o-p_A}{p_A^o}=\dfrac{n}{N}$ $\quad(\because n << N)$

A = Volatile component of solution,

B = non-volatile component of solution or the solute

n = moles of B, N = moles of A.

AN IDEAL SOLUTION :

The solution which (I) Obey Raoult's law at all temperatures and concentrations (II) $\Delta H_{mix} = 0$ i.e. no heat is evolved or absorbed when components are mixed to form the solution (III) $\Delta V_{mix} = 0$ i.e. no change in volume. In ideal solution the A–B intermolecular interactions are the same as A–A and B–B inter-molecular interactions. Strictly, there is no ideal solution. The following pairs almost behave as ideal solutions.

(a) benzene and toluene
(b) ethyl bromide and ethyl chloride
(c) n-Heptane and n-hexane
(d) chlorobenzene and bromobenzene
(e) ethylene chloride and ethylene bromide.

For ideal solutions the **vapour pressure of the solution** always lies between the vapour pressure of the pure components and generally **dilute solutions behave as ideal solutions.**

NON IDEAL SOLUTIONS :

Solutions which (I), do not obey Raoult's law, (II) $\Delta H_{mix} \neq 0$ (III) $\Delta V_{mix} \neq 0$.

TYPES OF NON IDEAL SOLUTIONS :

They are of two types

(i) **Showing positive deviations :** For such solutions (a) A–B inter-molecular interactions are weaker than A–A and B–B intermolecular interactions (b) ΔH_{mix} is +ve (c) ΔV_{mix} is +ve

Examples :

Carbon tetrachloride + benzene
Carbon tetrachloride + chloroform
Carbon tetrachloride + Toluene
Acetone + Carbon disulphide
Acetone + Ethyl alcohol
Acetone + Benzene
Methyl alcohol + Water
Ethyl alcohol + Water

(ii) **Showing negative deviations :** For such solutions (a) A–B intermolecular interactions are stronger than A–A and B–B intermolecular interactions (b) ΔH_{mix} is –ve (c) ΔV_{mix} is –ve.

Examples :

Chloroform + Acetone
Chloroform + Benzene
Chloroform + Diethyl ether
Acetone + Aniline
HCl + Water
HNO_3 + Water

AZEOTROPIC MIXTURE OR CONSTANT BOILING MIXTURE :

A mixture of two or more components which like a pure chemical compound boils and distills over completely at the same temperature without change in their chemical composition is called an azeotrope. Non ideal solutions form azeotropes.

AZEOTROPIC MIXTURE WITH MINIMUM BOILING POINT :

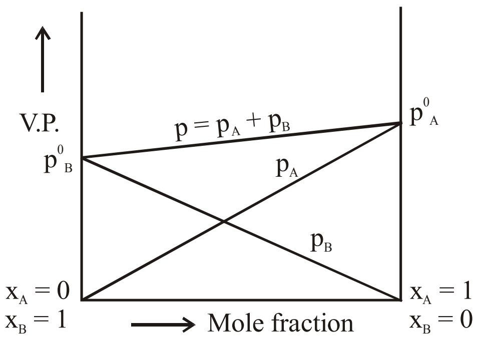
It is formed by liquids showing positive deviation. An intermediate composition of liquids having highest vapour pressure, hence lowest boiling point gives this azeotrope. Such azeotropes have boiling points lower than either of the pure component e.g. Rectified spirit (ethanol 95.5% + H_2O 4.50%) bpt 351.5 K.

AZEOTROPIC MIXTURE WITH MAXIMUM BOILING POINT :

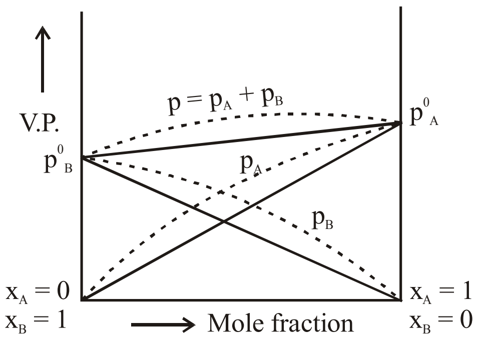
It is formed by liquids showing negative deviation. An intermediate composition of liquids having minimum vapour pressure, hence highest boiling point gives this azeotrope. Such azeotropes have boiling points higher than either of the pure components e.g. Water & HNO_3 (HNO_3 68% + H_2O 32%) bpt 393.5K.

GRAPHICAL REPRESENTATION OF IDEAL AND NON IDEAL SOLUTIONS :

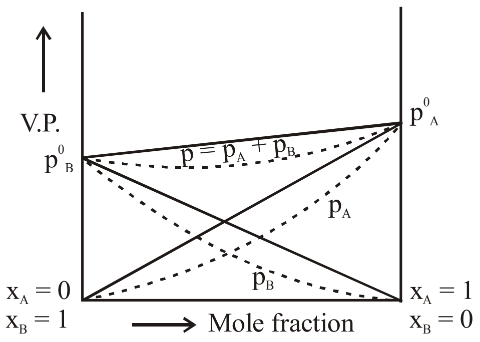
Ideal Solution



Positive Deviation



Negative Deviation



COLLIGATIVE PROPERTIES :

Properties which depend upon the number of particles irrespective of their nature (ions or molecules) are called colligative properties. These are

(i) Relative lowering of vapour pressure
(ii) Osmotic pressure
(iii) Elevation in boiling point
(iv) Depression in freezing point

RELATIVE LOWERING OF VAPOUR PRESSURE :

It is measured by **Ostwald and Walker's** method (Gas saturation method)

$$\frac{p^o - p}{p^o} = \text{mole fraction of non volatile solute} = \frac{w_2}{w_1 + w_2}$$

w_2 = loss in weight of solvent
w_1 = loss in weight of solution

OSMOSIS :

The spontaneous flow of the solvent through a semi-permeable membrane from pure solvent to solution or from a dilute solution to concentrated solution is known as osmosis.

Some natural semipermeable membranes are pig's bladder, skin round white of an egg, membrane round the red blood corpuscle and in the cell of the plant.

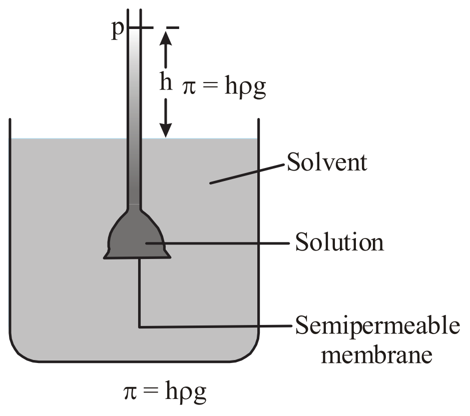
Cupric ferrocyanide $Cu_2[Fe(CN)_6]$ is artificially prepared semi-permeable membrane
($CuSO_4 + K_4[Fe(CN)_6]$)

$$2Cu^{++} + Fe(CN)_6^{4-} \longrightarrow Cu_2[Fe(CN)_6]\downarrow$$

It is not suitable for non aqueous solution as it gets dissolved. Another artificial semipermeable membrane is $Ca_3(PO_4)_2$.

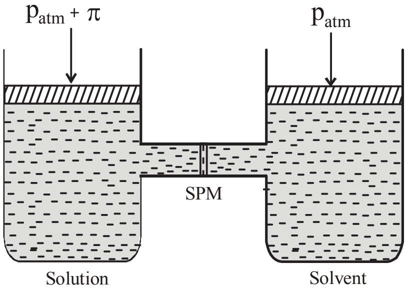
OSMOTIC PRESSURE (π) :

The hydrostatic pressure developed on the solution which just prevents the osmosis of pure solvent into the solution through a semipermeable membrane is called osmotic pressure.



$\Pi = h\rho g$
Or

The minimum external pressure applied to the solution to just stop the process of osmosis is known as osmotic pressure.



Or

The minimum external pressure applied on solution to make its vapour pressure equal to that of solvent is known as osmotic pressure.

DETERMINATION OF OSMOTIC PRESSURE :

(i) **Pfeffer's method**
(ii) **Berkeley and Hartley's method** (most common)
(iii) **Morse and Frazer's method**
(iv) **Townsend's negative pressure method**
(v) **De. Vries method**

ISOTONIC SOLUTIONS :

Solutions having the same osmotic pressure. 0.91% NaCl solution is isotonic with human RBC's.

HYPOTONIC SOLUTION :

Solution having lower Osmotic pressure.

HYPERTONIC SOLUTION :

Solution having higher osmotic pressure.

VAN'T HOFF'S THEORY OF DILUTE SOLUTIONS :

Dilute solutions behave like gases and gas laws can be applied to them.

BOYLE-VAN'T HOFF LAW :

Osmotic pressure of a solution is directly proportional to its concentration at constant given temperature.

$$\pi \propto C \propto \frac{1}{V}$$

CHARLE'S-VAN'T HOFF LAW :

Osmotic pressure of a solution is directly proportional to its temperature at fixed concentration.

$$\pi \propto T$$

VAN'T HOFF EQUATION FOR SOLUTIONS :

$$\pi \propto CT \qquad \therefore \pi = SCT$$

S = Solution constant having same value as gas constant

C = Molar concentration

T = Absolute temperature and π = Osmotic pressure

AVOGADRO-VAN'T HOFF LAW FOR SOLUTIONS :

Equal volumes of solutions having the same osmotic pressure and temperature contain equal number of moles i.e. have same concentration.

RELATION BETWEEN OSMOTIC PRESSURE (π) AND LOWERING OF VAPOUR PRESSURE :

Relative lowering of vapour pressure is directly proportional to osmotic pressure

$$\frac{p^o - p}{p^o} = \frac{\pi \times M}{dRT} \qquad \therefore \frac{p^o - p}{p^o} \propto \pi \left(\text{since } \frac{M}{dRT} \text{ Constant}\right)$$

OSMOLARITY :

Osmotic behaviour of solutes undergoing association or dissociation is equal to molarity × number of particles produced per formula unit of solute known as osmolarity.

REVERSE OSMOSIS :

When the external pressure applied on the solution is more than osmotic pressure, the solvent flows from the solution to the pure solvent which is called reverse osmosis. Desalination of sea water is done by reverse osmosis to make it potable.

PLAMOLYSIS :

The flow of the fluid from the plant cell when placed in a hypertonic solution is called plamolysis. The plant cell undergoes shrinkage.

EXO-OSMOSIS :

Outward osmotic flow of fluid from a cell through semipermeable memberane e.g. grape in conc. NaCl solution.

ENDO-OSMOSIS :

Inward osmotic flow of fluid from a cell through semipermeable membranes e.g. grape in water.

SILICA GARDEN :

When coloured salts e.g. Copper Sulphate, Cobalt Nitrate, Manganese Chloride, Nickel Chloride and Ferrous sulphate etc. are placed in Sodium silicate solution of density 1.1, a colloidal and semipermeable shell of Silicates is formed round the crystal. Inside this, there is strong solution of salt and outside weak solution of sodium silicate. Water permeates into the shell, pressure rises and the shell bursts out, the salt solution escapes but immediately reacts with sodium silicate to form again semipermeable shell of the metallic silicate. The process is repeated again and again and projection of coloured silicates continues to grow.

KONOWALOFF'S RULE :

The mole fraction of the more volatile component is always greater in the vapour phase than in the solution phase.

RELATION BETWEEN THE TOTAL PRESSURE AND MOLE FRACTIONS OF VOLATILE COMPONENTS IN LIQUID PHASE :

$$P = p_A^o . x_A + p_B^o . x_B$$

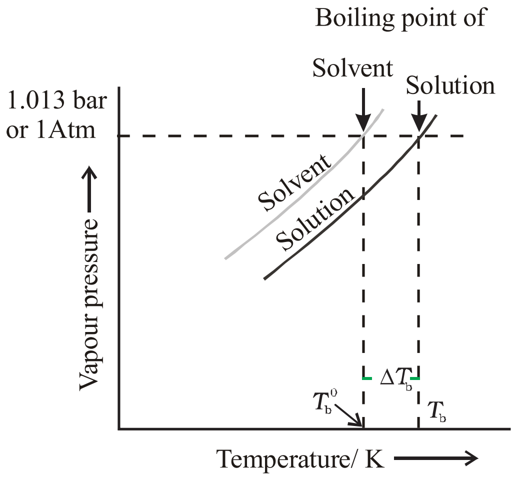
RELATION BETWEEN THE TOTAL PRESSURE AND MOLE FRACTIONS OF VOLATILE COMPONENTS IN VAPOUR PHASE :

$$\frac{1}{P} = \frac{Y_A}{p_A^o} + \frac{Y_B}{p_B^o}$$

BOILING POINT AND ELEVATION IN BOILING POINT :

The temperature at which the vapour pressure of a liquid becomes equal to atmospheric pressure is known as the boiling point of the liquid.

Addition of non volatile solute in a solvent lowers the vapour pressure and increases the boiling point. The increase in boiling point is directly proportional to the molality of solution,



The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.

$$\Delta T_b \propto m \text{ or } \Delta T_b = K_b \times m = \frac{K_b \times w \times 1000}{M \times W}$$

K_b = molal elevation constant or ebullioscopic constant. It is characteristic for given solvent. When

$$m = 1, \Delta T_b = K_b.$$

Thus **molal elevation constant** or **ebullioscopic** constant is defined as the elevation in boiling point caused by one molal solution. Its value is given by

$$K_b = \frac{RT_0^2}{1000\, l_v} = \frac{M_A . RT_0^2}{\Delta H_{vap} \times 1000}$$

Units of K_b = K kg mol^{-1}

R = gas constant, T_0 = normal boiling point l_v = latent heat of vaporisation per gram of pure solvent. K_b is constant for given solvent.

M_A = molecular mass of solvent, ΔH_v = Enthalpy of vaporisation of solvent

MOLAL ELEVATION CONSTANTS OF SOME COMMON SOLVENTS :

Solvents	*Value of K_b in K kg mol^{-1}*
Water	0.52
Methyl alcohol	0.80
Acetone	1.72
Benzene	2.53
Carbon tetrachloride	5.03
Chloroform	3.63
Ethyl alcohol	1.20
Ethyl ether	2.11

DETERMINATION OF MOLECULAR WEIGHT FROM BOILING POINT ELEVATION :

$$M = \frac{K_b \times w \times 1000}{\Delta T_b \times W}$$

K_b = molal elevation constant,

w = weight of solute,

W = weight of solvent,

ΔT_b = Elevation in bpt.

The method employed is known as **ebullioscopic method**. The common methods are

(i) Landsberger's method

(ii) Coltrell's method

FREEZING POINT AND DEPRESSION IN FREEZING POINT :

The temperature at which the vapour pressure of the solvent in its liquid and solid phase becomes the same is known as freezing point of solvent.

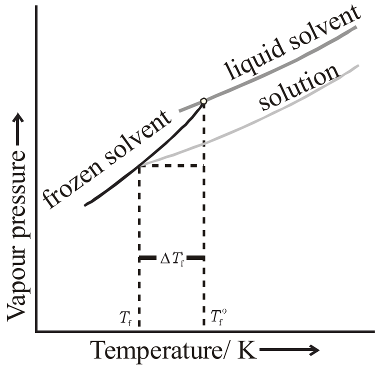


Diagram showing ΔT_f, depression of the freezing point of a solvent in a solution.

When non volatile solute is dissolved in a solvent, the freezing point decreases. Depression in freezing point is given by

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f \times m = \frac{K_f \times w \times 1000}{M \times W}$$

K_f is molal depression constant or molal Cryoscopic constant.

When m (molality) = 1 then $\Delta T_f = K_f$

Hence molal depression constant or **molal Cryoscopic** constant is equal to depression in freezing point caused by one molal solution. Its value is given by

$$K_f = \frac{RT_0^2}{1000\ l_f} = \frac{M_A RT_0^2}{\Delta H_{fusion} \times 1000} \quad \text{Units of } K_f = K\,.\,Kg\ mol^{-1}$$

R = gas constant,

T_0 = normal freezing point,

l_f = heat of fusion per gram of solvent.

K_f is freezing point constant for a given solvent.

MOLAL DEPRESSION CONSTANTS OF SOME COMMON SOLVENTS :

Water	1.86	Naphthalene	6.90
Acetic acid	3.90	Bromoform	14.40
Phenol	7.27	Cyclohexane	20.00
Benzene	5.12	Camphor	37.70

DETERMINATION OF MOLECULAR WEIGHT BY DEPRESSION IN FREEZING POINT :

$$M = \frac{K_f \times w \times 1000}{\Delta T_f \times W}$$

K_f = Molal depression constant, w = weight of non-volatile solute, ΔT_f = depression in freezing point, W = weight of solvent

The method employed is known as Cryoscopic method. The common methods are

(i) The Beckmann method

(ii) The Rast Method

RELATION BETWEEN OSMOTIC PRESSURE AND OTHER COLLIGATIVE PROPERTIES :

(i) $\pi = \left(\frac{p_A^o - p_A}{p_A^o}\right) \times \frac{dRT}{M_B}$ Relative lowering of vapour pressure

(ii) $\pi = \Delta T_b \times \frac{dRT}{1000K_b}$ Elevation in boiling point

(iii) $\pi = \Delta T_f \times \frac{dRT}{1000K_f}$ Depression in freezing point

π = Osmotic pressure,

d = Density of solution at temperature T,

R = Gas constant,

M_B = Molecular mass of solute,

K_b = Molal elevation constant of solvent,

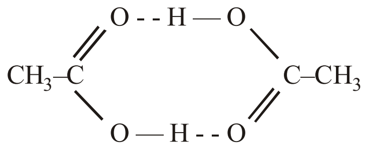
K_f = Molal depression constant of solvent.

ABNORMAL MOLECULAR MASS AND COLLIGATIVE PROPERTIES :

When solutes undergo association or dissociation in solution, there is decrease or increase in number of particles and there are discrepencies between observed and calculated values of colligative properties.

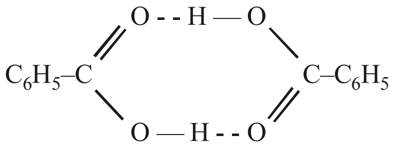
Colligative property $\propto \frac{1}{\text{Molecular mass of solute}}$, hence higher values are obtained for molecular masses in case of association.

Acetic acid in benzene associates and its observed molecular mass is 120.



Acetic acid

Benzoic acid in benzene associates and its observed molecular mass is 244.



Benzoic acid

KCl in water dissociates and its observed molecular mass is 37.25.

$$KCl \rightleftharpoons \overset{+}{K} + \overset{-}{Cl}$$

These observed values are corrected by multiplying by Van't Hoff factor *i*.

VAN'T HOFF FACTOR (*i*) :

Its value is obtained by any of the following expression

(i) $i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$

(ii) $i = \frac{\text{Observed Value of Colligative property}}{\text{Calculated Value of Colligative property}}$

(iii) $i = \frac{\text{No. of particles after association or dissociation}}{\text{No. of particles before association or dissociation}}$

DEGREE OF DISSOCIATION :

Fraction of total number of molecules undergoing dissociation,

$$\alpha = \frac{i-1}{m-1}$$

m = number of particles of electrolyte given in solution.

i = Van't Hoff factor *i*.

DEGREE OF ASSOCIATION :

Fraction of the total number of molecules undergoing association.

$$\alpha = \frac{i-1}{\frac{1}{m}-1}$$

RELATION BETWEEN RELATIVE LOWERING OF VAPOUR PRESSURE AND MOLALITY OF SOLUTION:

$$\frac{p^o - p}{p^o} = \frac{m \times M_1}{1000}$$

Where m = molality of solution

M_1 = Molecular weight of solvent

RELATION BETWEEN WEIGHTS OF TWO IMMISCIBLE LIQUIDS IN THE DISTILLATE :

$$\frac{w_A}{w_B} = \frac{p_A \times M_A}{p_B + p_B}$$

where w = weight of liquid

p = partial pressure

M = Molecular weight

CONJUGATE SOLUTIONS :

When two partially miscible liquids A and B are mixed with each other, two layers are formed. First, Solution of A in B and Second, Solution of B in A. Such solutions co-existing together are called conjugate solutions. For example solution of phenol and water.

CRITICAL SOLUTION TEMPERATURE OR CONSOLUTE TEMPERATURE :

On heating the conjugate solution the mutual solubility of A and B increases. A temperature is reached when two phases disappear and one homogeneous phase is left. This temperature is known as **Critical solution temperature** or **Consolute Temperature**. It is of two types :

(i) **Upper Consolute temperature :** For example water-phenol system.

(ii) **Lower Consolute temperature :** In some cases it is also possible to have a lower temperature of similar kind. For example Trimethylamine-water is a **lower consolute** temperature.

Miscellaneous Solved Examples

1. The solublity of KCl in water is 45.5 g per 100 g water at 55°C. What is the mass percent of KCl.

Sol. Mass % of KCl = $\frac{\text{mass of KCl}}{\text{Total mass of all components}} \times 100$

$$= \frac{45.5}{45.5 + 100} \times 100 = 31.27$$

2. Find the molarity and molality of a 15% solution of H_2SO_4 (density of H_2SO_4 = 1.10 g/ml).

Sol. Molarity $= \frac{\text{Wt} \times 1000}{\text{M. Wt} \times \text{Volume}} = \frac{15 \times 1000}{98 \times 100} = 1.53 \text{ M}$

Molality $= \frac{\text{Wt of solute} \times 1000}{\text{M. Wt} \times \text{Wt. of solvent}}$

Mass of 100 ml soln. = 1.10 × 100 = 110 g

Mass of solvent=110 – 15 = 95 g

$$m = \frac{15 \times 1000}{98 \times 95} = 1.64$$

3. A solution contains 25% water, 25% ethanol and 50% ethanoic acid by mass. Calculate the mole fraction of each component.

Sol. Moles of water $n_A = \frac{25}{18} = 1.388$

Moles of ethanol $n_B = \frac{25}{46} = 0.543$

Moles of ethanoic acid $= \frac{50}{60} = 0.833$

Total moles $n_A + n_B + n_C = 1.388 + 0.543 + 0.833 = 2.764$

Mole fraction of water $= \frac{1.388}{2.764} = 0.5022$

Mole fraction of ethanol $= \frac{0.543}{2.764} = 0.196$

Mole fraction of ethanoic acid $= \frac{0.833}{2.764} = 0.301$

4. The density of a 3M Sodium thiosulphate ($Na_2S_2O_3$) is 1.25 g/l. Calculate (I) the percentage by mass of sodium thiosulphate (II) the mole fraction of sodium thiosulphate (III) molalities of Na^+ and $S_2O_3^{2-}$ ions.

Sol. Mass of 1000 ml. of $Na_2S_2O_3$ solution = 1000 × 1.25 = 1250 g

(I) Mass of $Na_2S_2O_3$ in 1000 ml = 3 × 158 (M. Wt) = 474 g

Mass % of $Na_2S_2O_3 = \frac{474 \times 100}{1250} = 37.92$

(II) Moles of $Na_2S_2O_3$ = 3

Mass of water = (1250 – 474) = 776 g

Moles of water $= \frac{776}{18} = 43.1$

Total moles = 3 + 43.1 = 46.1

Moles fraction of $Na_2S_2O_3 = \frac{3}{46.1} = 0.065$

(III) Number of moles of Na^+ ions = 2 × 3 = 6

$$\text{Molality of } Na^+ = \frac{6 \times 1000}{776} = 7.73 \text{ m}$$

Number of moles of $S_2O_3^{2-}$ ions = 3

$$\text{Molality of } S_2O_3^{2-} = \frac{3 \times 1000}{776} = 3.86 \text{ m}$$

5. 0.080575 kg of Glauber's Salt is dissolved in water to obtain 1 dm^3 of solution of density 1.0772 $kgdm^{-3}$. Calculate the molarity, molality and mole fraction of Na_2SO_4 in solution.

Sol. Molecular mass of Glauber's salt = 322 g/mol = 0.322 kg mol^{-1}

$$\text{Moles of Glauber's salt} = \frac{0.080575}{0.322} = 0.2502$$

Moles of Na_2SO_4 will be same i.e. 0.2502.

$$\therefore \text{ Molarity of solution} = \frac{0.2502}{1} = 0.2502 \text{ M}$$

Mass of 1 litre solution = V × d = 1 dm^3 × 1.0772 kg dm^{-3}

= 1.0772 kg

Mass of Na_2SO_4 = 0.2502 × 142 (M. wt of Na_2SO_4 = 142)

= 0.03552 kg

Mass of solvent = (1.0772 – 0.0355) Kg = 1.0417 kg

$$\text{Molality m} = \frac{0.2502}{1.0417} = 0.24 \text{ m}$$

$$\text{Moles of solvent} = \frac{1041.7}{18} = 57.87$$

$$\text{Mole fraction of } Na_2SO_4 = \frac{0.2502}{0.2502 + 57.87} = 4.3 \times 10^{-3}$$

6. How much concentrated H_2SO_4 of density 1.84 g cm^{-3} which contains 98 mass percent of H_2SO_4 must be diluted to prepare 100 cm^3 of the 20 mass percent H_2SO_4 of density 1.14 g cm^{-3}.

Sol. Molarity of first sample of H_2SO_4

$$M = \frac{98 \times 1000 \times 1.84}{98 \times 100} = 18.4$$

Molarity of second sample of H_2SO_4

$$M = \frac{20 \times 1000 \times 1.14}{98 \times 100} = 2.32 \text{ ; } M_1V_1 = M_2V_2$$

V × 18.4 = 2.32 × 100 V = 12.6 cm^3

7. (a) 10g of a certain non-volatile solute were dissolved in 100 g H_2O at 20°C. The vapour pressure was lowered from 17.3555 mm Hg to 17.2350 mm Hg. Calculate molecular wt. of solute.

(b) The vapour pressure of pure water at 25°C is 23.62 mm Hg what will be vapour pressure of a solution of 1.5 g of urea in 50 g of water.

Sol. (a)

$$\frac{p^o - p_s}{p^o} = \frac{n}{N} = \frac{w}{m} \times \frac{M}{W}$$

$$\text{or } \frac{17.3555 - 17.2350}{17.3555} = \frac{10}{m} \times \frac{18}{100}$$

$$0.006943 = \frac{1.8}{m}$$

$$\therefore m = 259.25$$

(b)

$$\frac{p^o - p_s}{p^o} = \frac{w \times M}{m \times w}$$

$$\text{or } \frac{23.62 - P_s}{23.62} = \frac{1.5 \times 18}{60 \times 50}$$

$$\therefore P_s = 23.407 \text{ mm Hg}$$

8. The vapour pressure of water at 20°C is 17.54 mm Hg. When 20g of solute was added in 50 g water, the V.P. was found to lower by 0.30 mm Hg. Calculate M wt of solute.

Sol.

$$\frac{p^o - p_s}{p^o} = \frac{w \times M}{m \times W}$$

$$\text{or } \frac{0.30}{17.54} = \frac{20 \times 18}{m \times 50}$$

$$\therefore m = 420.96$$

9. Find the molality of a solution containing non volatile solute if the vapour pressure is 2% below the vapour pressure of pure water. **(DHANBAD 1990)**

Sol. Apply $\frac{p^o - p_s}{p^o} = \frac{m \times M}{1000}$

where m = molality of solution;

M = Molecular weight of solvent.

$$\therefore m = \frac{2 \times 1000}{100 \times 18} = 1.111$$

$$\text{or } \frac{2}{100} = \frac{m \times 18}{1000}$$

$$\therefore m = \frac{2 \times 1000}{100 \times 18} = 1.111$$

10. An aqueous solution of glucose boils at 100.01°C. The K_b for water is 0.5 K mol^{-1} Kg. What is the number of glucose molecules in the solution containing 100 g water.

Sol. $\Delta T_b = \frac{K_b \times w \times 1000}{M \times W}$; $0.01 = \frac{0.5 \times w \times 1000}{180 \times 100}$

w = 0.36 g

180 g glucose contains = 6.023 × 10^{23} molecules

$$0.36 \text{ g glucose contains} = \frac{6.023 \times 10^{23}}{180} \times 0.36$$

$$= 1.2 \times 10^{21} \text{ molecules}$$

11. The freezing point of a solution containing 50 cm^3 of ethylene glycol in 50 g of water is found to –34°C. Assuming ideal behaviour calculate the density of ethylene glycol.

K_f for water = 1.86 K kg mol^{-1}

Sol. Ethylene glycol = 50 cm^3

Weight of ethylene glycol = 50 × d

Molecular weight of ethylene glycol = 62 g

Weight of water = 50 g

$$\Delta T_f = \frac{K_f \times w \times 1000}{M \times W}; \qquad 34 = \frac{1.86 \times 50 \times d \times 1000}{62 \times 50}$$

d = 1.133 g/cm^3

12. Calculate the freezing point of an aqueous solution of non electrolyte having an osmotic pressure 2.0 atm at 900 K.

K_f = 1.86 K mol^{-1} kg and S = 0.0821 litre atm $K^{-1}mol^{-1}$.

Sol. π = CST where C = Molar concentration, π = 2 atm, S = 0.0821 litre atm K^{-1} mol^{-1}, T = 300 K

$\therefore$ 2 = C × 0.0821 × 300 $\qquad$ $\therefore$ C = 0.0812 mol lit^{-1}

$\Delta T_f = K_f \times$ molality

For dilute solutions molarity = molality

ΔT_f = 1.86 × 0.0812 = 0.151

Freezing point = T – ΔT_f = 0 – 0.151 = –0.151°C

13. A decimolar solution of potassium ferrocyanide is 50% dissociated at 300K. Calculate the osmotic pressure of the solution. Given S = 8.314 JK^{-1} mol^{-1}.

Sol. Given C = 0.1 mol lit^{-1} = $\frac{0.1}{10^{-3}} = 10^2$ mol m^{-3}

$$\pi = 10^2 \times 8.314 \times 300 \text{ Nm}^{-2}$$

But, $K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$

1 – 0.5 $\qquad$ 4×0.5 $\qquad$ 0.5

$$\text{Van't Hoff's factor } i = \frac{1-0.5+2.0+0.5}{1} = 3$$

$$\therefore \pi = 10^2 \times 8.314 \times 300 \times 3 = 7.483 \times 10^5 \text{Nm}^{-2}$$

14. 0.85%, aqueous solution of $NaNO_3$ is apparently 90% dissociated at 27°C. Calculate the osmotic pressure. (R = 0.0821 atm K^{-1} mol^{-1})

Sol. Molecular weight of $NaNO_3$ = 85

$$\text{Molarity} = \frac{\text{Wt} \times 1000}{\text{M. wt} \times \text{V}} = \frac{0.85 \times 1000}{85 \times 100} = 0.1 \text{ mol lit}^{-1}$$

$NaNO_3$ solution is 90% dissociated

$NaNO_3 \rightleftharpoons Na^+ + NO_3^-$

1 – 0.9 $\qquad$ 0.9 $\qquad$ 0.9

Van't Hoff factor i = 1 – 0.9 + 0.9 + 0.9 = 1.9

$$\therefore \pi = 1.9 \times 0.1 \times 0.0821 \times 300 = 4.68 \text{ atm}$$

15. A 1.2% solution (wt/volume) of NaCl is isotonic with 7.2% solution (wt/volume) of glucose. Calculate degree of ionisation and Van't Hoff factor of NaCl.

Sol. Since glucose is non electrolyte its osmotic pressure is

$$\pi_1 = CRT = \left(\frac{7.2 \times 1000}{180 \times 100}\right) \times 0.0821 \times T \quad \left(\because C = \frac{7.2 \times 1000}{180 \times 100}\right)$$

NaCl is electrolyte and let α be the degree of ionisation then

$NaCl \rightleftharpoons Na^+ + Cl^-$

$1 - \alpha$ $\qquad$ α $\qquad$ α

$$\text{Van't Hoff's factor } i = \frac{1-\alpha+\alpha+\alpha}{1} = 1+\alpha$$

Osmotic pressure of NaCl is

$$\pi_2 = (1+\alpha)\left(\frac{1.2 \times 1000}{58.5 \times 100}\right) \times 0.0821 \times T$$

For isotonic solutions $\pi_1 = \pi_2$

$$\left(\frac{7.2 \times 1000}{180 \times 100}\right) \times 0.0821 \times T = \left(\frac{1.2 \times 1000}{58.5 \times 100}\right) \times 0.0821 \times T(1+\alpha)$$

$\therefore \alpha = 0.95$ and $i = 1.95$

16. The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution containing 7g of salt per 100 g of water at 100°C is 70%. Calculate the vapour pressure of solution.

Sol. $Ca(NO_3)_2 \rightleftharpoons Ca^{++} + 2NO_3^-$

1 – 0.7 $\qquad$ 0.7 $\qquad$ 2 × 0.7

Van't Hoff factor i = 1 – 0.7 + 0.7 + 1.4 = 2.4

$$\text{Van't Hoff factor } i = \frac{\text{Normal M.wt}}{\text{Obs. M.wt}}$$

$$\therefore \text{Obs. M.wt} = \frac{164}{2.4} = 68.33$$

$$\text{Now } \frac{p^o - p_s}{p^o} = \frac{w}{m} \times \frac{M}{W} = \frac{7 \times 18}{68.33 \times 100} = 0.0184$$

$$\frac{p^o - p_s}{p^o} = 0.0184$$

$$\frac{760 - p_s}{760} = 0.0184$$

$\therefore$ p_s = 746.01 mm Hg

17. To 500 cm^3 of water 3.0 × 10^{-3} Kg of acetic acid is added. If 23% acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86K kg^{-1} mol^{-1} and 0.997 g cm^{-3} respectively.

Sol. Mass of acetic acid = 3×10^{-3} kg = 3.0 g
Molecular mass of acetic acid = 60 g
Mass of Solvent = 500 × 0.997 = 498.5 g

$$\begin{array}{llll} CH_3COOH & \rightleftharpoons CH_3COO^- + & H^+ & \\ 1-0.23 & 0.23 & 0.23 & i=1.23 \end{array}$$

$$\therefore \Delta T_f = K_f \times \text{molality} \times i = 1.86 \times \frac{3\times1000}{60\times498.5} \times 1.23 = 0.229$$

18. Calculate the molality of a 1 litre solution of 93% H_2SO_4 (mass/volume). The density of the solution is 1.84 g/ml

Sol. Molarity of 93% H_2SO_4 is $= \frac{93\times1000}{98\times100} = 9.48$

The relation between M and m is as follows

$$M = \frac{m\times d}{1+\frac{mM_2}{1000}};$$

$$9.48 = \frac{m\times1.84}{1+\frac{m\times98}{1000}}$$

On solving
$m = 10.30$

19. What mass of non volatile solute urea (NH_2CONH_2) must be dissolved in 100 g of water in order to decrease the vapour pressure of water by 25%. What will be the molality of the solution?

Sol. Let the mass of urea be w g
Now use the alternate formula

$$\frac{p^0-p}{p} = \frac{n}{N}$$

$$\frac{100-75}{75} = \frac{W/60}{100/18}$$

or $w = \frac{6000}{54} = 111.11$ g

$$\text{Molality of urea} = \frac{111.11\times1000}{60\times100}$$

$= 18.5 \text{ mol kg}^{-1}$

20. The vapour pressure of pure benzene at 25°C is 639.7 mm Hg and the vapour pressure of a solution of a solute in benzene at the same temperature is 631.9 mm Hg. Calculate the molality of the solution.

Sol. From Raoult's law $p_A = x_A P_A^o$

$$\therefore \quad x_1 = \frac{631.9}{639.7} = 0.988$$

$\therefore$ Mole fraction of solute = (1 – 0.988) = 0.012 = x_2

now apply the formula $m = \frac{x_2\times1000}{x_1M_1}$

$$m = \frac{1000\times0.012}{0.988\times78};$$

$m = 0.156 \text{ mol kg}^{-1}$

21. Addition of 0.643 g of a compound to 50 ml of benzene (density 0.879 g mol^{-1}), lower the freezing point from 5.51°C to 5.03°C. If K_f for benzene is 5.12 kg mol^{-1}, Calculate the molecular mass of the compound

Sol. Molecular mass $= \frac{K_f\times w\times1000}{\Delta T_f\times W}$

$$= \frac{5.12\times0.643\times1000}{0.48\times50\times0.879}$$

= 156.06 g/mol

(ΔT_f = (5.51 – 5.03) = 0.48 and Mass of solvent $= V\times d = 50\times0.879$)

22. At 100°C benzene and toluene have vapour pressure of 1375 and 558 torr, respectively. Assuming these two form an ideal solution calculate the composition of the solution that boils at 1 atm and 100°C. What is the composition of vapour issuing at these conditions.

Sol. Let x_A and x_B be the mole fraction of benzene and toluene respectively

then, $P = x_A p_A^o + (1-x_A)p_B^o$

$760 = x_A \times 1375 + (1 - x_A)\, 558$

$x_A = 0.247$

Mole fraction of benzene in the vapour phase

$$= \frac{x_A p_A^o}{P} = \frac{0.247\times1375}{760} = 0.447$$

Mole fraction of toluene in solution
$(1-0.247) = 0.753$

Mole fraction of toluene in vapour
$(1-0.447) = 0.553$

23. The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. The non volatile solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molar mass of the solid substance?

Sol. Apply the formula

$$\frac{P^o-P}{P} = \frac{n}{N}$$

$$\frac{640-600}{600} = \frac{2.175/M}{39/78}$$

M = 65.25 g/mol

24. A 0.1 molar solution of NaCl is found to be isotonic with 1% urea solution. Calculate

(a) degree of dissociation of sodium chloride.

(b) Van't Hoff factor and

Assume density of 1% urea equal to 1 g cm $^{-3}$

Sol. (a) $NaCl \rightleftharpoons Na^+ + Cl^-$

$C(1-\alpha) \quad C\alpha \quad C\alpha$

Total concentration of species in solution

$= C(1+\alpha) = 0.1(1+\alpha)$

Osmotic pressure of NaCl

$= 0.1\,(1+\alpha)RT$

Osmotic pressure of urea solution

$$= \frac{1}{60 \times 0.1} RT$$

Since two solutions are isotonic, then

$$0.1\,(1+\alpha)RT = \frac{1}{60 \times 0.1} RT$$

$\therefore\ \alpha = 0.667$

(b) Again Van't Hoff's factor

$$i = \frac{C(1+\alpha)}{C} = 1.667$$

25. What minimum weight of ethane -1, 2-diol must be mixed with 10 gallons of water to protect it from freezing at – 24°C? Ethane 1, 2 - diol is an antifreeze addition

(1 gallon = 3.785 liters, K_f for $H_2O = 1.86$ K mol^{-1} kg)

Sol. $\Delta T_f = K_f \times m \qquad$ (m = Molality)

$$\therefore\ m = \frac{24}{1.86} = 12.90$$

Freezing point of water = 0.0°C

$\therefore$ 1 kg of water should contain 12.90 mole of ethane-1, 2-diol

10 gallons of water = 10 × 3.785

= 37.85 liters

Moles of ethane – 1, 2-diol in 37.85 liters

= 12.9 × 37.85mol

$$= \frac{12.9 \times 37.85 \times 62}{1000}\,\text{kg} \quad \left(\because \text{molar mass of ethane } 1,2-\text{diol} = 62 \text{ g mol}^{-1}\right)$$

= 30.272 kg

26. A decinormal solution of sodium chloride exerts an osmotic pressure of 4.6 atm at 300 K Calculate the degree of dissociation

(R = 0.0821 atm litre K^{-1}mol^{-1})

Sol. $\pi = CRT$

π calculated = 0.1 × 0.0821 × 300 = 2.46 atm

π observed = 4.6 atm

Van't Hoff factor

$$i = \frac{4.6 \text{ atm}}{2.46 \text{ atm}} = 1.87$$

$NaCl \rightleftharpoons Na^+ + Cl^-$

$1-\alpha \qquad \alpha \quad \alpha$

$$i = \frac{1-\alpha+\alpha+\alpha}{1};\ 1+\alpha = 1.87$$

$\therefore\ \alpha = 0.87$ or 87%

27. The freezing point of a solution containing 0.2 g of ethanoic acid in 20 g of benzene is lowered by 0.45°C. Calculate the degree of association of ethanoic acid in benzene. Assume ethanoic acid dimerises in the solvent benzene. K_f for benzene = 5.12 K mol^{-1} kg

Sol. $$M = \frac{K_f \times w \times 1000}{\Delta T_f \times W} = \frac{5.12 \times 0.2 \times 1000}{0.45 \times 20} = 113.77$$

Van't Hoff factor

$$i = \frac{\text{Normal M.wt}}{\text{Observed M.wt}} = \frac{60}{113.77} = 0.53$$

$2\,CH_3COOH \rightleftharpoons (CH_3COOH)_2$

$1-\alpha \qquad \frac{\alpha}{2}$

$$\text{Van't Hoff factor } i = \frac{1-\alpha+\alpha/2}{1} = 0.53$$

$$\text{or}\quad 1-\frac{\alpha}{2} = 0.53$$

$\therefore$ Degree of association $\alpha = 0.94 = 94\%$

28. The degree of dissociation of calcium nitrate in dilute solution containing 7 g per 100 g of water at 100°C is 70%. Calculate the vapour pressure of solution.

Sol. $Ca(NO_3)_2 \rightleftharpoons Ca^{++} + 2\,NO_3^-$

$1-\alpha \qquad \alpha \qquad 2\alpha$

Moles at equilibrium

$1-\alpha+\alpha+2\alpha = 1+2\alpha$

$= 1+2 \times 0.7 = 2.4$

Again

$$\frac{M_{normal}}{M_{observed}} = 1+2\alpha = 2.4;$$

$$M_{observed} = \frac{164}{2.4} = 68.33$$

From Raoult's law

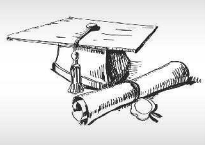
$$\frac{P^o - Ps}{P^o} = \frac{n}{N};$$

$$1 - \frac{Ps}{P^o} = \frac{\frac{7}{68.33}}{100/18} = 0.0184$$

$P_s = (1-0.0184)\,760$

= 746.016 mm Hg

Exercise-1 | NCERT Based Questions



Very Short/Short Answer Questions

1. Why is the osmotic pressure considered to be a colligative property?

2. If glycerine [$C_3H_5(OH)_3$] and ethylene glycol ($C_2H_6O_2$) are sold at same price per kg, which would be cheaper for preparing an antifreeze solution for the radiator of an automobile?

3. Why is liquid ammonia bottle first cooled in ice before opening it?

4. At the same temperature, hydrogen is more soluble in water than helium. Which of them will have a higher value of K_H and Why ? (K_H = Henry's constant).

5. Two liquids X and Y have boiling points 110 °C and 130 °C respectively. Which one of them has higher vapour pressure at 50 °C ?

6. CCl_4 and H_2O are immiscible whereas C_2H_5OH and H_2O are miscible in all proportions. Correlate this behaviour with the molecular structures of the three compounds.

7. An aqueous solution freezes at 272·4 K while pure water at 273 K. Determine

(*a*) the molality of solution

(*b*) boiling point of solution

(*c*) lowering of vapour pressure of water at 298 K.

[Given $K_f = 1{\cdot}86$ K kg mol^{-1}, $K_b = 0{\times}512$ K mg mol^{-1}, vapour pressure of pure water is 23·756 mm Hg].

8. Vapour pressure of pure water at 35 °C is 31. 82 mm Hg. When 27. 0 g of solute is dissolved in 100 g of water (at same temperature), vapour pressure of solution thus formed is 30. 95 mm Hg. Calculate molecular mass of the solute.

9. What do you expect to happen when Red Blood Corpuscles (RBC's) are placed in following solutions:

(*i*) 1% NaCl solution

(*ii*) 0.5% NaCl solution

10. Find the boiling point of a solution containing 0.520 g of glucose ($C_6H_{12}O_6$) dissolved in 80.2 g of water.
[Given K_b for water = 0.52 K/m]

11. Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

12. A 1.00 molal aqueous solution of trichloroacetic acid (CCl_3COOH) is heated to its boiling point. The solution has the boiling point of 100.18°C. Determine the Van't Hoff factor for trichloro-acetic acid. (K_b for water = 0.512 K kgmol^{-1})

13. 18 g of glucose, $C_6H_{12}O_6$ (Molar Mass = 180 g mol^{-1}) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil?
(K_b for water = 0.52 K kg mol^{-1}, boiling point of pure water = 373.15 K).

Long Answer Questions

14. Define osmotic pressure. Arrange the following in increasing order of osmotic pressure and give reasons in support of your answer:

(*a*) 34·2 g per litre of sucrose (M . Wt = 342)

(*b*) 90·0 g per litre of glucose (M. Wt = 180)

(*c*) 5·85 g per litre of NaCl (M . Wt = 58·5)

15. (*a*) In a solution of three components A, B and C, mole fraction of A is 0·5 and that of C is 0·2. What is mole fraction of B?

(*b*) Under what condition, molality and molarity of a solution are equal?

(*c*) Calculate the osmotic pressure of mixture of 100 mL of 6% urea solution and 100 mol of 18% glucose solution at 27°C. [R = 0·0821 L atm mol^{-1} K^{-1}].

16. (a) Define the following terms:

(i) Mole fraction

(ii) Ideal solution

(b) 15.0 g of an unknown molecular material is dissolved in 450 g of water. The resulting solution freezes at – 0.34°C. What is the molar mass of the material?
(K_f for water = 1.86 K mol^{-1})

17. (a) Explain the following:

(i) Henry's law about dissolution of a gas in a liquid

(ii) Boiling point elevation constant for a solvent

(b) A solution of glycerol ($C_3H_8O_3$) in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42°C. What mass of glycerol was dissolved to make this solution? (K_b for water = 0.512 K kg mol^{-1})

18. (a) State Raoult's law for a solution containing volatile components.

How does Raoult's law become a special case of Henry's law?

(b) 1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. Find the molar mass of the solute. (K_f for benzene = 5.12 kg mol^{-1})

19. (a) Define the following terms:

(i) Ideal solution   (ii) Azeotrope

(iii) Osmotic pressure

(b) A solution of glucose ($C_6H_{12}O_6$) in water is labelled as 10% by weight. What should be the molality of the solution? (Molar mass of glucose = 180 g mol^{-1})

Multiple Choice Questions

20. When mercuric iodide is added to the aqueous solution of potassium iodide then
(a) freezing point is raised.
(b) freezing point is lowered.
(c) freezing point does not change.
(d) boiling point does not change.

21. Which one of the following salts will have the same value of van't Hoff factor (i) as that of $K_4[Fe(CN)_6]$.
(a) $Al_2(SO_4)_3$ (b) NaCl
(c) $Al(NO_3)_3$ (d) Na_2SO_4.

22. For a dilute solution, Raoult's law states that
(a) the lowering of vapour pressure is equal to the mole fraction of the solute
(b) the relative lowering of vapour pressure is equal to the mole fraction of the solute
(c) the relative lowering of vapour pressure is proportional to the amount of solute in solution
(d) the vapour pressure of the solution is equal to the mole fraction of the solvent

23. The normality of 10% (weight/volume) acetic acid is
(a) 1 N (b) 10 N
(c) 1.7 N (d) 0.83 N

24. Osmotic pressure of a sugar solution at 24°C is 2.5 atmosphere. The concentration of the solution in gm mole per litre is
(a) 10.25 (b) 1.025
(c) 102.5 (d) 0.1025

25. A solution is obtained by dissolving 12 gm of urea (mol. wt. 60) in a litre of water. Another solution is obtained by dissolving 68.4 gm of cane sugar (mol. wt. 342) in a litre of water at the same temperature. The lowering of vapour pressure in the first solution is
(a) same as that of 2nd solution
(b) nearly one-fifth of the 2nd solution
(c) double that of 2nd solution
(d) nearly five times that of 2nd solution

26. Freezing point of an aqueous solution is (–0.186)°C. Elevation of boiling point of the same solution is K_b = 0.512°C, K_f = 1.86°C, find the increase in boiling point.
(a) 0.186°C (b) 0.0512°C
(c) 0.092°C (d) 0.2372°C.

27. The relationship between osmotic pressure at 273 K when 10g glucose (P_1), 10 g urea (P_2), and 10g sucrose (P_3) are dissolved in 250 ml of water is
(a) $P_1 > P_2 > P_3$ (b) $P_3 > P_1 > P_2$
(c) $P_2 > P_1 > P_3$ (d) $P_2 > P_3 > P_1$

Exercise-2 | CONCEPTUAL MCQs

1. Which of the following modes of expressing concentration is independent of temperature?
(a) Molarity (b) Formality
(c) Normality (d) Molality

2. The solubility of a gas in water depends on
(a) nature of the gas (b) temperature
(c) pressure of the gas (d) All of these

3. If one mole of a substance is present in 1 kg of solvent, then its concentration is called
(a) Molar conc. (b) Molal conc.
(c) Normality (d) Strength wt/wt.

4. Equal volumes of 0.1 M HCl and 0.1M NaOH are mixed. The concentration of the resulting solution will be
(a) 0.1 M (b) 0.05 M
(c) 0.2 M (d) 0.0 M

5. When the solute is present in trace quantities the following expression is used
(a) gram per million (b) milligram percent
(c) microgram percent (d) parts per million

6. For preparing 0.1 N solution of a compound from its impure sample of which the percentage purity is known, the weight of the substance required will be
(a) more than the theoretical weight
(b) less than the theoretical weight
(c) same as theoretical weight
(d) None of the above

7. What is the molarity of H_2SO_4 solution that has a density 1.84 gm/cc at 35°C and contains 98% H_2SO_4 by weight?
(a) 4.18 M (b) 8.14 M
(c) 18.4 M (d) 18 M

8. The amount of oxalic acid (mol. wt. 63) required to prepare 500 ml of its 0.10 N solution is
(a) 0.315 g (b) 3.150 g
(c) 6.300 g (d) 63.00 g

9. The molarity of the solution containing 7.1 g of Na_2SO_4 in 100 ml of aqueous solution is
(a) 2 M (b) 0.5 M
(c) 1 M (d) 0.05 M

10. A solution of $CaCl_2$ is 0.5 mol/litre, then the moles of chloride ions in 500 ml. will be
(a) 0.25 (b) 0.50
(c) 0.75 (d) 1.00

11. What will be the molality of a solution having 18 g of glucose (mol. wt. = 180) dissolved in 500 g of water?

(a) 1 m (b) 0.5 m
(c) 0.2 m (d) 2 m

12. 50 ml of 10N H_2SO_4, 25 ml of 12 N HCl and 40 ml of 5 N HNO_3 were mixed together and the volume of the mixture was made 1000 ml by adding water. The normality of the resulting solution will be

(a) 1 N (b) 2 N
(c) 3 N (d) 4 N

13. An aqueous solution of 6.3 g oxalic acid dihydrate is made upto 250 ml. The volume of 0.1 N NaOH required to completely neutralize 10 ml of this solution is

(a) 40 ml (b) 20 ml
(c) 10 ml (d) 4 ml

14. 2.5 litre of 1 M NaOH solution are mixed with another 3 litre of 0.5 M NaOH solution. Then the molarity of the resulting solution is

(a) 0.80 M (b) 1.0 M
(c) 0.73 M (d) 0.50 M

15. 12g of urea is dissolved in 1 litre of water and 68.4 g of sucrose is dissolved in 1 litre of water. The lowering of vapour pressure of first case is

(a) equal to second (b) greater than second
(c) less than second (d) double that of second

16. Which of the following statement is correct if the intermolecular forces in liquids A, B and C are in the order $A < B < C$?

(a) B evaporates more readily than A
(b) B evaporates less readily than C
(c) A and B evaporates at the same rate
(d) A evaporates more readily than C

17. The aqueous solution that has the lowest vapour pressure at a given temperature is

(a) 0.1 molal sodium phosphate
(b) 0.1 molal barium chloride
(c) 0.1 molal glucose
(d) 0.1 molal acetic acid

18. Vapour pressure of CCl_4 at 25°C is 143 mm Hg. 0.5 g of a non-volatile solute (mol. wt. 65) is dissolved in 100 ml of CCl_4. Find the vapour pressure of the solution. (Density of CCl_4 = 1.58 g/cm^3)

(a) 141.93 mm Hg (b) 94.39 mm Hg
(c) 199.34 mm Hg (d) 143.99 mm Hg

19. The vapour pressure of solvent decreases by 10 mm of mercury when a non-volatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2. What should be the mole fraction of the solvent if the decrease in vapour pressure is to be 20 mm of mercury ?

(a) 0.8 (b) 0.6
(c) 0.4 (d) 0.4

20. The vapour pressure of a solvent A is 0.80 atm. When a non-volatile substance B is added to this solvent its vapour pressure drops to 0.6 atm. the mole fraction of B in the solution is

(a) 0.25 (b) 0.50
(c) 0.75 (d) 0.90

21. At a particular temperature, the vapour pressures of two liquids A and B are respectively 120 and 180 mm of mercury. If 2 moles of A and 3 moles of B are mixed to form an ideal solution, the vapour pressure of the solution at the same temperature will be (in mm of mercury)

(a) 156 (b) 145
(c) 150 (d) 108

22. At room temperature, the mole fraction of a solute is 0.25 and the vapour pressure of a solvent is 0.80 atm. Then the lowering of vapour pressure is

(a) 0.75 (b) 0.60
(c) 0.20 (d) 0.80

23. Which of the following is not correct for ideal solution?

(a) $\Delta S_{mixing} = 0$ (b) $\Delta V_{mixing} = 0$
(c) $\Delta H_{mixing} = 0$ (d) It obeys Raoult's law

24. Which of the following does not show positive deviation from Raoult's law?

(a) Benzene-Chloroform
(b) Benzene-Acetone
(c) Benzene-Ethanol
(d) Benzene-Carbon tetrachloride

25. Identify the mixture that shows positive deviation from Raoult's law

(a) $CHCl_3 + (CH_3)_2CO$
(b) $(CH_3)_2CO + C_6H_5NH_2$
(c) $CHCl_3 + C_6H_6$
(d) $(CH_3)_2CO + CS_2$

26. Azeotropic mixture of HCl and H_2O has

(a) 48% HCl (b) 22.2% HCl
(c) 36% HCl (d) 20.2% HCl

27. Which of the following is not a colligative property?

(a) Depression in freezing point
(b) Elevation of boiling point
(c) Osmotic pressure
(d) Modification of refractive index

28. Which of the following is a colligative property?

(a) Change in free energy (b) Change in pressure
(c) Heat of vapourisation (d) Osmotic pressure

29. Which of the following colligative properties can provide molar mass of proteins (or polymers or colloids) with greatest precision?

(a) Depression in freezing point
(b) Osmotic pressure
(c) Relative lowering of vapour pressure
(d) Elevation of boiling point

30. Isotonic solutions have same

(a) molar concentration (b) molality
(c) normality (d) None of these

31. When mango is placed in dilute aqueous solution of hydrochloric acid, it

(a) shrinks (b) swells
(c) bursts (d) Nothing happens

32. As a result of osmosis, the volume of the solution

(a) gradually decreases (b) gradually increases
(c) is not affected (d) Any of the three

33. The relationship between osmotic pressure at 273 K when 10g glucose (P_1), 10 g urea (P_2), and 10g sucrose (P_3) are dissolved in 250 ml of water is

(a) $P_1 > P_2 > P_3$ (b) $P_3 > P_1 > P_2$
(c) $P_2 > P_1 > P_3$ (d) $P_2 > P_3 > P_1$

34. 0.1 M NaCl and 0.1 M CH_3COOH are kept in separate containers. If their osmotic pressures are P_1 and P_2 respectively then what is the correct statement?

(a) $P_1 > P_2$ (b) $P_1 = P_2$
(c) $P_1 < P_2$ (d) $P_1 = P_2 = 0$ atm.

35. What happen when isotonic solution of A (mol. wt. 342) and B (mol. wt. 60) are put into communication through semipermeable membrane?

(a) Transference of solvent from solution of A to that of B takes place
(b) Transference of solvent from solution of B to that of A takes place
(c) No transference of solvent from solution of A to that of B takes place
(d) Change in temperature of the solutions takes place

36. Which among the following will show maximum osmotic pressure?

(a) 1 M NaCl (b) 1 M $MgCl_2$
(c) 1 M $(NH_4)_3PO_4$ (d) 1 M Na_2SO_4

37. Isotonic solutions have

(a) same boiling point (b) same vapour pressure
(c) same melting point (d) same osmotic pressure

38. An aqueous solution of sucrose, $C_{12}H_{22}O_{11}$, containing 34.2 g/ litre has an osmotic pressure of 2.38 atmospheres at 17°C. For an aqueous solution of glucose, $C_6H_{12}O_6$ to be isotonic with this solution, it would have

(a) 34.2 g/lit of glucose (b) 17.1 g/lit of glucose
(c) 18.0 g/lit of glucose (d) 36.0 g/lit of glucose

39. The osmotic pressure of 5% (mass-volume) solution of cane sugar at 150°C (mol. mass of sugar = 342) is

(a) 4 atm (b) 5.07 atm
(c) 3.55 atm (d) 2.45 atm

40. A 1% aqueous solution (mass by volume) of a certain substance is isotonic with a 3% solution of dextrose i.e. glucose (molar mass 180) at a given temperature. The molar mass of the substance is

(a) 60 (b) 120
(c) 180 (d) 360

41. A 5% solution of cane sugar (mol. wt. = 342) is isotonic with 1% solution of substance X. The molecular weight of X is

(a) 34.2 (b) 171.2
(c) 68.4 (d) 136.8

42. If the solution boils at a temperature T_1 and the solvent at a temperature T_2 the elevation of boiling point is given by

(a) $T_1 + T_2$ (b) $T_1 - T_2$
(c) $T_2 - T_1$ (d) $T_1 + T_2$

43. Which of the following will have highest boiling point at 1 atm pressure?

(a) 0.1 M NaCl (b) 0.1 M Sucrose
(c) 0.1 M $BaCl_2$ (d) 0.1 M Glucose

44. A solution of 1 molal concentration of a solute will have maximum boiling point elevation when the solvent is

(a) ethyl alcohol (b) acetone
(c) benzene (d) chloroform

45. The normal boiling point of water is 373 K (at 760 mm Hg). Vapour pressure of water at 298 K is 23 mm Hg. If enthalpy of vaporisation is 40.656 kJ mol^{-1}, the boiling point of water at 23 mm Hg pressure will be

(a) 250 K (b) 294.4 K
(c) 51.6 K (d) 12.5 K

46. If the elevation in boiling point of a solution of 10 gm of solute (mol. wt. = 100) in 100 gm of water is ΔT_b, the ebullioscopic constant of water is

(a) 10 (b) $10\,\Delta T_b$
(c) ΔT_b (d) $\frac{\Delta T_b}{10}$

47. The rise in the boiling point of a solution containing 1.8 g of glucose in 100 g of solvent is 0.1°C. The molal elevation constant of the liquid is

(a) 0.01 K/m (b) 0.1 K/m
(c) 1 K/m (d) 10 K/m

48. The boiling point of a solution of 0.11 g of a substance in 15 g of ether was found to be 0.1°C higher than that of pure ether. The molecular weight of the substance will be (K_b = 2.16°K kg mol^{-1})

(a) 148 (b) 158
(c) 168 (d) 178

49. The boiling point of 0.1 molal $K_4[Fe(CN)_6]$ solution will be (Given K_b for water = 0.52°K kg mol^{-1})

(a) 100.52°C (b) 100.104°C
(c) 100.26°C (d) 102.6°C

50. The freezing point of equimolal aqueous solution will be highest for

(a) $C_6H_5NH_3^+Cl^-$ (b) $Ca(NO_3)_2$
(c) $La(NO_3)_2$ (d) $C_6H_{12}O_6$

51. If all the following four compounds were sold at the same price, which would be cheapest for preparing an antifreeze solution for a car radiator?

(a) CH_3OH (b) C_2H_5OH
(c) $C_2H_4(OH)_2$ (d) $C_3H_5(OH)_3$

52. Which of the following 0.10 m aqueous solution will have the lowest freezing point?

(a) $Al_2(SO_4)_3$ (b) $C_6H_{10}O_5$
(c) KI (d) $C_{12}H_{22}O_{11}$

53. Which of the following aqueous solution will have highest depression in freezing point?
(a) 0.1 M Urea (b) 0.1 M Sucrose
(c) 0.1 M $AlCl_3$ (d) 0.1 M $K_4[Fe(CN)_6]$

54. The depression in freezing point for 1 M urea, 1 M glucose and 1 M NaCl are in the ratio
(a) 1 : 2 : 3 (b) 3 : 2 : 2
(c) 1 : 1 : 2 (d) None of these

55. Which one of the following aqueous solutions will have the lowest freezing point?
(a) 0.1 molal solution of urea
(b) 0.1 molal solution of sucrose
(c) 0.1 molal solution of sodium chloride
(d) 0.1 molal solution of calcium chloride

56. The depression of freezing point is directly proportional to
(a) mole fraction of the solution
(b) molarity of the solution
(c) molality of the solution
(d) molarity of the solvent

57. A 0.5 molal solution of ethylene glycol in water is used as coolant in a car. If the freezing point constant of water be 1.86°C per mole, the mixture shall freeze at
(a) 0.93°C (b) –0.93°C
(c) 1.86°C (d) –1.86°C

58. An aqueous solution freezes at –0.186°C (K_f = 1.86, K_b = 0.512) what is the elevation in boiling point?
(a) 0.186 (b) 0.512
(c) 0.86 (d) 0.0512

59. The molal freezing point constant for water is 1.86°C/m. Therefore, the freezing point of 0.1 M NaCl solution in water is expected to be
(a) –1.86°C (b) –0.186°C
(c) –0.372°C (d) +0.372°C

60. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to
(a) ionization of benzoic acid
(b) dimerization of benzoic acid
(c) trimerization of benzoic acid
(d) solvation of benzoic acid

61. The van't Hoff factor for 0.1 M $Ba(NO_3)_2$ solution is 2.74. The degree of dissociation is
(a) 91.3% (b) 87%
(c) 100% (d) 74%

62. Formation of a solution from two components can be considered as
(i) pure solvent → separated solvent molecules, ΔH_1
(ii) pure solute → separated solute molecules, ΔH_2
(iii) separated solvent and solute molecules → solution, ΔH_3
Solution so formed will be ideal if
(a) $\Delta H_{soln} = \Delta H_1 + \Delta H_2 - \Delta H_3$
(b) $\Delta H_{soln} = \Delta H_1 - \Delta H_2 - \Delta H_3$
(c) $\Delta H_{soln} = \Delta H_3 - \Delta H_1 - \Delta H_2$
(d) $\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$

63. If liquids A and B form an ideal solution
(a) the enthalpy of mixing is zero
(b) the entropy of mixing is zero
(c) the free energy of mixing is zero
(d) the free energy as well as the entropy of mixing are each zero

64. 25 ml of a solution of barium hydroxide on titration with a 0.1 molar solution of hydrochloric acid gave a titre value of 35 ml. The molarity of barium hydroxide solution was
(a) 0.07 (b) 0.14
(c) 0.28 (d) 0.35

65. During depression of freezing point in a solution the following are in equilibrium
(a) liquid solvent, solid solvent
(b) liquid solvent, solid solute
(c) liquid solute, solid solute
(d) liquid solute, solid solvent

Exercise-3 | PAST COMPETITION MCQs

1. A 0.0020 m aqueous solution of an ionic compound $Co(NH_3)_5(NO_2)Cl$ freezes at – 0.00732 °C. Number of moles of ions which 1 mol of ionic compound produces on being dissolved in water will be (K_f = – 1.86°C/m) **[CBSE-PMT 2009]**
(a) 3 (b) 4 (c) 1 (d) 2

2. An aqueous solution is 1.00 molal in KI. Which change will cause the vapour pressure of the solution to increase? **[CBSE-PMT 2010]**
(a) Addition of NaCl (b) Addition of Na_2SO_4
(c) Addition of 1.00 molal KI (d) Addition of water

3. A solution of sucrose (molar mass = 342 g mol^{-1}) has been prepared by dissolving 68.5 g of sucrose in 1000 g of water. The freezing point of the solution obtained will be (K_f for water = 1.86 K kg mol^{-1}). **[CBSE-PMT 2010]**
(a) – 0.372°C (b) – 0.520°C
(d) + 0.372°C (d) – 0.570°C

4. 25.3 g of sodium carbonate, Na_2CO_3 is dissolved in enough water to make 250 mL of solution. If sodium carbonate dissociates completely, molar concentration of sodium ions, Na^+ and carbonate ions, CO_3^{2-} are respectively (Molar mass of $Na_2CO_3 = 106\ g\ mol^{-1}$) **[CBSE-PMT 2010]**

(a) 0.955 M and 1.910 M
(b) 1.910 M and 0.955 M
(c) 1.90 M and 1.910 M
(d) 0.477 M and 0.477 M

5. The freezing point depression constant for water is $-1.86°C\ m^{-1}$. If 5.00 g Na_2SO_4 is dissolved in 45.0 g H_2O, the freezing point is changed by $-3.82°C$. Calculate the van't Hoff factor for Na_2SO_4 **[CBSE-PMT 2011]**

(a) 2.05
(b) 2.62
(c) 3.11
(d) 0.381

6. The van't Hoff factor i for a compound which undergoes dissociation in one solvent and association in other solvent is respectively : **[CBSE-PMT 2011]**

(a) less than one and greater than one.
(b) less than one and less than one.
(c) greater than one and less than one.
(d) greater than one and greater than one.

7. Mole fraction of the solute in a 1.00 molal aqueous solution is **[CBSE-PMT 2011]**

(a) 0.1770
(b) 0.0177
(c) 0.0344
(d) 1.7700

8. A 0.1 molal aqueous solution of a weak acid is 30% ionized. If K_f for water is 1.86°C/m, the freezing point of the solution will be : **[CBSE-PMT 2011 M]**

(a) $-0.18°C$
(b) $-0.54°C$
(c) $-0.36°C$
(d) $-0.24°C$

9. 200 mL of an aqueous solution of a protein contains its 1.26 g. The osmotic pressure of this solution at 300 K is found to be 2.57×10^{-3} bar. The molar mass of protein will be ($R = 0.083\ L\ bar\ mol^{-1}\ K^{-1}$) **[CBSE-PMT 2011 M]**

(a) $51022\ g\ mol^{-1}$
(b) $122044\ g\ mol^{-1}$
(c) $31011\ g\ mol^{-1}$
(d) $61038\ g\ mol^{-1}$

10. P_A and P_B are the vapour pressure of pure liquid components, A and B, respectively of an ideal binary solution. If X_A represents the mole fraction of component A, the total pressure of the solution will be. **[CBSE-PMT 2012]**

(a) $P_A + X_A(P_B - P_A)$
(b) $P_A + X_A(P_A - P_B)$
(c) $P_B + X_A(P_B - P_A)$
(d) $P_B + X_A(P_A - P_B)$

11. Freezing point of an aqueous solution is (–0.186)°C. Elevation of boiling point of the same solution is $K_b = 0.512°C, K_f = 1.86°C$, find the increase in boiling point. **[AIEEE 2002]**

(a) 0.186°C
(b) 0.0512°C
(c) 0.092°C
(d) 0.2372°C.

12. In mixture A and B components show -ve deviation as **[AIEEE 2002]**

(a) $\Delta V_{mix} > 0$
(b) $\Delta H_{mix} < 0$
(c) $A-B$ interaction is weaker than $A-A$ and $B-B$ interaction
(d) $A-B$ interaction is stronger than $A-A$ and $B-B$ interaction.

13. A pressure cooker reduces cooking time for food because **[AIEEE 2003]**

(a) boiling point of water involved in cooking is increased
(b) the higher pressure inside the cooker crushes the food material
(c) cooking involves chemical changes helped by a rise in temperature
(d) heat is more evenly distributed in the cooking space

14. In a 0.2 molal aqueous solution of a weak acid HX the degree of ionization is 0.3. Taking k_f for water as 1.85, the freezing point of the solution will be nearest to **[AIEEE 2003]**

(a) $-0.360°C$
(b) $-0.260°C$
(c) $+0.480°C$
(d) $-0.480°C$

15. Which one of the following aqueous solutions will exihibit highest boiling point ? **[AIEEE 2004]**

(a) 0.015 M urea
(b) 0.01 M KNO_3
(c) 0.01 M Na_2SO_4
(d) 0.015 M glucose

16. 6.02×10^{20} molecules of urea are present in 100 ml of its solution. The concentration of urea solution is **[AIEEE 2004]**

(a) 0.02 M
(b) 0.01 M
(c) 0.001 M
(d) 0.1 M

(Avogadro constant, $N_A = 6.02 \times 10^{23}\ mol^{-1}$)

17. To neutralise completely 20 mL of 0.1 M aqueous solution of phosphorous acid (H_3PO_3), the value of 0.1 M aqueous KOH solution required is **[AIEEE 2004]**

(a) 40 mL
(b) 20 mL
(c) 10 mL
(d) 60 mL

18. For which of the following parameters the structural isomers C_2H_5OH and CH_3OCH_3 would be expected to have the same values? **[AIEEE 2004]**

(Assume ideal behaviour)

(a) Boiling points
(b) Vapour pressure at the same temperature
(c) Heat of vapourization
(d) Gaseous densities at the same temperature and pressure

19. Which of the following liquid pairs shows a positive deviation from Raoult's law ? **[AIEEE 2004]**

(a) Water - nitric acid
(b) Benzene - methanol
(c) Water - hydrochloric acid
(d) Acetone - chloroform

20. Which one of the following statements is **FALSE?** **[AIEEE 2004]**

(a) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is

$BaCl_2 > KCl > CH_3COOH >$ Sucrose

(b) The osmotic pressure (π) of a solution is given by the equation $\pi = MRT$, where M is the molarity of the solution

(c) Raoult's law states that the vapour pressure of a component over a solution is proportional to its mole fraction

(d) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression

21. If α is the degree of dissociation of Na_2SO_4, the Vant Hoff's factor (i) used for calculating the molecular mass is **[AIEEE 2005]**

(a) $1-2\alpha$ (b) $1+2\alpha$
(c) $1-\alpha$ (d) $1+\alpha$

22. Benzene and toluene form nearly ideal solution. At 20°C, the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapour pressure of benzene at 20°C for a solution containing 78 g of benzene and 46 g of toluene in torr is **[AIEEE 2005]**

(a) 53.5 (b) 37.5
(c) 25 (d) 50

23. Two solutions of a substance (non electrolyte) are mixed in the following manner. 480 ml of 1.5 M first solution + 520 ml of 1.2 M second solution. What is the molarity of the final mixture? **[AIEEE 2005]**

(a) 2.70 M (b) 1.344 M
(c) 1.50 M (d) 1.20 M

24. Equimolar solutions in the same solvent have **[AIEEE 2005]**

(a) different boiling and different freezing points
(b) same boiling and same freezing points
(c) same freezing point but different boiling point
(d) same boiling point but different freezing point

25. Density of a 2.05M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is **[AIEEE 2006]**

(a) 2.28 mol kg^{-1} (b) 0.44 mol kg^{-1}
(c) 1.14 mol kg^{-1} (d) 3.28 mol kg^{-1}

26. 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water. The vapour pressure of water for this aqueous solution at 100°C is **[AIEEE 2006]**

(a) 76.00 Torr (b) 752.40 Torr
(c) 759.00 Torr (d) 7.60 Torr

27. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm Hg at 300 K. The vapour pressure of propyl alcohol is 200 mm Hg. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm Hg) at the same temperature will be **[AIEEE 2007]**

(a) 360 (b) 350 (c) 300 (d) 700

28. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm^{-3}, molar mass of the substance will be **[AIEEE 2007]**

(a) 210.0 g mol^{-1} (b) 90.0 g mol^{-1}
(c) 115.0 g mol^{-1} (d) 105.0 g mol^{-1}.

29. At 80° C, the vapour pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mm Hg. If a mixture solution of 'A' and 'B' boils at 80° C and 1 atm pressure, the amount of 'A' in the mixture is (1 atm = 760 mm Hg) **[AIEEE 2008]**

(a) 52 mol percent (b) 34 mol percent
(c) 48 mol percent (d) 50 mol percent

30. The vapour pressure of water at 20°C is 17.5 mm Hg. If 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20°C, the vapour pressure of the resulting solution will be **[AIEEE 2008]**

(a) 17.325 mm Hg (b) 15.750 mm Hg
(c) 16.500 mm Hg (d) 17.500 mm Hg

31. A binary liquid solution is prepared by mixing *n*-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution? **[AIEEE 2009]**

(a) The solution is non-ideal, showing – ve deviation from Raoult's Law.

(b) The solution is non-ideal, showing + ve deviation from Raoult's Law.

(c) *n*-heptane shows + ve deviation while ethanol shows – ve deviation from Raoult's Law.

(d) The solution formed is an ideal solution.

32. Two liquids *X* and *Y* form an ideal solution. At 300 K, vapour pressure of the solution containing 1 mol of *X* and 3 mol of *Y* is 550 mm Hg. At the same temperature, if 1 mol of *Y* is further added to this solution, vapour pressure of the solution increases by 10 mm Hg. Vapour pressure (in mm Hg) of *X* and *Y* in their pure states will be, respectively: **[AIEEE 2009]**

(a) 300 and 400 (b) 400 and 600
(c) 500 and 600 (d) 200 and 300

33. If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f), when 0.01 mol of sodium sulphate is dissolved in 1 kg of water, is (K_f = 1.86 K kg mol^{-1}) **[AIEEE 2010]**

(a) 0.372 K (b) 0.0558 K (c) 0.0744 K (d) 0.0186 K

34. On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25.0 g of heptane and 35 g of octane will be (molar mass of heptane = 100 g mol^{-1} and of octane = 114 g mol^{-1}) **[AIEEE 2010]**

(a) 72.0 kPa (b) 36.1 kPa (c) 96.2 kPa (d) 144.5 kPa

35. A 5% solution of cane sugar (molar mass 342) is isotonic with 1% of a solution of an unknown solute. The molar mass of unknown solute in g/mol is : **[AIEEE 2011RS]**

(a) 171.2 (b) 68.4 (c) 34.2 (d) 136.2

36. K_f for water is 1.86 K kg mol^{-1}. If your automobile radiator holds 1.0 kg of water, how many grams of ethylene glycol ($C_2H_6O_2$) must you add to get the freezing point of the solution lowered to –2.8°C ? **[AIEEE 2012]**

(a) 72 g (b) 93 g (c) 39 g (d) 27 g

37. The molarity of a solution obtained by mixing 750 mL of 0.5(M) HCl with 250 mL of 2(M) HCl will be : **[JEE M 2013]**

(a) 0.875 M (b) 1.00 M (c) 1.75 M (d) 0.975 M

38. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene (K_f = 1.72 K kg mol^{-1}), a freezing point depression of 2 K is observed. The Van't Hoff factor (*i*) is **[IIT-JEE 2007]**

(a) 0.5 (b) 1 (c) 2 (d) 3

39. The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water at 298 K and 5 atm pressure is **[IIT-JEE 2009]**

(a) 4.0×10^{-4} (b) 4.0×10^{-5}

(c) 5.0×10^{-4} (d) 4.0×10^{-6}

40. Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of the solution is **[IIT-JEE 2011]**

(a) 1.78 M (b) 2.00 M (c) 2.05 M (d) 2.22 M

41. The freezing point (in °C) of a solution containing 0.1 g of $K_3[Fe(CN)_6]$ (Mol. wt. 329) in 100 g of water (K_f = 1.86 K kg mol^{-1}) is **[IIT-JEE 2011]**

(a) -2.3×10^{-2} (b) -5.7×10^{-2}

(c) -5.7×10^{-3} (d) -1.2×10^{-2}

42. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take K_b = 0.76 K kg mol^{-1}) **[IIT-JEE 2012]**

(a) 724 (b) 740 (c) 736 (d) 718

Exercise-4 | Applied MCQs

1. An X molal solution in carbon tetrachloride show the mole fraction of solute equal to 0.23527 . The value of X is

(a) 1.55 (b) 1.82

(c) 2.00 (d) 2.16

2. 3.0 molal sodium hydroxide solution has a density of 1.110 gm L^{-1} . The molarity of this solution is

(a) 2.97 (b) 3.05

(c) 3.65 (d) 4.11

3. For a solution of two liquids A and B it was proved that $P_S = x_A(p°_A - p°_B) + p°_B$. The resulting solution will be

(a) Non -ideal (b) ideal

(c) semi-ideal (d) None of these

4. The vapour pressure of water at 50°C is 92.5 torr. What will be the vapour pressure of solution which consists of 1 mole of nonvolatile solute in 100 g of water at 50°C

(a) 906 .5 torr (b) 94.2 torr

(c) 91.8 torr (d) 90.8 torr.

5. When 200g of 10% solution was cooled part of the solute precipitated and the concentration of solution become 6% . The mass of the precipitated solute is

(a) 6.2 g (b) 8.5 g

(c) 12.6 g (d) 14.0 g

6. At 30°C and 40°C the vapour pressure of a liquid are 0.025 and 0.050 atm respectively. Calculate the heat of vaporization of the liquid.

(a) 14.06 cal/mol (b) 13060 cal/mol

(c) 140.8 cal /mol (d) 2160 cal/ mol

7. The equilibrium vapour pressure of water vapour over a 0.20 mole sample of water (l) is 35 torr at 27°C. If the amount of the liquid water is decreased to 0.10 mole, the equilibrium vapour pressure of it would be

(a) 17.5 torr (b) 35.0 torr

(c) 51.5 torr (d) None of these

8. A flask is partially evacuated to 400 torr pressure of air. A small amount of benzene is introduced into the flask in order that some liquid will remain after equilibrium has been established. The vapour pressure of benzene at 25°C is 220 torr. . What is the total pressure in the flask at equilibrium at 25°C ?

(a) 120 torr (b) 510 torr

(c) 620 torr (d) 480 torr

9. Which of the following solutions will have the highest boiling point?

(a) 0.5 molal $BaCl_2$

(b) 1.0 molal KBr

(c) 1.8×10^{24} glucose molecules per litre.

(d) 100 g powdered glucose in one litre water

10. Two 1-litre flask A and B are connected to each other by a valve which is closed. Flask A has benzene in equilibrium with its vapours at 30°C. The flask B, is evacuated, and the valve is opened. Which of the following is true. If temperature is kept constant.'

(a) Some of the benzene molecules would move to flask B from flask A.

(b) Vapour pressure will be half the initial value.

(c) The vapour pressure remains unchanged

(d) Some more of the liquid benzene in flask A would evaporate.

11. The vapour pressure of ethanol and methanol are 42.0 mm and 88.5 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 46.0 g of ethanol with 16.0 g of methanol. What is the mole fraction of methanol vapour ?

(a) 0.467 (b) 0.502

(c) 0.513 (d) 0.556

12. Which of the following solutions will have the maximum lowering of vapour pressure at 300 K

(a) 1 M $CaCl_2$ (b) 1 M NaCl

(c) 1 M Phenol (d) 1 M sucrose

13. Two Aqueous solutions S_1 and S_2 are separated by a semipermeable membrane. Solution S_1 has got a greater vapour pressure than solution S_2. Water will be flowing

(a) from S_1 to S_2

(b) from S_2 to S_1

(c) in both the directions

(d) in either direction depending upon the nature of the solute

14. What is the degree of dissociation of sodium chloride, if the molar mass determined by a cryoscopic method was found to be 31.80 g mol^{-1} [Atomic mass Na = 23 g mol^{-1} Cl = 35.5 g mol^{-1}] ?

(a) 0.58 (b) 0.73

(c) 0.84 (d) 0.92

15. Consider the following statements

1. Isotonic solutions have the same molar concentration at a given temperature
2. The molal elevation constant K_b is a characteristic of a solvent, and is independent of the solute added
3. The freezing point of a 0.1 M aqueous KCl solution is more than that of a 0.1 M aqueous $AlCl_3$ solution.

Which of these statements is correct?

(a) 1 and 2 (b) 2 and 3

(c) 1 and 3 (d) 1, 2 and 3

16. The vapour pressure of pure liquid is 70 torr at 300 K. It forms an ideal solution with another liquid Y. The mole fraction of Y in the solution is 0.2 and total pressure of solution is 84 torr at 300 K. The vapour pressure of pure liquid Y at 27° C

(a) 70 torr (b) 560 torr

(c) 140 torr (d) 154 torr

17. The molecular mass of a solute cannot be calculated by which of the following?

(a) $M_B = \dfrac{W_B \times RT}{\pi V}$ (b) $M_B = \dfrac{p^o\, W_B M_A}{(p^o - p) W_A}$

(c) $M_B = \dfrac{\Delta T_b W_B \times 1000}{K_b W_A}$ (d) $M_B = \dfrac{K_b W_B \times 1000}{\Delta T_b \times W_A}$

18. At certain hill station pure water boils at 99.725 ° C. If K_b for water is 0.513 ° C kg mol^{-1}, the boiling point of 0.69 m solution of urea will be

(a) 103 °C (b) 100.079 °C

(c) 100.359 °C (d) unpredictable

19. Two elements A and B form compounds of formula AB_2 and AB_4. When dissolved in 20.0 g of benzene 1.0 g of AB_2 lowers F. pt. by 2.3° C whereas 1.0 g of AB_4 lowers F. pt. by 1.3° C. The K_f for benzene is 5.4. The atomic masses of A and B are

(a) 25, 42 (b) 42, 25

(c) 52, 48 (d) 48, 52

20. The heat of vaporisation of benzene is 7353 cal mol^{-1}. The approximate bpt. of benzene is

(a) 77.1 °C (b) 87.1 °C

(c) 101 °C (d) 95 °C

21. The vapour pressure of a solution of the liquids A ($p° = 80$ mm Hg and $x_A = 0.4$) and B ($p° = 120$ mm Hg and $x_B = 0.6$) is found to be 100 mm Hg. It shows that the solution exhibits

(a) positive deviation from ideal behaviour

(b) negative deviation from ideal behaviour

(c) ideal behaviour

(d) positive deviation for lower conc. and negative for higher conc.

22. Plot of $\frac{1}{x_A}$ Vs $\frac{1}{Y_A}$ (x_A mole fraction of A in liquid state and Y_A in vapour state) is linear whose slope and intercept respectively are given

(a) $p_B^o / p_A^o, \frac{p_B^o - p_A^o}{p_B^o}$

(b) $p_A^o - p_B^o, \frac{p_A^o - p_B^o}{p_B^o}$

(c) $p_B^o - p_A^o, \frac{p_B^o - p_A^o}{p_B^o}$

(d) $p_B^o / p_A^o, \frac{p_A^o - p_B^o}{p_B^o}$

23. How many grams of sucrose (M. wt. 342) must be dissolved in 100 g water to produce a solution with a 105.0°C difference between the freezing point & the boiling point temperature ?

(a) 460 g (b) 342 g

(c) 72 g (d) 34.2 g

24. Coolent used in car radiator is aqueous solution of ethylene glycol. In order to prevent the solution from freezing at – 0.3 °C. How much ethylene glycol must be added to 5 kg of water ? ($K_f = 1.86$ K kg mol^{-1})

(a) 50 kg (b) 55 g

(c) 45 g (d) 40 g

25. The total vapour pressure of a solution of components A and B is 600 torr. The mole fraction of component A in liquid and vapour phase are 0.70 and 0.35 respectively. The vapour pressure of pure A and B are

(a) 300 torr, 130 torr (b) 1300 torr, 300 torr

(c) 300 torr, 1300 torr (d) 300 torr, 300 torr

26. A current of dry air is passed through a solution of 2.64 g of a non volatile solute in 30.0 g of ether and then through pure ether. The loss in weight of solution was 0.645 g and of the ether 0.0345 g. The molecular weight of the solid is

(a) 122 g (b) 12.2 g

(c) 244 g (d) 135 g

27. An ideal solution of 1 mol A and 2 mol B has vapour pressure 250 torr at 50° C. If 1 mole of A is added to the solution, the V. P. of solution becomes 300 torr. What will be the V. P. if 1 mole of B is added to the solution instead of 1 mole of A

(a) 150 torr (b) 225 torr

(c) 275 torr (d) 175 torr

Hints & Solutions

EXERCISE 1

7. (a) 0·322 mol/kg.
   (b) 373·165 K.
   (c) 0·137 mm Hg.
8. 177·38 g mol^{-1}
9. (i) They will shrink due to plasmolysis.
   (ii) They will swell and may even burst.
14. Sucrose < NaCl < Glucose

20. **(a)** **21.** **(a)** **22.** **(c)** **23.** **(c)** **24.** **(d)**
25. **(a)** **26.** **(b)** **27.** **(c)**

EXERCISE 2

1. **(d)** Molality involves weight of solute and solvent, hence it is independent of temperature.

2. **(d)** All are correct. See Henry's law.

3. **(b)** If one mole of solute is present in 1 Kg of solvent the conc. is 1 m.

4. **(b)** Solution will be neutral. Concentration of each will be 0.05 M since volume got doubled.

5. **(d)** For very dil. solution the concentration is expressed in ppm.

6. **(a)** Since the compound is impure more than theoretical weight is required.

7. **(c)** $M = \dfrac{\text{Wt}\times 1000}{\text{M.Wt}\times V} = \dfrac{98\times 1000}{98\times 100}\times 1.84 = 18.4$

8. **(b)** $M = \dfrac{\text{Wt}\times 1000}{\text{E.wt.}\times V};\quad 0.10 = \dfrac{\text{Wt}\times 1000}{63\times 500};$

$\text{Wt} = 3.150\ \text{g}$

9. **(b)** $M = \dfrac{\text{Wt}\times 1000}{\text{M.Wt.}\times V};\quad M = \dfrac{7.1\times 1000}{142\times 100} = 0.5\text{M}$

10. **(b)** $\text{CaCl}_2 \rightleftharpoons \text{Ca}^{++} + 2\text{Cl}^-$.

Moles of CaCl_2 in 500 ml $= 0.25$ and $\text{Cl}^- = 0.50$.

11. **(c)** Apply $m = \dfrac{\text{Wt.}\times 1000\text{g}}{\text{M.Wt}\times \text{Wt. of Solvent}}$

12. **(a)** $N = \dfrac{N_1V_1 + N_2V_2 + N_3V_3}{\text{Total volume}}$

$= \dfrac{50\times 10 + 25\times 12 + 40\times 5}{1000} = 1\text{N}$

13. **(a)** Normality of oxalic acid $= \dfrac{6.3\times 1000}{63\times 250} = 0.4$

$N_1V_1 = N_2V_2;\ 0.1\times V_1 = 0.4\times 10.\ \therefore\ V_1 = 40\ \text{ml}$

14. **(c)** $M_3V_3 = M_1V_1 + M_2V_2$

$\therefore\ M_3\times 5.5 = 2.5\times 1 + 3\times 0.5.\ \therefore\ M_3 = 0.727.$

15. **(a)** Moles of urea $= \dfrac{12}{60} = 0.2$

Moles of sucrose $= \dfrac{68.4}{342} = 0.2$

Both are non electrolyte hence lowering of V.P. will be same.

16. **(d)** Lesser the intermolecular forces, the more the volatile character.

17. **(a)** 0.1 m $\text{Na}_3\text{PO}_4 = 0.4$ m (Van't Hoff factor $i = 4$)

$\therefore$ Lowering of vapour pressure will be maximum.

18. **(a)** Relative lowering of V.P. = mole fraction of Solute

$\dfrac{p^o - p_s}{p^o} = x_2$

$\dfrac{143 - p_s}{143} = \dfrac{0.5/65}{158/154};\ p_s = 141.93\,\text{mm Hg}$

19. **(b)** $\dfrac{\Delta p}{p^o} = x_2;\ \dfrac{\Delta p}{\Delta p'} = \dfrac{x_2}{x'_2};\ \dfrac{10}{20} = \dfrac{0.2}{x'_2};$

$\therefore\ x'_2 = 0.4,\ x'_1 = 1 - 0.4 = 0.6$

sum of mole fractions is always 1

20. **(a)** $\dfrac{0.80 - 0.6}{0.80} = x_B;\ x_B = 0.25$

21. **(a)** Vapour pressure of solution $= P_A + P_B$

$= p_A^o x_A + p_B^o x_B = \dfrac{120\times 2}{5} + \dfrac{180\times 3}{5} = 156\ \text{mm Hg}$

22. **(c)** $\dfrac{\Delta p}{p^o} = x_B;\quad \therefore\ \Delta p = 0.25\times 0.80 = 0.20$

23. **(a)** $\Delta S_{\text{mixing}} \neq 0$ for ideal solution. On mixing two solutions the entropy increases.

24. (a) Benzene + chloroform, show negative deviation.

25. (d) $CH_3COCH_3 + CS_2$

26. (d) Azeotrope of $HCl + H_2O$ contains 20.2% HCl.

27. (d) Modification of refractive index is not a colligative property.

28. (d) Osmotic pressure.

29. (b) Osmotic pressure.

30. (a) Isotonic solutions have same molar concentration at given temperature provided the Van't Hoff factor (i) is same

31. (b) Mango swells due to osmosis.

32. (b) Increases

33. (c) Moles of glucose $\frac{10}{180} = 0.05$,

$$\text{urea} = \frac{10}{60} = 0.16, \quad \text{Sucrose} = \frac{10}{342} = 0.029 \cdot$$

Hence osmotic presure $p_2 > p_1 > p_3$ $(\pi \propto c)$

34. (a) NaCl is strong electrolyte and CH_3COOH weak electrolyte.

$\therefore p_1 > p_2$ (value of i will be more in case of NaCl)

35. (c) Since solutions are isotonic, hence no transference of solvents.

36. (c) Vant Hoff factor $i = 4$ in case of $(NH_4)_3PO_4$,

$$(NH_4)_3PO_4 \rightleftharpoons 3\overset{+}{N}H4 + PO_4^{3-}$$

37. (d) For isotonic solutions $\pi_1 = \pi_2$

38. (c) For isotonic solutions $\pi_1 = \pi_2$ or $C_1 = C_2$;

$$\frac{34.2}{342} = 0.1; \ \frac{18.0}{180} = 0.1 \cdot$$

Hence 18 gL^{-1} glucose is 0.1 M.

39. (b) $\pi = CRT \quad \pi = \frac{5}{342} \times \frac{1000}{100} \times 0.0821 \times 423 = 5.07$ atm.

40. (a) $\frac{30}{180} = \frac{10}{M_2} \quad \therefore M_2 = 60$

41. (c) $\frac{10}{m} = \frac{50}{342}; \ \therefore m = 68.4$

42. (b) Solution always boil at higher temperature $T_1 - T_2 = \Delta T_b$

43. (c) Conc. of particles will be highest in $BaCl_2$ (Van't Hoff factor $i = 3$).

44. (d) $\Delta T_b = K_b \times m$

when m = 1 $\Delta T_b = K_b$. Higher the value of K_b, the more is value of ΔT_b.

45. (b) Clapeyron Clausius equation $\log\frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$.

$$\log\frac{760}{23} = \frac{40656}{2.303 \times 8.314}\left(\frac{373 - T_1}{373T_1}\right)$$

$T_1 = 294.4K$

46. (c) $\Delta T_b = \frac{K_b \times w \times 1000}{M \times W}; \ \therefore K_b = \frac{\Delta T_b \times 100 \times 100}{10 \times 1000} = \Delta T_b$

47. (c) $K_b = \frac{0.1 \times 180 \times 100}{1.8 \times 1000} = 1\ K/m$

48. (b) $M = \frac{K_b \times w \times 1000}{\Delta T_b \times W} = \frac{2.16 \times 0.11 \times 1000}{0.1 \times 15} = 158.4$

49. (c) $\Delta T_b = K_b \times m \times i = 0.52 \times 0.1 \times 5 = 0.26;$

$\therefore$ b.pt. = 100.26°C

50. (d) Glucose is non electrolyte hence depression in freezing point will be minimum, hence freezing point will be highest.

51. (a) $\Delta T_f = \frac{K_f \times w \times 1000}{M \times W}$. Other things being equal, the smaller the molecular weight, the more is the ΔT_f

52. (a) $\Delta T_f = K_f \times w \times i$ van't Hoff factor $i = 5$ for $Al_2(SO_4)_3$ hence lowest freezing point.

53. (d) For $K_4[Fe(CN)_6]$, i = 5 hence lowest freezing point.

54. (c) Urea and glucose are non electrolytes and 1 M NaCl $\equiv$ 2M non electrolyte. $\therefore 1:1:2$. (for NaCl i = 2)

55. (d) 0.1 m $CaCl_2$. Concentration of particles = 0.3 m (Since $i = 3$).

56. (c) $\Delta T_f \propto m$ (m = molality of solution)

57. (b) $\Delta T_f = K_f \times m = 1.86 \times 0.5 = 0.93; \quad T_f = -0.93°C$

58. (c) $0.186 = 1.86 \times m; \ \therefore m = 0.1;$

$\therefore \Delta T_b = 0.512 \times 0.1 = 0.0512°C$

59. (c) $\Delta T_f = 2 \times K_f \times m = 2 \times 1.86 \times 0.1 = 0.372;$

$\therefore T_f = -0.372°C$

60. (b) Benzoic acid forms a dimer in benzene.

61. (b) $$\begin{array}{lcc} Ba(NO_3)_2 \rightleftharpoons & Ba^{++} + & 2NO_3^- \\ 1-\alpha & \alpha & 2\alpha \end{array}$$

$$i = \frac{1 - \alpha + \alpha + 2\alpha}{1} = 2.74; \ \therefore \alpha = 0.87 = 87\%$$

62. (d)

63. (a) For ideal solution $\Delta H_{mix} = 0$.

64. (b) $M_1V_1 = M_2V_2 \qquad M_1 \times 25 = 0.1 \times 35;$

$\therefore M_1 = 0.14$

65. (a) Liquid solvent and solid solvent are in equilibrium.

EXERCISE 3

1. **(d)** $\Delta T_f = 0-(0.00732°C) = 0.00732$
$\Delta T_f = i \times K_f \times m$
$$i = \frac{\Delta T_f}{K_f \times m} = \frac{0.00732}{1.86 \times 0.002} = 1.97 \approx 2$$

2. **(d)** When the aqueous solution of one molal KI is diluted with water, concentration decreases, therefore the vapour pressure of the resulting solution increases.

3. **(a)** $\Delta T_f = K_f \frac{1000 W_2}{M_2 W_1} = \frac{1.86 \times 1000 \times 68.5}{342 \times 1000} = 0.372$
$T_f = T°_f - \Delta T_f$
$T_f = -0.372°C$

4. **(b)** Concentration of $Na_2CO_3 = \frac{25.3}{106} \times \frac{1000}{250} = 0.955\ M$
$$[Na^+] = 2 \times 0.955 = 1.91\ M$$
$$\left[CO_3^{2-}\right] = 0.955\ M$$

5. **(b)** Given $K_f = -1.86°C\ m^{-1}$, mass of solute = 5.00 g, mass of solvent = 45.0 g and $\Delta T_f = -3.82°C$
$\Delta T_f = i \times K_f . m$
$3.82 = i \times 1.86 \times \frac{5 \times 1000}{142 \times 45}$
$\therefore i = 2.62$ (Molecular mass of $Na_2SO_4 = 142$ g)

6. **(c)** If compound dissociates in solvent $i > 1$ and on association $i < 1$.

7. **(b)** 1 molal solution means 1 mole of solute dissolved in 1000 gm solvent.
$\therefore\ n_{solute} = 1 \qquad w_{solvent} = 1000$ gm
$\therefore\ n_{solvent} = \frac{1000}{18} = 55.56$
$$x_{solute} = \frac{1}{1 + 55.56} = 0.0177$$

8. **(d)** Given $\alpha = 30\%$ i.e., 0.3
$$\begin{array}{lll} HA & \longrightarrow H^+ & + A^- \\ 1-\alpha & \alpha & \alpha \\ 1-0.3 & 0.3 & 0.3 \end{array}$$
$i = 1 - 0.3 + 0.3 + 0.3$
$i = 1.3$
$\Delta T_f = 1.3 \times 1.86 \times 0.1 = 0.2418$
$T_f = 0 - 0.2418 = -0.2418\ °C$

9. **(d)** $M = \frac{WRT}{\pi V} = \frac{1.26 \times 0.083 \times 300}{2.57 \times 10^{-3} \times 200 \times 10^{-3}}$
$$= \frac{31.374 \times 10^6}{514} = 61038\ g$$

10. **(d)** $p = p_A x_A + p_B x_B$
$= p_A x_A + p_B (1 - x_A)$
$\Rightarrow\ p_A x_A + p_B - p_B x_A$
$\Rightarrow\ p_B + x_A (p_A - p_B)$

11. **(b)** $\Delta T_b = K_b \frac{W_B}{M_B \times W_A} \times 1000$;
$$\Delta T_f = K_f \frac{W_B}{M_B \times W_A} \times 1000;$$
$$\frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f} = \frac{\Delta T_b}{-0.186} = \frac{0.512}{1.86} = 0.0512°C.$$

12. **(b)** $[\Delta H_{mix} < 0]$

13. **(a)** On increasing pressure, the temperature is also increased. Thus in pressure cooker due to increase in pressure the b.p. of water increases.

14. **(d)** $\Delta T_f = K_f \times m \times i$;
$\Delta T_f = 1.85 \times 0.2 \times 1.3 = 0.480°C$
$\therefore T_f = 0 - 0.480 = -0.480°C$
$$(\underset{1-0.3}{HX} \rightleftharpoons \underset{0.3}{\overset{+}{H}} + \underset{0.3}{X^-},\ i = 1.3)$$
$$i = 1 - 0.3 + 0.3 + 0.3 = 1.3$$

15. **(c)** $\Delta T_b = K_b \times m \times i$.
The value of i for $Na_2SO_4 = 3$,
for $KNO_3 = 2$, for urea = 1 and for glucose = 1

16. **(b)** $M = \frac{6.02 \times 10^{20} \times 1000}{6.02 \times 10^{23} \times 100} = 0.01M$

17. **(a)** $N_1V_1 = N_2V_2$ (H_3PO_3 is dibasic $\therefore M = 2N$)
$20 \times 0.2 = 0.1 \times V$
$\therefore V = 40\ ml$

18. **(d)** Gaseous densities of ethanol and dimethyl ether would be same at same temperature and pressure. The heat of vaporisation, V.P. and b.pt. will differ due to H - bonding in ethanol.

19. **(b)** A mixture of benzene and methanol show positive deviation from Raoult's law

20. **(d)** $\Delta T_f = K_f \times m \times i$. Since K_f has different values for different solvents, hence even if the m is the same ΔT_f will be different

21. **(b)** $\underset{1-\alpha}{Na_2SO_4} \rightleftharpoons \underset{2\alpha}{2Na} + \underset{\alpha}{SO_4^-}$
$$\text{Vant. Hoff's factor } i = \frac{1 - \alpha + 2\alpha + \alpha}{1} = 1 + 2\alpha$$

22. (d) Given

Vapour pressure of benzene= 75 torr

Vapour pressure of toluene = 22 torr

mass of benzene in = 78g

hence moles of benzene $= \frac{78}{78} = 1\text{mole}$

(mol.wt of benzene = 78)

mass of toluene in solution = 46g

hence moles of toluene $= \frac{46}{92} = 0.5$ mole

now partial pressure of benzene $= P_b^o.X_b$

$$= 75 \times \frac{1}{1+0.5} = 50 \text{ torr} = 75 \times \frac{1}{1.5} = 78 \times \frac{2}{3}$$

23. (b) From the molarity equation.

$M_1V_1 + M_2V_2 = MV$

$$M = \frac{M_1V_1 + M_2 V_2}{V} \quad \text{where } V = V_1 + V_2$$

$$M = \frac{480 \times 1.5 + 520 \times 1.2}{480 + 520} = 1.344 \text{ M}$$

24. (d) Equimolar solutions of normal solutes in the same solvent will have the same b. pts and same f. pts.

25. (a) Apply the formula $d = M\left(\frac{1}{m} + \frac{M_2}{1000}\right)$

$$\therefore\ 1.02 = 2.05\left(\frac{1}{m} + \frac{60}{1000}\right)$$

On solving we get, m = 2.288 mol/kg

26. (b) Moles of glucose $= \frac{18}{180} = 0.1$

Moles of water $= \frac{178.2}{18} = 9.9$

Total moles = 0.1 + 9.9 = 10

$$p_{H_2O} = \text{Mole fraction} \times \text{Total pressure} = \frac{9.9}{10} \times 760$$

$$= 752.4 \text{ Torr}$$

27. (b) $p_A^\circ = ?$, Given $p_B^\circ = 200$ mm of Hg, $x_A = 0.6$,

$x_B = 1 - 0.6 = 0.4, P = 290$ of Hg

$$P = P_A + P_B = P_A^\circ x_A + P_B^\circ x_B$$

$$\Rightarrow 290 = P_A^\circ \times 0.6 + 200 \times 0.4 \ \therefore\ p_A^\circ = 350 \text{ mm of Hg.}$$

28. (a) Osmotic pressure (π) of isotonic solutions are equal. For solution of unknown substance C_1(concentration).

$$C_1 = \frac{5.25/M}{V}$$

Where M represents molar mass.

For solution of urea, C_2 (concentration) $= \frac{1.5/60}{V}$

Given, $\pi_1 = \pi_2$ $\quad\because \pi = CRT$

$$\therefore\ C_1RT = C_2RT \text{ or } C_1 = C_2 \text{ or } \frac{5.25/M}{V} = \frac{1.5/60}{V}$$

$\therefore\ M = 210$ g/mol

29. (d) At 1 atmospheric pressure the boiling point of mixture is 80°C.

At boiling point the vapour pressure of mixture, $p_T = 1$ atmosphere = 760 mm Hg.

Using the relation,

$p_T = p_A^\circ x_A + p_B^\circ x_B$, we get

$p_T = 520x_A + 1000(1 - x_A)$

$\{\because p_A^o = 520 \text{ mm Hg},$

$p_B^\circ = 1000 \text{ mm Hg},\ x_A + x_B = 1\}$

or $760 = 520x_A + 1000 - 1000x_A$ or $480x_A = 240$

or $x_A = \frac{240}{480} = \frac{1}{2}$ or 50 mol. percent

i.e., the correct answer is (d)

30. (a) The vapour pressure of a solution of glucose in water can be calculated using the relation

$$\frac{p^\circ - p_s}{p_s} = \frac{\text{Moles of glucose in solution}}{\text{Moles of water in solution}}$$

$$\text{or } \frac{17.5 - p_s}{p_s} = \frac{18/180}{178.2/18} \qquad [\because p^\circ = 17.5]$$

or $17.5 - p_s = \frac{0.1 \times p_s}{9.9}$ or $p_s = 17.325$ mm Hg.

Hence (a) is correct answer.

31. (b) For this solution intermolecular interactions between *n*-heptane and ethanol are weaker than *n*-heptane-*n*-heptane & ethanol-ethanol interactions hence the solution of *n*-heptane and ethanol is non-ideal and shows positive deviation from Raoult's law.

32. (b) $p_{\text{total}} = p_A^\circ x_A + p_B^\circ x_B$

$$550 = p_A^\circ \times \frac{1}{4} + p_B^\circ \times \frac{3}{4}$$

$$p_A^\circ + 3p_B^\circ = 550 \times 4 \qquad \text{...(i)}$$

In second case

$$p_{\text{total}} = p_A^\circ \times \frac{1}{5} + p_B^\circ \times \frac{4}{5}$$

$p_A^\circ + 4p_B^\circ = 560 \times 5$ ...(ii)

Subtract (i) from (ii)

$\therefore p_B^\circ = 560 \times 5 - 550 \times 4 = 600$

$\because p_A^\circ = 400$

33. (b) Sodium sulphate dissociates as

$Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{--}$

hence van't hoff factor $i = 3$

Now $\Delta T_f = iK_f.m$

$= 3 \times 1.86 \times 0.01 = 0.0558\,K$

34. (a) $p_{Total} = p^\circ_A x_A + p^\circ_B x_B$

$= p^\circ_{Heptane}\, x_{Heptane} + p^\circ_{Octane}\, x_{Octane}$

$$= 105 \times \frac{25/100}{\frac{25}{100}+\frac{35}{114}} + 45 \times \frac{35/114}{\frac{25}{100}+\frac{35}{114}}$$

$$= 105 \times \frac{0.25}{0.25+0.3} + 45 \times \frac{0.3}{0.25+0.3}$$

$$= \frac{105 \times 0.25}{0.55} + \frac{45 \times 0.3}{0.55} = \frac{26.25 + 13.5}{0.55}$$

$= 72$ kPa

35. (b) For isotonic solutions

$\pi_1 = \pi_2$

$C_1 = C_2$

$$\frac{5/342}{0.1} = \frac{1/M}{0.1}$$

$$\frac{5}{342} = \frac{1}{M}$$

$$\Rightarrow M = \frac{342}{5} = 68.4 \text{ gm/mol}$$

36. (b) $\Delta T_f = i \times K_f \times m$

Given $\Delta T_f = 2.8$, $K_f = 1.86$ K kg mol^{-1} $i = 1$

(ethylene glygol is a non- electrolyte)

wt. of solvent = 1 kg

Let of wt of solute = x

Mol. wt of ethylene glycol = 62

$$2.8 = 1 \times 1.86 \times \frac{x}{62 \times 1}$$

$$\text{or } x = \frac{2.8 \times 62}{1.86} = 93 \text{ gm}$$

37. (a) From molarity equation :

$M_1V_1 + M_2V_2 = M \times V$

$M = \frac{M_1V_1 + M_2V_2}{V}$ where V = total volume

$$= \frac{750 \times 0.5 + 250 \times 2}{1000}$$

$= 0.875$ M

38. (a) Molecular weight of naphthoic acid

$C_{11}H_8O_2 = 172$ g mol^{-1}.

The theoretical value of depression in freezing point

$$= K_f \times \text{ molality} = 1.72 \times \frac{20 \times 1000}{172 \times 50} = 4K$$

Van't Hoff factor,

$$i = \frac{\text{Observed value of colligative property}}{\text{Theoretical value of colligative property}}$$

$$= \frac{2}{4} = 0.5.$$

39. (a) $P_{N_2} = \kappa_H x_{N_2}$

$0.8 \times 5 = 1 \times 10^5 \times x_{N_2}$

$\therefore x_{N_2} = 4 \times 10^{-5}$

Solubility in 10 moles = 4×10^{-4}.

40. (c) Number of moles of urea = $\frac{120}{60} = 2$

Total mass of solution = 1000 + 120 = 1120 g

$$\text{Total volume of solution (in L)} = \frac{\text{Mass}}{\text{Density}}$$

$$= \frac{1120}{1.15 \times 10^3} = \frac{112}{115} L$$

$$\text{Molarity of the solution} = \frac{\text{Number of moles}}{\text{Volume of solution in litre}}$$

$$= \frac{2 \times 115}{112} = 2.05 \text{ mol } L^{-1}$$

41. (a) $\Delta T_f = i \times K_f \times m$

Where m = Molality of the solution

(*i.e.* number of moles of solute per 1000 g of the solvent)

Here $m = \frac{0.1}{329} \times 10$

Thus $\Delta T_f = 4 \times 1.86 \times \frac{0.1 \times 10}{329} = 2.3 \times 10^{-2}$

Thus $T_f = 0 - 2.3 \times 10^{-2} = -2.3 \times 10^{-2}$ °C

42. (a) From Raoult law

$$\frac{p^\circ - p}{p^\circ} = \frac{\text{No.of moles of solute}}{\text{No. of moles of solvent+ No. of moles of solute}}$$

When the concentration of solute is much lower than the concentration of solvent,

$$\frac{p^\circ - p}{p^\circ} = \frac{\text{No. of moles of solute}}{\text{No. of moles of solvent}}$$

$\Delta T_b = K_b \times m$

$$m = \frac{\text{Number of moles of the solute}}{\text{Mass of solvent in grams}} \times 1000$$

$$\Delta T_b = K_b \times \frac{\text{Number of moles of the solute}}{\text{Mass of solvent in grams}} \times 1000$$

Number of moles of solute

$$= \frac{\Delta T_b \times \text{Mass of solvent in grams}}{K_b \times 1000}$$

$$= \frac{2 \times 100}{0.76 \times 1000} = 0.26,$$

Number of moles of solvent $= \frac{100}{18} = 5.56$

From equation (i) we get, $\frac{760 - p}{760} = \frac{0.26}{5.56}$

On solving, $p = 724.46 \approx 724$

EXERCISE 4

1. **(c)** Use the formula, $m = \frac{1000X_2}{X_1M_1}$;

Given $X_2 = 0.23527, X_1 = (1 - 0.23527) = 0.76473$

Molecular weight of $CCl_4 = 153.82$,

$$m = \frac{1000 \times 0.23527}{0.76473 \times 153.82} = 2.00$$

2. **(a)** Use the formula

$$M = \frac{md}{1 + \frac{m.M_2}{1000}}; M = \frac{3.1 \times 1.110}{1 + \frac{3 \times 40}{1000}}; M = 2.97$$

3. **(b)** $p_s = X_A(p_A^o - p_B^o) + p_B^o$;

$p_s = p_A^o \times x_A - p_B^o \times x_A + p_B^o$;

$p_s = p_A^o \times x_A - p_B^o(1 - x_B) + p_B^o$

$\therefore p_s = p_A^o \times x_A + p_B^o \times x_B$.

This is condition for ideal solution.

4. **(d)** Moles of water $\frac{1000}{18} = 55.5$;

Mole fraction of water $= \frac{55.5}{55.5 + 1} = 0.982$

$p_A = 0.982 \times 92.5$; $p_A = 90.8$ torr

5. **(b)** 10% soln contains 10g solute in 90 gm solvent or 20 g solute in 180 g solvent

6% solution contains 6 g solute in 94g solvent. For 60% the amount of

solute in 180g solvent. $= \frac{6}{94} \times 180 = 11.48$;

Amount precipitated $= 8.52$ g

6. **(b)** Apply claypeyron equation,

$$\log\frac{0.050}{0.25} = \frac{\Delta H_v}{2.303R}\left(\frac{313 - 303}{313 \times 303}\right) = 13060 \text{cal/mol}$$

7. **(b)** The equilibrium vapour pressure will remain the same. It is independent of the quantity of substance

8. **(c)** The total pressure will be the sum of pressures of air and benzene

9. **(c)** For electrolytes multiply the concentration by Van't Hoff's factor i

(a) $0.5 \times 3 = 1.5$ for $BaCl_2$

(b) $1.0 \times 2 = 2$ for KBr,

(c) $\frac{1.8 \times 10^{24}}{6.023 \times 10^{23}} = 2.98$ for glucose

(d) $\frac{100}{180} = 0.55$ for glucose

Hence highest bpt will be observed in case of (c)

10. **(c)** There is no change in vapour pressure.

11. **(c)**

C_2H_5OH	CH_3OH
42.0 mm Hg	88.5 mm Hg
46.0g	16.0 g
1 Mole	0.5 Mole
Total Moles	$1 + 0.5 = 1.5$

Total pressure $P = 42 \times \frac{1}{1.5} + \frac{88.5 \times 0.5}{1.5}$;

$(p_A = p_A^o \times x_A)$

$p = 28 + 29.5 = 57.5$

Mole fraction in vapour phase p_A

$= x_A \times$ Total pressure

$\therefore x_A = \frac{29.5}{57.5} = 0.513$

12. **(a)** Maximum lowering of vapour pressure will be given by the substance giving maximum number of particles in solution. In case of electrolytes do not forget. To multiply the molarity by Van't Hoff factor i.

13. **(a)** In case of osmosis the flow of the solvent, from lower concentration to higher concentration.

14. **(c)** Let α be the give of dissociation then

$$\underset{1-\alpha}{NaCl} \rightleftharpoons \underset{\alpha}{Na^+} + \underset{\alpha}{Cl^-}$$

Van't Hoff's factor $i = \frac{1 - \alpha + \alpha + \alpha}{1} = 1 + \alpha$

Again Van't Hoff's factor

$$= \frac{\text{Normal mol.wt}}{\text{Observed mol.wt}} = \frac{58.5}{31.8} = 1.83$$

Equating to both values of i, $\therefore 1 + \alpha = 1.83$

$\therefore \alpha = 0.83$

15. (d) All the statements are correct (see text)

16. (c) $P = p^{o}_{A}.x_{A} + p^{o}_{B}.x_{B}$,

$84 = 0.2\, p^{o}_{Y} + 70.0 \times 0.8$

$\therefore\ p^{o}_{Y} = 140$ torr

17. (c) $M_{B} = \frac{\Delta T_{b} \times W_{B} \times 1000}{K_{b} \times W_{A}}$ is wrong. The correct form is

$$M_{B} = \frac{K_{b} \times W_{B} \times 1000}{\Delta T_{b} \times W_{A}}$$

18. (b) $\Delta T_{b} = K_{b} \times m = 0.513 \times 0.69 = 0.3539°\,C$

$\therefore$ bpt. of solution $= 99.725°\,C + 0.3539°\,C$

$= 100.079°\,C$

19. (a) Let the masses of A and B be a and b. The mass of AB_{2} will be $(a + 2b)\,g\,mol^{-1}$ and AB_{4} will be $(a + 4b)\,g\,mol^{-1}$

For AB_{2}, $2.3 = \frac{5.1 \times 1 \times 1000}{(a + 2b) \times 20}$ .... (I)

For AB_{4}, $1.3 = \frac{5.1 \times 1 \times 1000}{(a + 4b) \times 20}$ .... (II)

On solving (I) and (II),

$a = 25.49$ and $b = 42.64$

20. (a) Trouton's rule is $\frac{\Delta H_{evp}}{T_{b}} = 21$ cal. $K^{-1}\,mol^{-1}$

$$T_{b} = \frac{7353}{21} = 350.1\,K = 77.1°\,C$$

21. (b) $P_{total} = p^{o}_{A} \times x_{A} + p^{o}_{B} \times x_{B}$

$= 80.0 \times 0.4 + 120.0 \times 0.6 = 104$ mm Hg

The observed P_{total} is 100 mm Hg which is less than 104 mm Hg. Hence the solution shows negative deviation.

22. (c) $p_{A} = p^{o}_{A} \times x_{A} =$ Total pressure $\times\ y_{A}$

$p_{B} = p^{o}_{B} \times x_{B} =$ Total pressure $\times\ y_{B}$

Where x and y represent mole fraction in liquid and vapour phase respectively.

$$\therefore\ \frac{p^{o}_{B}\, x_{B}}{p^{o}_{B}\, x_{A}} = \frac{y_{B}}{y_{A}},$$

$$\frac{p^{o}_{B}(1 - x_{A})}{p^{o}_{A}\, x_{A}} = \frac{1 - y_{A}}{y_{A}}$$

$$\frac{1}{x_{A}} - 1 = \frac{p^{o}_{A}}{p^{o}_{B}}\left(\frac{1}{y_{A}} - 1\right)$$

$$= \frac{p^{o}_{A}}{p^{o}_{B}}\, \frac{1}{y_{A}} - \frac{p^{o}_{A}}{p^{o}_{B}}$$

$$\text{or,}\quad \frac{1}{x_{A}} = \frac{p^{o}_{A}}{p^{o}_{B}} \cdot \frac{1}{y_{A}} + \left(1 - \frac{p^{o}_{A}}{p^{o}_{B}}\right)$$

$$= \frac{p^{o}_{A}}{p^{o}_{B}} \cdot \frac{1}{y_{A}} + \frac{p^{o}_{B} - p^{o}_{A}}{p^{o}_{B}}$$

This is equation of straight line.

Slope $= \frac{p^{o}_{A}}{p^{o}_{B}}$, Intercept $= \frac{p^{o}_{B} - p^{o}_{A}}{p^{o}_{B}}$

23. (c) B. pt. $= 100 + \Delta T_{b} = 100 + K_{b}\, m$

F. pt. $= 0 - \Delta T_{f} = 0 - K_{f}\, m$

$T_{b} - T_{f} = 100 + K_{b}\, m - (-\ K_{f}\, m)$

$105 = 100 + 0.51\, m + 1.86\, m$

$\therefore\quad m = \frac{5}{2.37} = 2.11$

Weight of sucrose to be dissolved in 100 g water

$$= \frac{2.11 \times 342 \times 100}{1000} = 72\,g$$

24. (b) $\Delta T_{f} = 0.3°\,C$

$$\Delta T_{f} = 0.3°\,C = \frac{K_{f} \times W_{B} \times 1000}{M_{B} \times W_{A}}$$

$$= \frac{1.86 \times W_{B} \times 1000}{62 \times 5000}$$

$\therefore\quad W_{B} = 50\,g$

The amount used should be more than 50 g.

25. (c) $X_{A} = 0.70$ $\quad\therefore\ X_{B} = 0.30;$

$Y_{A} = 0.35$ $\quad\therefore\ Y_{B} = 0.65$

$p_{A} = 600 \times 0.35$ $\quad\therefore\ \frac{600 \times 0.35}{0.70} = p^{o}_{A}$

$\therefore\ p^{o}_{A} = 300$ torr

$p_{B} = 600 \times 0.65$ $\quad\therefore\ \frac{600 \times 0.65}{0.30} = p^{o}_{B}$

$\therefore\ p^{o}_{B} = 1300$ torr

26. (a) Ostwald and Walker's method

$$\frac{p^\circ - p_s}{p^\circ} = \frac{W_2}{W_1 + W_2} = \frac{W_2 / m}{W_2 / m + W_1 / M}$$

W_1 = loss of weight of solution,

W_2 = loss of weight of solvent

$$\therefore \quad \frac{0.0345}{0.645 + 0.0345} = \frac{2.64 / m}{2.64 / m + 30 / 74}$$

m = 122 g

27. (b) V. P. of solution $P = p_A^o x_A + p_B^o x_B$

or $\quad 250 = p_A^o \cdot \frac{1}{3} + p_B^o \cdot \frac{2}{3}$

$$p_A^o + 2 p_B^o = 750 \qquad \text{...............(i)}$$

When 1 mole of A is added

$$x_A = \frac{2}{4} = \frac{1}{2} \text{ and } x_B = \frac{2}{4} = \frac{1}{2}$$

$$\therefore \quad p_A^o \cdot \frac{1}{2} + p_B^o \cdot \frac{1}{2} = 300$$

$$\therefore \quad p_A^o + p_B^o = 600 \qquad \text{.............(ii)}$$

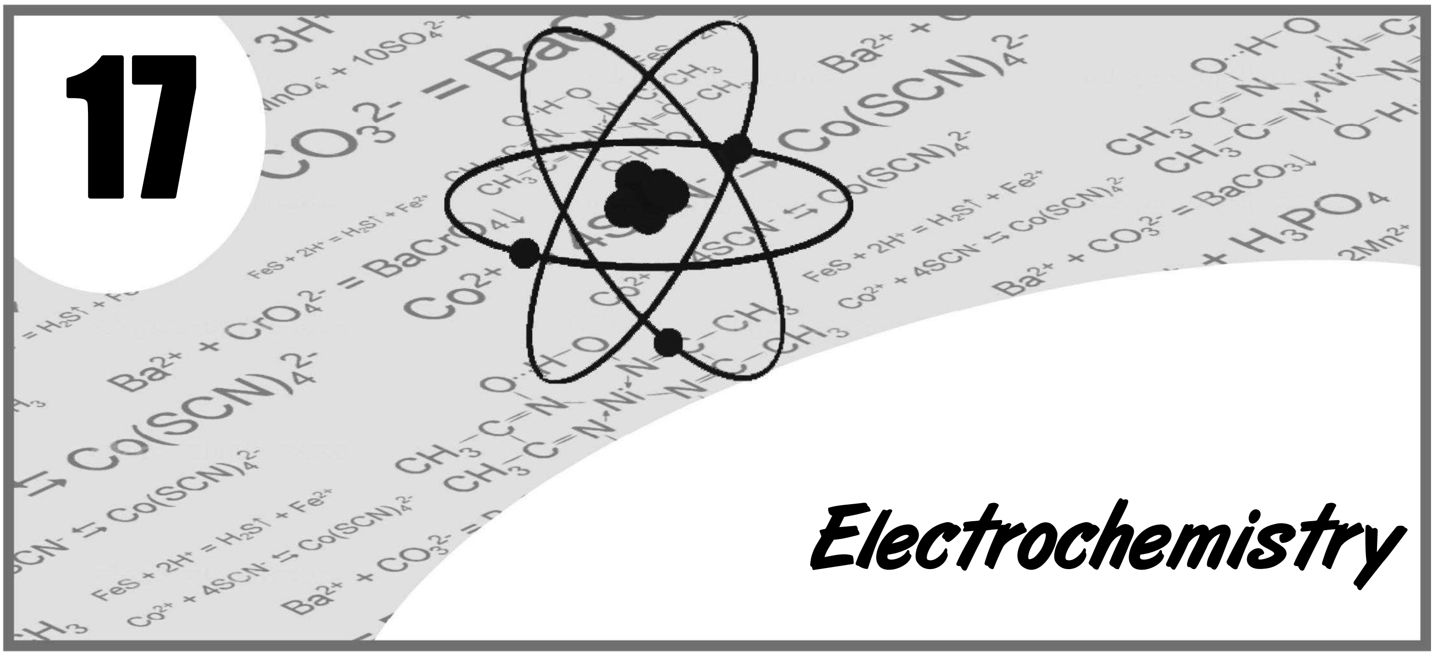
From (i) and (ii),

$p_B^o = 150$ and $p_A^o = 450$

When 1 mole of B is added

$$x_A = \frac{1}{4}, \; x_B = \frac{3}{4}$$

$$\therefore \quad P = 150 \times \frac{3}{4} + 450 \times \frac{1}{4} = 225$$



17

Electrochemistry

ELECTROLYTES AND ELECTROLYSIS :

A substance which decomposes as a result of the passage of electric current is called an ***electrolyte*** and phenomenon of decomposition by electricity is called ***electrolysis.***

ELECTROLYTIC CELL :

The apparatus used to carry out electrolysis is known as electrolytic cell. The main features of electrolytic cell are :

Feature	*Cathode*	*Anode*
Sign	Negative since attached to negative end of external battery	Positive since attached to positive end of external battery
Direction of movement of electrons	into the cell	out of the cell
Direction of movement of ions	Cations	Anions
Half-Reaction	Reduction	Oxidation

OXIDATION :

Loss of electrons is called oxidation.

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$

REDUCTION :

Gain of electrons is called reduction.

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

FARADAY'S LAWS OF ELECTROLYSIS :

(I) **First law :** The amount of the substance deposited or liberated at an electrode is directly proportional to the quantity of electricity passed through an electrolyte

$$W \propto I \times t = I \times t \times Z = Q \times Z$$

I = Current strength in amp., t = time in sec.,

Q = Quantity of charge (coulombs)

Z is a constant known as Electrochemical equivalent

When I = 1 amp., t = 1 sec. then Q = 1 coulomb, then W = Z.

Thus Electrochemical equivalent is the amount of the substance deposited or liberated by 1 ampere current passing for 1 second (i.e. 1 coulomb, I × t = Q)

(II) **Second law :** When the same quantity of electricity is passed through different electrolytes, the amounts of the products obtained at the electrodes are directly proportional to their chemical equivalents or equivalent weights. Thus

$$\frac{\text{Mass of A}}{\text{Mass of B}} = \frac{\text{Eq. wt of A}}{\text{Eq. wt of B}};\ \frac{m_1}{m_2} = \frac{E_1}{E_2} = \frac{Z_1 Q}{Z_2 Q} = \frac{Z_1}{Z_2}$$

Hence electrochemical equivalent $\propto$ Equivalent wt.

ONE FARADAY :

$E \propto Z$; $E = FZ$ F = Known as Faraday's constant

One Faraday is the quantity of charge carried by one mole of electrons

$$IF = 1.6023 \times 10^{-19} \times 6.023 \times 10^{23} = 96500 \text{ Coulombs}$$

AMOUNT OF THE SUBSTANCE 'm' LIBERATED OR DEPOSITED AT AN ELECTRODE :

$$m = \frac{\text{Eq. wt of the Sub.} \times I \times t}{96500} = \frac{\text{Eq. wt} \times Q}{96500}$$

Ex.1: Three electrolytic cells A, B and C containing electrolytes $AlCl_3$, $CuSO_4$ and $AgNO_3$ respectively were connected in series. A steady current of 1.287 ampere was passed through the cells for a definite time. After electrolysis 2.158 g of silver were deposited at the cathode of cell. Calculate.

(I) total charge passed during electrolysis.

(II) time period for which the current is passed

(III) Mass of aluminium deposited at cathode of cell A

(IV) Mass of Copper deposited at cathode of cell B

Sol.: (I) Amt. deposited $= \dfrac{\text{Eq. wt} \times \text{total charge (Q)}}{96500}$

$$2.158 = \frac{107.9}{96500} \times \text{total charge}$$

$$\therefore Q = \frac{2.158 \times 96500}{107.9} = 1930 \text{ C}$$

(II) Charge = Current × time; $\therefore$ time $= \dfrac{1930 \text{ C}}{1.287 \text{A}} = 1499.6 \text{ s}$

(III) $\dfrac{\text{mass of Al}}{\text{mass of Ag}} = \dfrac{\text{Eq. wt of Al}}{\text{Eq. wt of Ag}}$;

$$\therefore \text{mass of Al} = \frac{9 \times 2.158}{107.9} = 0.18 \text{ g}$$

(IV) Mass of copper deposited $= \dfrac{31.75 \times 2.158}{107.9} = 0.635 \text{ g}$

Ex.2 : The same quantity of electrical charge that deposited 0.583 g of Ag was passed through solution of gold salt and 0.355 gold was deposited. Find the oxidation state of gold in the solution.

Sol.: $Au^{n+} + ne^- \longrightarrow Au$

Eq. wt. of Au $= \dfrac{197}{n}$

$$\frac{m_1}{m_2} = \frac{E_1}{E_2}; \quad \frac{0.583}{0.355} = \frac{107.9}{\frac{197}{n}};$$

$\therefore n = 3, \ \therefore$ Oxidation state of gold = 3

Ex.3: Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline if current efficiency is 50%. If the potential drop across the cell is 3.0 volt, how much energy will be consumed.

Sol.: $C_6H_5NO_2 + 6H^+ + 6e^- \longrightarrow C_6H_5NH_2 + 2H_2O$

Eq. wt of nitrobenzene $= \dfrac{M}{6} = \dfrac{123}{6}$

$$W = \frac{E \times i \times t}{96500} \Rightarrow 12.3 = \frac{123}{6} \times \frac{i \times t \times 50}{100 \times 96500} \left(i = \frac{2 \times 50}{100} \right)$$

(given current efficiency is 50 %)

Q = i × t = 115800 coulombs

Now energy used = Q × V = 115800 × 3 = 347.4 kJ

Ex.4: A current of 1.70 amp. is passed through 300 ml of 0.160 M solution of $ZnSO_4$ for 230 sec with a current efficiency of 90%. Find the molarity of Zn^{++} after the deposition of Zn assuming no change in volume during electrolysis.

Sol. $i = \dfrac{1.70 \times 90}{100}$ amp.

Eq. of Zn^{++} deposited =

$$\frac{i \times t}{96500} = \frac{1.70 \times 90 \times 230}{100 \times 96500} = 3.646 \times 10^{-3}$$

M_{eq}. of Zn^{++} deposited = 3.646

Initial M_{eq} of Zn^{++} = 300 × 0.160 × 2 = 96

($\because$ M × 2 = N for Zn^{++})

M_{eq}. of Zn^{++} left in solution 96 – 3.646 = 92.354

$$[ZnSO_4] = \frac{92.354}{2 \times 300} = 0.154 M$$

COMPARISION OF ELECTROLYTIC AND METALLIC CONDUCTORS :

Property	*Metallic Conductor*	*Electrolytic Conductor*
1. Conduction	due to movement of electrons	due to movement of ions
2. Transfer of matter	No transfer of matter	there is transfer of matter
3. Chemical property	No change in chemical property	there is chemical change
4. Resistance	Resistance is offered by atomic Kernels	Resistance is offered by interionic attractions, viscosity of solvent
5. Temperature	decreases with increase of temperature	increases with increase of temperature
6. Magnitude	generally high	generally low
7. Solvation	No solvation	Ions are solvated

FACTORS AFFECTING ELECTROLYTIC CONDUCTION :

Please refer to the properties discussed above viz. viscosity, temperature, solvation of ions etc.

OHM'S LAW :

The potential difference across the conductor is directly proportional to the current flowing through it.

Potential difference $\propto$ current

$$V \propto I; \quad V = RI$$

where R is a constant and known as resistance of the conductor

$$R = \frac{V}{I}$$

Law is applicable to metallic as well as electrolytic conductors. R is expressed in Ohms also designated as Ω.

RESISTANCE (R) :

It offers obstruction to the passage of electric current. It is directly proportional to the length (l) and inversely proportional to the area of cross section (a) of the conductor.

$$R \propto \frac{l}{a} = \rho \times \frac{l}{a}$$

where ρ is a constant, called ***resistivity*** or ***specific resistance***.

when $l = 1$ cm and $a = 1 \text{ cm}^2$ then ρ = R

SPECIFIC RESISTANCE (ρ) :

The resistance offered by 1 cm^3 of the conductor is known as specific resistance.

$$\text{Units of } \rho = \frac{R.a}{l} = \frac{\text{Ohm} \times \text{cm}^2}{\text{cm}} = \text{Ohm cm or } \Omega \text{ cm}$$

CONDUCTANCE (C) :

It is ease of flow of electric current through the conductor and reciprocal of resistance R.

$$C = \frac{1}{R} \text{ units ohm}^{-1}\text{, mhos or } \Omega^{-1}$$

SPECIFIC CONDUCTIVITY κ (KAPPA) :

It is the reciprocal of specific resistance.

$$\kappa = \frac{1}{\rho} = \frac{l}{R.a} = C \times \frac{l}{a} = C \times \text{cell constant} \quad \left(\frac{l}{a} = \text{cell constant}\right)$$

Hence specific conductivity κ (Kappa) = Conductance × cell constant

Units κ = Ohm^{-1} cm^{-1} = Ω^{-1} cm^{-1} = S cm^{-1} (Ω^{-1} = S, Seimens)

EFFECT OF DILUTION ON CONDUCTANCE :

The number of current carrying particles or ions per ml decrease on dilution and specific conductivity, being the conductance of one centimetre cube of solution, decreases with dilution.

CELL CONSTANT AND ITS DETERMINATION :

The quantity $\frac{l}{a}$ is known as cell constant. Its direct measurement is very difficult. It is measured by using standard solution of KCl whose conductivity is known at different concentrations and temperatures. Specific conductance of KCl solutions :

Concentration	*Specific conductance (Ω^{-1} cm^{-1}) at*		
	0°C	*18°C*	*25°C*
0.1M	0.007154	0.011192	0.012886
0.01M	0.0007751	0.0012227	0.0014114

$$\text{Hence cell constant} = \frac{\text{Specific conductance}}{\text{Measured conductance}}$$

Ex.5: Specific conductance of a decinormal solution of KCl at 18°C is 0.0112 Ohm^{-1} cm^{-1}. The resistance of the cell containing the solution at 18°C was found to be 55 Ohm. What is the cell constant.

Sol. Cell constant = $\frac{\text{Specific conductance}}{\text{Measured conductance}}$

$$= \frac{0.0112}{\frac{1}{55}} = 0.616 \text{ cm}^{-1}$$

EQUIVALENT CONDUCTIVITY (Λ_{eq}) :

The conductivity of all the ions produced when 1 gram equivalent of an electrolyte is dissolved in V ml of solution is known as equivalent conductivity

or

'The conductance of a solution containing 1 gm. equivalent of electrolyte placed between two large electrodes one centimetre apart'.

RELATION BETWEEN EQUIVALENT CONDUCTIVITY (Λ_{eq}) AND SPECIFIC CONDUCTIVITY (κ)

$$\Lambda_{eq} = \kappa \times V = \frac{\kappa \times 1000}{\text{Normality of solution}} = \frac{\kappa \times 1000}{N}$$

where V is the volume in cm^3 or ml containing 1 gev. of the electrolyte.

UNITS OF EQUIVALENT CONDUCTIVITY :

Ohm^{-1} cm^2 eq^{-1} or Ω^{-1} cm^2 eq^{-1} or S cm^2 eq^{-1}

EFFECT OF DILUTION ON EQUIVALENT CONDUCTIVITY :

Since the degree of dissociation of the electrolyte increases with dilution, the equivalent conductivity also increases. The increase is more in case of weak electrolytes than strong electrolytes.

The equivalent conductivity increases and specific conductivity decreases with dilution.

IMPORTANCE OF EQUIVALENT CONDUCTIVITY :

It helps to compare the conductivity of different electrolytes, since solutions of different electrolytes having 1 gram equivalent each in the same volume will have the same total charge of electricity. One mole of NaCl yields ions carrying 2 faradays of electricity and one mole of Na_2SO_4 yields ions carrying 4 faradays of electricity. But 1 gram equivalent of each will produce ions carrying 2 faradays of electricity

(Equivalent wt. of $Na_2SO_4 = \frac{\text{Mol wt. of } Na_2SO_4}{2}$).

Hence conductivity of different electrolytes can only be compared if their solutions have equivalent concentrations.

MOLAR CONDUCTIVITY (Λ_m) :

The conductivity of all the ions produced when 1 mole of an electrolyte is dissolved in V ml of solution is known as molar conductivity.

or

'The conductance of a solution containing one gram-mole of electrolyte placed between two large electrodes one centimeter apart'.

RELATION BETWEEN MOLAR CONDUCTIVITY (Λ_m) AND SPECIFIC CONDUCTIVITY (κ) :

$$\Lambda_m = \kappa \times V = \frac{\kappa \times 1000}{M}$$

where V is the volume in cm^3 or ml containing 1 mole of the electrolyte.

UNITS OF MOLAR CONDUCTIVITY (Λ_m) :

Ohm^{-1} cm^2 mol^{-1} or Ω^{-1} cm^2 mol^{-1} or S cm^2 mol^{-1}

EFFECT OF DILUTION ON MOLAR CONDUCTIVITY:

Since the degree of dissociation of electrolyte increases with dilution, Λ_m also increases but less in case of strong electrolytes and more in case of weak electrolytes.

DEBYE-HUCKEL ONSAGAR EQUATION :

Relation between molar conductivity Λ_m at a particular concentration and molar conductivity Λ_m^{∞} at infinite dilution is given by

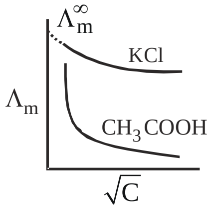
$$\Lambda_m = \Lambda_m^{\infty} - b\sqrt{C}$$

where b is constant. It depends upon nature of solvent and temperature.

FACTORS AFFECTING THE MOLAR CONDUCTIVITY Λ_m :

(I) **Nature of electrolyte :** The strong electrolytes like KNO_3, KCl, NH_4NO_3, HCl, H_2SO_4, NaOH, KOH etc are completely ionised in aqueous solution and have high values of Λ_m. The weak electrolytes are ionised to lesser extent in aqueous solution and have lower values of Λ_m.

(II) Concentration of the solution : The concentrated solutions of strong electolytes have significant inter-ionic attractions, which reduce the speed of ions and lower the value of Λ_m. The dilution decreases such attractions and increases the value of Λ_m. The limiting value Λ_m(Λ_m^{∞} the molar conductivity at zero concentration or at infinite dilution) can be obtained by extrapolating the graph.



In case of weak electrolytes, the degree of ionisation increases which increases the value of Λ_m. The limiting value Λ_m^{∞} cannot be obtained by extrapolating the graph. The limiting value, Λ_m^{∞}, for weak electrolytes is obtained by Kohlrausch law.

(III) **Temperature :** The increase of temperature decreases inter-ionic attractions, solvation of ions, viscosity and increases kinetic energy of ions and their speed. Thus Λ_m increases with temperature.

(IV) **Viscosity of solvent :** The higher the value of viscosity the lower is the value of Λ_m.

(V) **Dielectric constant of solvent :** The higher the value of dielectric constant of solvent, the more is the value of Λ_m. The former decreases interionic attractions.

DEGREE OF DISSOCIATION (α) :

For weak electrolytes

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^{\infty}} = \frac{\text{Molar conductivity at a given concentration}}{\text{Molar conductivity at infinite dilution}}$$

Ex.6: The resistance of $\frac{N}{2}$ solution of an electrolyte in a cell was found to be 45 ohm. Find the equivalent conductance of the solution if the electrodes in the cell are 2.3 cm apart and have a area of cross section 3.8 cm^2.

Sol. Conductance of solution C = $\frac{1}{45}$ ohm^{-1}

Cell constant $\frac{l}{a} = \frac{2.3}{3.8} = 0.6052$

Specific conductance

$$= 0.6052 \times \frac{1}{45} = 0.01345 \text{ Ohm}^{-1}\text{cm}^{-1}$$

$$\Lambda_{eq} = \frac{0.01345 \times 1000}{\frac{1}{2}} = 26.90 \text{ Ohm}^{-1}\text{cm}^2\text{eq}^{-1}$$

Ex.7: The specific conductance of an $\frac{N}{50}$ solution of KCl at 25°C is 0.002765 mho. If the resistance of a cell containing this solution is 400 ohms, what is the cell constant.

Sol.: Cell constant$= \frac{0.002765}{\text{Conductance}} = 0.002765 \times \text{Resistance}$

$$= 0.002765 \times 400 = 1.106$$

KOHLRAUSCH'S LAW :

At infinite dilution the molar conductivity of an electrolyte is the sum of the ionic conductivities of the cations and anions. e.g. for A_xB_y.

$$\Lambda_m^{\infty}(A_xB_y) = x\lambda^{\infty}\left(A^+\right) + y\lambda^{\infty}\left(B^-\right)$$

It is important to note that the source of cations (A^+) and anions (B^-) may be electrolyte itself or any other electrolyte.

$$\text{Thus } \Lambda_m^{\infty}\ (CH_3COOH) = \lambda_{CH_3COO^-}^{\infty} + \lambda_{H^+}^{\infty}$$

$$\text{(II) } \Lambda_m^{\infty}(Al_2(SO_4)_3) = 2\lambda_{Al^{3+}}^{\infty} + 3\lambda_{SO_4^{2-}}^{\infty}$$

APPLICATIONS OF KOHLRAUSCH'S LAW :

(I) **Calculation of molar conductivities of weak electrolytes at infinite dilution.**

Ex.8:Calculate the degree of dissociation of 0.01 M NH_4OH solution when its molar conductivity is 9.4 Ohm^{-1} cm^2 mol^{-1}. The molar conductivities at infinite dilution of NaCl, NH_4Cl and NaOH are 126, 130 and 217 Ohm^{-1} cm^2 mol^{-1} respectively.

Sol. $\Lambda_m^{\infty}(NaCl) = \lambda_{Na^+}^{\infty} + \lambda_{Cl^-}^{\infty} = 126 \text{ Ohm}^{-1}\text{cm}^2\text{mol}^{-1}\ (I)$

$$\Lambda_m^{\infty}(NH_4Cl) = \lambda_{NH_4^+}^{\infty} + \lambda_{Cl^-}^{\infty} = 130 \text{ Ohm}^{-1}\text{cm}^2\text{mol}^{-1}\ \text{(II)}$$

$$\Lambda_m^{\infty}(NaOH) = \lambda_{Na^+}^{\infty} + \lambda_{OH^-}^{\infty} = 217 \text{ Ohm}^{-1}\text{cm}^2\text{mol}^{-1}\ \text{(III)}$$

Add II and III and subtract I

$$\Lambda_m^{\infty}(NH_4OH) = (130+217)-(126) = 221 \text{ Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$$

Degree of dissociation

$$\alpha = \frac{\Lambda_m^c(NH_4OH)}{\Lambda_m^{\infty}(NH_4OH)} = \frac{9.4}{221} = 4.25\%$$

(II) Calculation of the solubility of sparingly soluble salts:

Very small amount of sparingly soluble salts like AgCl or $BaSO_4$ is present in their saturated solutions in completely ionised form. Their Λ_{eq} equal to κ V can be regarded as Λ_{eq}^{∞} at infinite dilution. According to Kohlrausch law its value is given by

$$\kappa V = \Lambda_{eq}^{\infty} = \lambda_a^{\infty} + \lambda_c^{\infty}$$

Hence knowing the value of κ (Kappa), V can be known which is the volume containing 1 gev of substance and solubility can be known.

(III) Calculation of degree of ionisation :

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^{\infty}} = \frac{\text{Molar conductivity at particular concentration}}{\text{Molar conductivity at infinite dilution}}$$

(IV) Calculation of absolute ionic mobilities :

The ionic mobility (U^{∞}) and ionic conductance (λ^{∞}) at infinite dilution are related to each other as below

$$U^{\infty} = \frac{\lambda^{\infty}}{F} = \frac{\lambda^{\infty}}{96500} \quad (\text{IF} = 96500 \text{ coulombs})$$

IONIC MOBILITY :

The distance travelled by an ion per second under a potential gradient of 1 volt per cm is known as ionic mobility.

$$\text{Ionic Mobility U} = \frac{\text{speed}}{\text{potential gradient}}$$

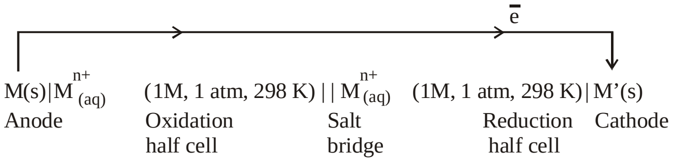
POTENTIAL GRADIENT :

Potential difference applied at the electrodes divided by the distance between the electrodes is known as *Potential gradient.*

GALVANIC CELL, ELECTROCHEMICAL CELL OR VOLTAIC CELL :

A device which converts chemical energy into electrical energy is called Galvanic, Electrochemical or voltaic cell. Main features of the cell are

General representation of an electrochemical cell



	Cathode	*Anode*
Sign	Positive due to consumption of electrons	Negative due to release of electrons
Reaction	Reduction	Oxidation
Movement of electrons	Into the cell	Out of cell

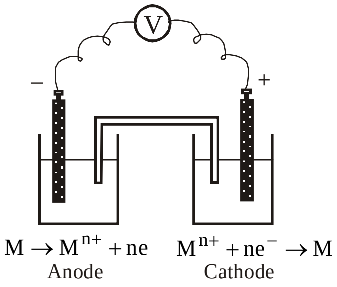
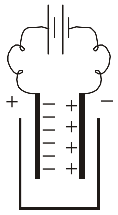
Other features of the electrochemical cell are :

(i) There is no evolution of heat

(ii) The solutions remain neutral on both side

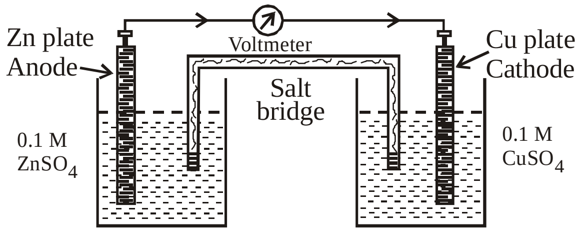
(iii) The reaction and flow of electrons stops after some time.

DIFFERENCE BETWEEN ELECTROCHEMICAL CELL AND ELECTROLYTIC CELL :

	Features	Electrochemical cell	Electrolytic cell
			
1.	Assembly	It is a combination of two half cells, containing the same or different electrodes in the same or different electrolytes.	It is a single cell containing the same electrodes present in the same electrolyte.
2.	Nature of electrodes	Anode is negative, Cathode is positive	Anode is positive, Cathode is negative
3.	Movement of electrons	From anode to cathode in external circuit	Electrons enter through cathode and leave through anode.
4.	Energy	It converts chemical energy into electrical energy, produced as a result of redox reaction.	It converts electrical energy into chemical energy. Energy is supplied to the electrolytic solution to bring about the redox reaction.
5.	Spontaneity	Cell reaction is spontaneous.	Cell reaction is non-spontaneous.
6.	Salt bridge	Salt bridge is required.	No salt-bridge is required.

DANIELL CELL :

An electrochemical cell of Zinc and copper metals is known as Daniell Cell. It is represented as



Zn (s) | Zn^{++} (aq.) | | Cu^{2+} (aqs.) | Cu (s)

LHS oxidation : $Zn \longrightarrow Zn^{2+} + 2e^-$

RHS reduction : $Cu^{2+} + 2e^- \longrightarrow Cu$

Overall reaction :

$$Zn + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu$$

By convention cathode is represented on the RHS and anode on the LHS. Two vertical lines represent the salt bridge.

FUNCTION OF SALT BRIDGE :

(I) Completes the circuit and allows the flow of current (II) It maintain the electrical neutrality on both sides. Salt-bridge generally contains solution of strong electrolyte such as KNO_3, KCl etc. KCl is preferred because the transport numbers of K^+ and Cl^- are almost same.

ELECTRODE POTENTIAL :

When an electrode is in contact with the solution of its own ions in a half cell, it has a tendency to lose or gain electrons which is known as electrode potential. It is expressed in volts.

Some standard electrode potentials (E° Red) at 298K (ECS)

Couple	*Half-Reaction*	*E° Volts*
Li^+/Li	$Li^+ + e^- \longrightarrow Li$	–3.05
M^+/M (K, Rb or Cs)	$M^+ + e^- \longrightarrow M$	–2.94
Ba^{++}/Ba	$Ba^{++} + 2e^- \longrightarrow Ba$	–2.90
Sr^{++}/Sr	$Sr^{++} + 2e^- \longrightarrow Sr$	–2.89
Ca^{++}/Ca	$Ca^{++} + 2e^- \longrightarrow Ca$	–2.76
Na^+/Na	$Na^+ + e^- \longrightarrow Na$	–2.71
Mg^{++}/Mg	$Mg^{++} + 2e^- \longrightarrow Mg$	–2.38
$\frac{1}{2}H_2 / H^-$	$\frac{1}{2}H_2 + e^- \longrightarrow H^-$	–2.23
Al^{3+}/Al	$Al^{3+} + 3e^- \longrightarrow Al$	–1.67
Zn^{++}/Zn	$Zn^{++} + 2e^- \longrightarrow Zn$	–0.76
Cr^{3+}/Cr	$Cr^{3+} + 3e^- \longrightarrow Cr$	–0.74
Fe^{3+}/Fe	$Fe^{3+} + 3e^- \longrightarrow Fe$	–0.41
Cd^{++}/Cd	$Cd^{++} + 2e^- \longrightarrow Cd$	–0.40
Ni^{++}/Ni	$Ni^{++} + 2e^- \longrightarrow Ni$	–0.25
Sn^{++}/Sn	$Sn^{++} + 2e^- \longrightarrow Sn$	–0.14
$H^+/\frac{1}{2}H_2$	$H^+ + e^- \longrightarrow \frac{1}{2}H_2$	0.00
Cu^{++}/Cu	$Cu^{++} + 2e^- \longrightarrow Cu$	0.34
$\frac{1}{2}I_2 / I$	$\frac{1}{2}I_2 + e^- \longrightarrow I$	0.54
Ag^+/Ag	$Ag^+ + e^- \longrightarrow Ag$	0.80
Hg^{++}/Hg	$Hg^{++} + 2e^- \longrightarrow Hg$	0.85
$\frac{1}{2}Br_2 / Br^-$	$\frac{1}{2}Br_2 + e^- \longrightarrow Br^-$	1.09
$\frac{1}{2}Cr_2O_7^{2-} / Cr^{3+}$	$\frac{1}{2}Cr_2O_7^{2-} + 7H^+ + 3e^- \longrightarrow Cr^{3+} + \frac{7}{2}H_2O$	1.33
$\frac{1}{2}Cl_2 / Cl^-$	$\frac{1}{2}Cl_2 + e^- \longrightarrow Cl^-$	1.36
MnO_4^- / Mn^{++}	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{++} + 4H_2O$	1.51
H_2O_2/H_2O	$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	1.77
$\frac{1}{2}F_2 / F^-$	$\frac{1}{2}F_2 + e^- \longrightarrow F^-$	2.87
$Hg_2^{++} / 2Hg$	$Hg_2^{++} + 2e^- \longrightarrow 2Hg$	0.79
$NO_3^- / NO, H_2O$	$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	0.97
Au^{3+}/Au	$Au^{3+} + 3e^- \longrightarrow Au$	1.42

→ Increasing Reactivity - Reducing Character

OXIDATION POTENTIAL :

The tendency to lose electrons in above case is known as Oxidation potential.

Oxidation potential of a half-cell is inversely proportional to the concentration of ions in the solution.

REDUCTION POTENTIAL :

The tendency to gain electrons in above case is known as reduction potential.

It is not possible to determine the absolute value of electrode potential. For this a reference electrode is required. The electrode potential is only the difference of potentials between two electrodes that we can measure by combining them to give a complete cell.

STANDARD REDUCTION POTENTIAL $(E^{o}_{M^{n+}/M})$:

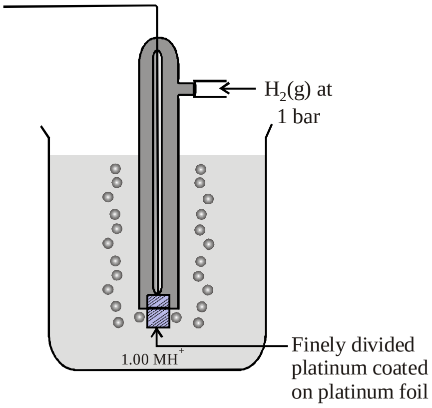
According to latest convention the electrode potential is always represented as reduction potential. If its value is negative, it means electrode has oxidation potential. The standard conditions are 1 molal solution, 298K temperature and 1 atm. pressure. According to IUPAC convention, the reduction potential alone be called as the electrode potential unless it is specifically mentioned.

REFERENCE ELECTRODE :

The following electrodes are used as reference electrodes for determining the standard reduction potentials.

(i) Standard hydrogen electrode (SHE) : Standard hydrogen electrode (SHE) also known as Normal Hydrogen Electrode (NHE), consists of platinum wire, carrying platinum foil coated with finely divided platinum black. The wire is sealed into a glass tube, placed in a beaker containing 1M HCl. The hydrogen gas at 1 atm pressure is bubbled through the solution at 298K. Half cell is Pt, H_2(1 atm)/H^+ (1M)

In SHE, at the surface of platinum, either of the following reactions can take place



$$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad \text{Reduction}$$

$$H_2(g) \longrightarrow 2H^+(aq) + 2e^- \qquad \text{Oxidation}$$

The electrode potential of SHE has been fixed as zero.

All other single electrode potentials are referred to as potentials on hydrogen scale.

Drawbacks of SHE

1. It is difficult to maintain H_2 at 1 atm. pressure.
2. It is difficult to maintain H^+ ion concentration at 1M
3. The platinum electrode is easily poisoned by traces of impurities.

Hence calomel and silver chloride electrodes are conveniently used as reference electrodes.

(ii) Calomel electrode (Hg, Hg_2Cl_2, KCl)

Half cell is Hg, Hg_2Cl_2(s) KCl(solution)

Oxidation :

$$2Hg(\ell) \rightarrow Hg_2^{2+} + 2e^-$$

$$Hg_2^{2+} + 2Cl^- \rightarrow Hg_2Cl_2$$

$$2Hg(\ell) + 2Cl \rightarrow Hg_2Cl_2(s) + 2e^-$$

Reduction :

$$Hg_2Cl_2(s) \rightarrow Hg_2^{2+} + 2Cl^-$$
$$Hg_2^{2+} + 2e^- \rightarrow 2Hg(\ell)$$

Overall reaction :

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(\ell) + 2Cl^- \qquad E^{o}_{Red} = 0.2422\ V$$

(iii) Silver-silver salt electrode

Half cell is Ag, AgCl(s), Cl^- (KCl or HCl)

Oxidation :

$$Ag \rightarrow Ag^+ + e^-$$

$$Ag^+ + Cl^- \rightarrow AgCl(s)$$

$$Ag + Cl^- \rightarrow AgCl(s) + e^-$$

Reduction :

$$AgCl(s) \rightarrow Ag^+ + Cl^-$$
$$Ag^+ + e^- \rightarrow Ag$$

$$AgCl(s) + e^- \rightarrow Ag + Cl^-$$

$$E^{o}_{Red} = 0.2225\ V$$

ELECTROMOTIVE FORCE (EMF) OF A CELL :

It is the difference between the electrode potentials of two half-cells and cause of flow of current from electrode at higher potential to electrode at lower potential. It is also the measure of free energy change. Standard EMF of a cell

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = E^{o}_{right} - E^{o}_{left}$$

ELECTROCHEMICAL SERIES :

It is the arrangement of electrodes in the increasing order of their Standard Reduction potential $E^{o}_{M^{n+}/M}$.

APPLICATIONS OF ELECTROCHEMICAL SERIES :

(I) The lower the value of E°, the greater the tendency to form cation

$$M - ne \longrightarrow M^{n+}$$

(II) Replacement (or evolution) of H_2 from hydro acids by metals. Metals placed below hydrogen in E.C.S. can not replace hydrogen from dil. acids but metals placed above hydrogen can replace hydrogen from dil. acids.

$$Ca + H_2SO_4 \longrightarrow CaSO_4 + H_2 \uparrow$$

possible

$$(Ca + 2H^+ \rightarrow Ca^{++} + H_2)$$

$$Cu + H_2SO_4 \longrightarrow CuSO_4 + H_2 \uparrow$$

not possible

$$(Cu + 2H^+ \rightarrow Cu^{++} + H_2)$$

(III) Metals placed above hydrogen evolve H_2 with H_2O or steam, but metals placed below hydrogen cannot.

(IV) Oxides of metals placed above hydrogen are not reduced by H_2 but oxides of iron and metals placed below iron are reduced by H_2
SnO, PbO, Fe_3O_4, CuO are reduced with H_2
CaO, MgO, K_2O are not reduced with H_2

(V) Oxides of Ag and metals below Ag are decomposed

$$2HgO \longrightarrow 2Hg + O_2$$

$$2Ag_2O \longrightarrow 4Ag + O_2$$

(VI) Reducing character decreases down the series.

(VII) Reactivity decreases down the series.

(VIII) Feasibility of redox reaction : A redox reaction can occur if the species losing the electrons lie above that which gains the electrons.

(IX) Determination of emf : Emf is the difference of reduction potentials of two half cells.
$E_{emf} = E_{RHS} - E_{LHS}$
If the value of e.m.f. is positive the reaction can take place spontaneously, otherwise not.

FUNCTIONING OF ELECTROCHEMICAL CELL :

With the passage of time the electrode potential of the cathode decreases and that of anode increases the difference becomes zero, the driving force of emf becomes zero and reaction stops.

TYPES OF ELECTRODES AND HALF-CELLS :

(I) Gas electrodes or gas Ion half cells :

Half-cell Reaction

Oxidation

$H^+(aq)/H_2(g)/Pt$: $H_2(g) \rightleftharpoons 2H^+ + 2e^-$

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

Reduction

$Cl^-(aq)/Cl_2(g)/Pt$: $Cl^-(aq) \rightleftharpoons \frac{1}{2}Cl(g) + e^-$

$$\frac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$$

(II) Metal-Metal ion electrode or half-cell : A metal rod dipped in the solution of its own ions

$Zn^{++}(aq)/Zn$: $Zn \rightarrow Zn^{++} + 2e^-$

$$Zn^{++} + 2e^- \longrightarrow Zn$$

$Ag^+(aq)/Ag$: $Ag \rightarrow Ag^+ + e^-$

$$Ag^+ + e^- \longrightarrow Ag$$

$Cu^{++}(aq)/Cu$: $Cu \rightarrow Cu^{++} + 2e^-$

$$Cu^{++} + 2e^- \longrightarrow Cu$$

(III) Metal-metal insoluble Salt-Salt anion :

$Cl^-(aq)/AgCl/Ag$:

$$Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$$

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$$

$Br^-(aq)/AgBr/Ag$:

$$Ag(s) + Br^-(aq) \rightarrow AgBr(s) + e^-$$

$$AgBr(s) + e^- \longrightarrow Ag(s) + Br^-(aq)$$

$Cl^-(aq)/Hg_2Cl_2(s)/Hg(Pt)$:

$$2Hg(\ell) + 2Cl^- \rightarrow Hg_2Cl_2(s) + 2e^-$$

$$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(\ell) + 2Cl^-(aq)$$

$OH^-(aq)/Cu(OH)_2(s)/Cu$:

$$Cu(s) + 2OH^-(aq) \rightarrow Cu(OH)_2 + 2e^-$$

$$Cu(OH)_2(s) + 2e^- \longrightarrow Cu(s) + 2OH^-(aq)$$

$SO_4^{--}(aq)/PbSO_4(s)/Pb$:

$$Pb(s) + SO_4^{--}(aq) \rightarrow PbSO_4(s) + 2e^-$$

$$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{--}(aq)$$

(IV) Redox electrodes half cells : An inert metal such as platinum wire dipped in a solution of ions of the same metal in different oxidation states

$Fe^{3+}(aq), Fe^{2+}(aq)/Pt$: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$$

$Sn^{4+}(aq), Sn^{2+}(aq)/Pt$: $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$

$$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$$

$Cr_2O_7^{2-}(aq), Cr^{3+}(aq), H^+(aq)/Pt$:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$$

$MnO_4^-(aq); Mn^{2+}(aq), H^+(aq)/Pt$:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$$

NERNST EQUATION FOR ELECTRODE POTENTIAL:

The relationship between the concentration of ions and electrode potential is given by Nernst equation.

$$M^{n+} + ne^- \rightarrow M$$

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}]}$$

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{2.303 \times 8.314 \times 298}{n \times 96500}\log\frac{1}{[M^{n+}]}$$

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{0.059}{n}\log\frac{1}{[M^{n+}]}$$

If we write the elcetrode reaction, in general, as

Oxidised state + $ne^- \rightleftharpoons$ Reduced State

The potential of electrode is given by

$$E_{cell} = E^o_{cell} - 2.303\frac{RT}{nF}\log\frac{[\text{Reduced state}]}{[\text{Oxidised state}]}$$

or $$E_{cell} = E^o_{cell} + \frac{2.303RT}{nF}\log\frac{[\text{Oxidised state}]}{[\text{Reduced state}]}$$

Ex.9: What is the electrode potential of a half cell for magnesium electrode dipped in a 0.1 M $MgSO_4$ solution at 25°C. ($E° = –2.36$).

Sol.: $$E_{Mg^{++}/Mg} = -2.36 - \frac{0.0591}{2}\log\frac{1}{0.1} = -2.389V$$

NERNST EQUATION FOR CELL POTENTIAL :

Consider a general cell reaction involving n electrons.

$$aA + bB \longrightarrow cC + dD$$

$$E_{cell} = E^o_{cell} - \frac{2.303RT}{nF}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Concentration of solids and liquids is taken as **unity**, concentration of ions **Mol L^{-1}** and concentration of gases as partial pressures in **Atmosphere**.

NERNST EQUATION AND EQUILIBRIUM CONSTANT (K_c) :

When E_{cell} drops to zero the concentration of ions will be equilibrium concentrations. We have for general cell reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$E_{cell} = E^o_{cell} - \frac{2.303RT}{nF}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$E^o_{cell} = \frac{2.303RT}{nF}\log K_c \qquad [\text{Since at equilibrium } E_{cell} = 0]$$

$$E^o_{cell} = \frac{0.0591}{n}\log K_c \text{ at 298K.}$$

RELATION BETWEEN ELECTRICAL ENERGY AND FREE ENERGY (ΔG) :

If n is the number of electrons liberated (or taken up) in a particular cell reaction, then n faradays (nF) of electricity will be generated in the complete reaction. If E is the EMF of the cell, then

Electrical energy supplied by the cell = nFE

According to Gibbs and Helmholtz, the decrease of free energy ($-\Delta G$) of the reaction occuring in the cell is equal to electrical energy

Hence, $-\Delta G = nFE$

The standard free energy and E^o_{cell} are related as

$$\Delta G^o = -nFE^o_{cell}$$

RELATIONSHIP BETWEEN FREE ENERGY CHANGE AND EQUILIBRIUM CONSTANT :

$$\Delta G^o = -2.303RT\log K_c$$

CONCENTRATION CELLS :

They are of two types

(I) **Electrode concentration cells :** Two electrodes of different concentrations are dipped in the same solution of electrolyte e.g.

$$\text{Pt, } H_2(P_{H_2} = p_1) \mid H^+ \mid H_2(P_{H_2} = p_2)\text{Pt} \qquad p_1 > p_2$$

$$E_{cell} = \frac{2.303RT}{nF}\log\frac{p_1}{p_2}$$

(II) **Electrolyte concentration cells :** Electrodes are the same but electrolyte solutions have different concentrations e.g.

$$\text{Zn, } Zn^{++}(c_1) \| Zn^{++}(c_2)\text{; Zn} \qquad c_2 > c_1$$

$$E_{cell} = \frac{2.303}{nF}RT\log\frac{c_2}{c_1} = \frac{0.0591}{n}\log\frac{c_2}{c_1}$$

APPLICATIONS OF THE CONCENTRATION CELLS :

(I) Determination of valency

(II) Determination of solubility of sparingly soluble salts.

(III) Determination of transition point.

OVERVOLTAGE :

The difference between the voltage at which a gas is actually evolved and theoretical value at which it ought to have been evolved during electrolysis is known as ***overvoltage***.

REVERSIBLE CELL :

When the cell reaction can be stopped or reversed by applying an emf exactly equal to or infinitesimally greater than that of the cell, it is called **reversible cell**.

Examples of **reversible electrodes**

1. **Metal-metal ion electrode :** Metal rod dipped into a solution of its own ions.

   $$M \rightleftharpoons M^+ + e^-$$

   The negative electrode (electrode reaction involving oxidation) increases M^+ ions in solution

   The positive electrode (electrode reaction involving reduction) decreases M^+ ions in solution.

   Thus, electrode is reversible with respect to M^+ ions

2. **Gas electrodes :**

   (a) ***Hydrogen electrode :*** Pt, H_2(g), H^+

   Reaction

   $$\frac{1}{2}H_2(g) \rightleftharpoons H^+ + e^-$$

   The electrode is reversible with respect to H^+ ions

   (b) ***Chlorine electrode :*** Pt, Cl_2(g), Cl^-

   Reaction

   $$\frac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$$

   The electrode is reversible with respect to Cl^- ion.

(c) ***Metal - Metal Salt Ion Electrode :***

i) ***Calomel Electrode***

Hg, $Hg_2Cl_2(s)$; KCl(solution)

Oxidation :

$$\begin{array}{l} 2Hg(\ell) \rightleftharpoons Hg_2^{2+} + 2e^- \\ Hg_2^{2+} + 2Cl^- \rightleftharpoons Hg_2Cl_2(s) \\ \hline 2Hg + 2Cl^- \rightleftharpoons Hg_2Cl_2(s) + 2e^- \end{array}$$

Oxidation decreases concentration of chloride ions.

Reduction :

$$\begin{array}{l} Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+} + 2e^- \\ Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(\ell) \\ \hline Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(\ell) + 2Cl^- \end{array}$$

Reduction increases the concentration of chloride ions

The electrode is reversible with respect to Cl^- ions.

ii) ***Silver-Silver Chloride Electrode :*** Ag, AgCl(s), Cl^-(KCl or HCl)

Oxidation :

$$\begin{array}{l} Ag \rightleftharpoons Ag^+ + e^- \\ Ag^+ + Cl^- \rightleftharpoons AgCl(s) \\ \hline Ag + Cl^- \rightleftharpoons AgCl(s) + e^- \end{array}$$

Oxidation decreases the concentration of Cl^- ions.

Reduction :

$$\begin{array}{l} AgCl(s) \rightleftharpoons Ag^+ + Cl^- \\ Ag^+ + e^- \rightleftharpoons Ag \\ \hline AgCl(s) + e^- \rightleftharpoons Ag + Cl^- \end{array}$$

Reduction increases the concentration of Cl^-

(d) ***Oxidation - Reduction Electrodes :*** Such electrodes are set up by inserting unattackable metal (eg Platinum) into a solution of ions in different oxidation states. The metal acquires a potential due to tendency of ions in one oxidation state to change into another stable oxidation state.

Electrode reaction :

$$\begin{array}{l} M^{n+} - me^- \rightleftharpoons M^{(n+m)+} \\ Fe^{2+} - e^- \rightleftharpoons Fe^{3+} \\ Sn^{2+} - 2e^- \rightleftharpoons Sn^{4+} \end{array}$$

IRREVERSIBLE CELL :

When the cell reaction cannot be stopped or reversed it is called irreversible cell e.g. cell of Zn and Ag electrodes immersed in solution of H_2SO_4.

Criteria of the formation of products in Electrolysis - Preferential discharge theory : Ions present in large excess conduct electricity and ions having lower discharge potentials are discharged at respective electrodes.

(I) Electrolysis of aqueous NaOH :

$NaOH \longrightarrow Na^+ + OH^-$ Completely dissociated

$H_2O \longrightarrow H^+ + OH^-$ Slightly dissociated

At cathode : $2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_2$

At anode : $2OH^- - 2e^- \longrightarrow H_2O + O;\ O + O \longrightarrow O_2$

Current is carried by Na^+ and OH^- ions.

(II) Electrolysis of aqueous H_2SO_4

$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$ Completely dissociated

$H_2O \longrightarrow H^+ + OH^-$ Slightly dissociated

At cathode : $2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_2$

At anode : $2OH^- - 2e^- \longrightarrow 2OH \longrightarrow H_2O + O;$

$O + O \longrightarrow O_2$

(III) Electrolysis of aqueous NaCl

$NaCl \longrightarrow Na^+ + Cl^-$ Completely dissociated

$H_2O \longrightarrow H^+ + OH^-$ Slightly dissociated

At cathode : $2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_2$

At anode : $2Cl^- - 2e^- \longrightarrow 2Cl \longrightarrow Cl_2$

Although the oxidation potential of OH^- is more than Cl^- yet Cl_2 is formed at anode due to overvoltage.

(IV) Electrolysis of aqueous $CuSO_4$ using Pt electrodes

$$CuSO_4 \longrightarrow Cu^{++} + SO_4^{--}$$

$$H_2O \longrightarrow H^+ + OH^-$$

At cathode $Cu^{++} + 2e^- \longrightarrow Cu$

At anode $2OH^- - 2e^- \longrightarrow 2OH \longrightarrow H_2O + O;$

$O + O \longrightarrow O_2$

(V) Electrolysis of $CuSO_4$ solution using copper electrodes

$CuSO_4 \longrightarrow Cu^{++} + SO_4^{--}$; $H_2O \longrightarrow H^+ + OH^-$

At Cathode $Cu^{++} + 2e^- \longrightarrow Cu$

At Anode $Cu \longrightarrow Cu^{++} + 2e^-$

Oxidation potential $\underset{-3.4}{Cu} > \underset{-1.23}{OH^-} > \underset{-2.01}{SO_4^{--}}$

FACTORS GOVERNING THE DISCHARGE POTENTIAL :

(I) Position in the electrochemical series

(II) Concentration of ions in the solution

(III) Nature of electrodes

Discharge potential of some ions

$$Li^+ < K^+ < Na^+ < Ca^{++} < Mg^{++} < Al^{++} < Zn^{++} < Fe^{++}$$

$$< Ni^{++} < H^+ < Cu^{++} < Hg^{++} < Ag^+$$

$$< Au^{+++} < SO_4^{--} < NO_3^- < OH^- < Cl^- < Br^- < I^-$$

TRANSPORT NUMBER :

The fraction of the total current carried by each ion is called its transport number.

The amount of electricity carried by a particular ion $\propto$ speed of particular ion.

Transport number of the cation n_c

$$= \frac{\text{Current carried by the cation}}{\text{Total current}} = \frac{U_c}{U_c + U_a}$$

Transport number of anion $n_a = \dfrac{U_a}{U_c + U_a}$

U_c = speed of cation and U_a = speed of anion.

Further $n_a + n_c = 1$

SOME COMMERCIAL CELLS AND THEIR TYPES :

They are broadly classified into two groups.

(I) **Primary cells :** They cannot be recharged and used again. Examples are

(a) ***Dry cell or Leclanche cell :*** Particulars are

Anode - Zinc Container

Cathode - graphite rod surrounded by MnO_2 powder

Electrolyte - paste of $NH_4Cl + ZnCl_2$

Cathode Reaction : $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

Anode Reaction : $Zn - 2e^- \longrightarrow Zn^{++}$

$$Zn^{2+} + 2NH_3 \longrightarrow [Zn(NH_3)_2]^{2+}$$

Cell potential 1.25V to 1.5V

(b) ***Mercury Cell :***

Anode - Zn-Hg amalgam

Cathode - paste of (HgO + C)

Electrolyte - moist paste of KOH-ZnO

Cathode Reaction :

$$HgO(s) + H_2O(\ell) + 2e^- \longrightarrow Hg(\ell) + 2OH^-$$

Anode Reaction : $Zn + 2OH^- \longrightarrow ZnO + H_2O(\ell) + 2e^-$

Net Reaction : $Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(\ell)$

cell potential = 1.30 volt

(II) **Secondary cells :** It can be recharged and can be used again and again. Examples

(a) ***Lead storage battery :***

Anode - Spongy lead

Cathode - grid of lead packed with PbO_2

Electrolyte - 38% H_2SO_4 by mass

Anode Reaction : $Pb + SO_4^{--} \longrightarrow PbSO_4 + 2e^-$

Cathode Reaction :

$$PbO_2 + SO_4^{--} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$$

Net Reaction :

$$Pb + PbO_2 + 4H^+ + 2SO_4^{--} \longrightarrow 2PbSO_4 + 2H_2O$$

When recharged the cell reactions are reversed.

(b) ***Nickel-cadmium storage cell***

Anode - Cadmium

Cathode - metal grid containing NiO_2

Electrolyte - KOH solution

Anode Reaction $Cd(s) + 2OH^- \rightarrow Cd(OH)_2(s) + 2e^-$

Cathode Reaction :

$$NiO_2(s) + 2H_2O(l) + 2e^- \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$$

Net Reaction :

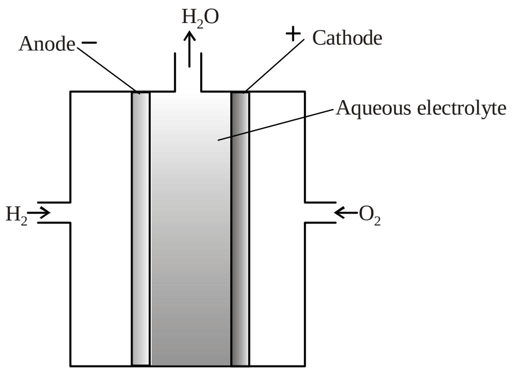
$$Cd(s) + NiO_2(s) + 2H_2O(\ell) \rightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

Cell potential = 1.4 V.

FUEL CELLS :

They convert chemical energy into electrical energy and the reactants are continuously fed and products are removed.

(a) **Hydrogen-Oxygen-Fuel Cell :** Electrodes are made of porous graphite impregnated with catalyst (Pt, Ag or a metal oxide).



Fuel cell using H_2 and O_2 produces electricity.

Electrolyte-aqueous solution of KOH or NaOH

Oxygen and hydrogen are continuously fed into the cell.

Oxidation (half-cell reaction) :

Reaction : $H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$

Reduction (half-cell reaction) :

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

Net Reaction : $2H_2 + O_2 \longrightarrow 2H_2O$

EMF of the cell 1 volt.

(b) **Hydrocarbon-oxygen fuel cell :** Based upon the combustion of hydrocarbons such as methane, ethane propane etc.

Oxidation (half cell reaction) :

$$C_3H_8 + 20\,OH^- \longrightarrow 3CO_2 + 14H_2O + 20e^-$$

Reduction (half cell reaction) :

$$(O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-) \times 5$$

Net Reaction $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$

ADVANTAGES OF FUEL CELLS :

I. Pollution free II. High efficiency

THERMODYNAMIC EFFICIENCY OF FUEL CELLS :

$$\eta = \frac{-\Delta G}{\Delta H} = \frac{-nFE^{o}_{cell}}{\Delta H}$$

For H_2–O_2 fuel cells it is 95%.

CORROSION :

Slow formation of undesirable compounds such as oxides, sulphides or Carbonates at the surface of metals by reaction with moisture and other atmospheric gases is known as *corrosion*.

FACTORS AFFECTING THE CORROSION :

(I) Reactivity of metals

(II) Presence of moisture and atmospheric gases like CO_2, SO_2 etc.

(III) Presence of impurities

(IV) Strains in the metal

(V) Presence of electrolyte

RUSTING OF IRON-ELECTROCHEMICAL THEORY :

An electrochemical cell known as corrosion cell is developed at the surface of iron.

Anode → Pure iron

Cathode → Impure Surface

Electrolyte :

$$CO_2 + H_2O \longrightarrow H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$SO_2 + H_2O \longrightarrow H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

Anode Reaction $\quad Fe \longrightarrow Fe^{++} + 2e^-$

Cathode Reaction $\quad 2H^+ + 2e^- \longrightarrow 2H$

$$2H + \frac{1}{2}O_2 \longrightarrow H_2O$$

Net Reaction, $Fe + 2H^+ + \frac{1}{2}O_2 \longrightarrow Fe^{++} + H_2O$

At surface $\quad 2Fe^{++} + \frac{1}{2}O_2 + 2H_2O \longrightarrow Fe_2O_3 + 4H^+$

$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3.xH_2O$$

Net reaction at surface

$$2Fe^{++} + \frac{1}{2}O_2 + (x+2)H_2O \longrightarrow \underset{\text{Rust}}{Fe_2O_3xH_2O} + 4H^+$$

PREVENTION OF CORROSION :

(I) ***Barrier protection*** *:* By painting, coating, electroplating

(II) ***Sacrificial protection*** *:* By galvanization, Sherardising

(III) ***Electrical protection***

(IV) ***Use of anti rust compounds.***

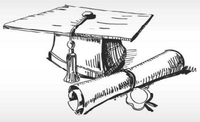
CALCULATION OF POTENTIAL OF INTERMEDIATE REACTION :

When two half-reactions having potential E_1 and E_2 which are combined to yield a third half reaction having potential E_3. Then E_3 is given by

$$E_3 = \frac{n_1E_1 + n_2E_2}{n}$$

Remember : The cell potentials are not thermodynamic functions and should not be added.

Exercise-1 | NCERT BASED QUESTIONS



Very Short/Short Answer Questions

1. Which is a better conductor, aqueous solution of NaCl or iron?

2. Can a nickel spatula be used to stir a solution of $CuSO_4$?
$(E^\circ_{Ni^{2+}/Ni} = -0\cdot25\ V;\ E_{Cu^{2+}/Cu} = +0\cdot34\ V)$

3. Why do the electrochemical cells stop working after sometime?

4. Can we find out the value of $\Lambda^\circ_{CH_3COOH}$ by extrapolating a graph of molar conductivity of CH_3COOH solution against $\sqrt{c}$?

5. Electrolysis of NaBr and NaI in aqueous solution liberate Br_2 and I_2 respectively while that of NaF liberates O_2 instead of F_2. Explain.

6. In each of the following pairs, which will provide greater conduction of electricity and why?
(*i*) Copper wire at 30 ºC or same copper wire at 100 ºC.
(*ii*) KCl solution at 25 ºC or same KCl solution at 50 ºC.
(*iii*) 0·1 M NH_4OH at 25ºC or 2M NH_4OH at 25 ºC.

7. Consider a cell composed of two half-cells:
(*i*) Cu(s) |Cu^{2+} (aq), and
(*ii*) Ag(s) |Ag^+ (aq).
Calculate
(*a*) the standard cell potential, and
(*b*) the cell potential when concentration of Cu^{2+} is 2M and concentration of Ag^+ is 0·05 M, at 298 K.

Given : $E^\circ_{Cu^{2+}/Cu} = +0.34V,\ E^\circ_{Ag^+/Ag} = 0{\cdot}80\ V,$
$R = 8{\cdot}314\ JK^{-1}\ mol^{-1}$ $F = 96500\ C\ mol^{-1}$

8. Silver is electrodeposited on a metallic surface area of 800 cm^2 by passing a current of 0·2A for 3 hours. Calculate the thickness of silver deposited. Density of silver is 10·47 g cm^3 and atomic mass of Ag = 108.

9. Express the relation among cell constant, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solution related to its conductivity?

10. Calculate the emf of the following cell at 298 K:
Fe(s) | Fe^{2+} (0.001 M) || H^+ (1 M) | H_2(g) (1bar), Pt (s)
$[\text{Given } E^\circ_{Cell} = +0.44\ V]$

11. For the cell
Zn (s) | Zn^{2+} (2M) || Cu^{2+} (0.5 M) | Cu (s)
(a) Write equation for each half-reaction.
(b) Calculate the cell potential at 25°C

$\left[\text{Given } E^\circ_{Zn^{2+}/Zn} = -0.76\ V;\ E^\circ_{Cu^{2+}/Cu} = +0.34\ V\right]$

Long Answer Questions

12. Explain why electrolysis of aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode. Write overall reaction.
$E^\circ_{Na^+/Na} = -2{\cdot}71V,\ E^\circ_{H_2O/H_2} = -0{\cdot}83V,$
$E^\circ_{Cl_2/Cl^-} = +1{\cdot}36V,\ E^\circ_{O_2/H_2O} = 1{\cdot}23V$

13. (a) What type of a battery is the lead storage battery? Write the anode and cathode reactions and the overall reaction occurring in a lead storage battery when current is drawn from it.
(b) In the button cell, widely used in watches, the following reaction takes place

$$Zn_{(s)} + Ag_2O_{(s)} + H_2O \rightarrow Zn^{2+}(aq) + 2\ Ag_{(s)} + 2OH^-_{(aq)}$$

Determine E° and ΔG° for the reaction.
$\left(\text{given} : E^\circ_{Ag^+/Ag} = +0.80V\right.$
$\left.E^\circ_{Zn^{2+}/Zn} = -0.76\ V\right)$

14. (a) Define molar conductivity of a solution and explain how molar conductivity changes with change in concentration of solution for a weak and a strong electrolyte.
(b) The resistance of conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCI solution at 298 K is $0.146 \times 10^{-3}\ S\ cm^{-1}$?

15. (a) State Kohlrausch law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrauch law.
(b) Calculate
$\wedge^\circ_m$ for acetic acid,
Given that
$\wedge^\circ_m$ (HCl) = 426 S cm^2 mol^{-1}
$\wedge^\circ_m$ (NaCl) = 126 S cm^2 mol^{-1}
$\wedge^\circ_m$ (CH_3COONa) = 91 S cm^2 mol^{-1}

16. (a) Write the anode and cathode reactions and the overall reaction occurring in a lead storage battery.
(b) A copper-silver cell is set up. The copper ion concentration is 0.10 M. The concentration of silver ion is not known. The cell potential when measured was 0.422 V. Determine the concentration of silver ions in the cell.

$\left(\text{Given } E^\circ_{Ag^+/Ag} = +0.80V, E^\circ_{Cu^{2+}/Cu} = +0.34\ V\right)$

Multiple Choice Questions

17. The standard electrode potentials of four elements A, B, C and D are –3.05, –1.66, –0.40 and +0.80. The highest chemical reactivity will be exhibited by :
(a) A (b) B
(c) C (d) D

18. The aqueous solution of which of the following decomposes on passing electric current
(a) cane sugar (b) urea
(c) methanol (d) potassium iodide

19. The standard electrode potential of the half cells are given below

$$Zn^{2+} + 2e^- \longrightarrow Zn \;; E = -7.62\text{ V}$$

$$Fe^{2+} + 2e^- \longrightarrow Fe \;; E = -7.81\text{ V}$$

The emf of the cell, $Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$ is
(a) 1.54 V (b) –1.54 V
(c) –0.19 V (d) +0.19 V

20. Two electrolytic cells, one containing acidified ferrous chloride and another acidified ferric chloride, are connected in series. The ratio of iron deposited at cathodes in the two cells will be :
(a) 3 : 1 (b) 2 : 1
(c) 1 : 1 (d) 3 : 2

21. A hypothetical electrochemical cell is shown below

$$\overset{\ominus}{A} \mid A^+(xM) \parallel B^+(yM) \mid \overset{\oplus}{B}$$

The emf measured is +0.20 V. The cell reaction is
(a) $A^+ + e^- \rightarrow A;\ B^+ + e^- \rightarrow B$
(b) The cell reaction cannot be predicted
(c) $A + B^+ \rightarrow A^+ + B$
(d) $A^+ + B \rightarrow A + B^+$

22. On heating one end of a piece of a metal, the other end becomes hot because of
(a) resistance of the metal
(b) mobility of atoms in the metal
(c) energised electrons moving to the other end
(d) minor perturbation in the energy of atoms

23. 4.5 g of aluminium (at. mass 27 amu) is deposited at cathode from Al^{3+} solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from H^+ ions in solution by the same quantity of electric charge will be
(a) 44.8 L (b) 22.4 L
(c) 11.2 L (d) 5.6 L

24. On passing 0.5 Faraday of electricity through molten sodium chloride, sodium deposited at cathode will be :
(a) 29.25 g (b) 11.50 g
(c) 58.50 g (d) 0.00 g

Exercise-2 | CONCEPTUAL MCQs

1. Which of the following is the use of electrolysis?
(a) Electrorefining (b) Electroplating
(c) Both (a) and (b) (d) Neither (a) nor (b)

2. Which of the following will form the cathode with respect to iron anode in an electrolytic cell?
(a) Mg (b) Al
(c) Cu (d) Zn

3. The number of coulombs required for the deposition of 107.870 g of silver is
(a) 96500 (b) 48250
(c) 193000 (d) 10000

4. An electrolytic cell contains a solution of Ag_2SO_4 and has platinum electrodes. A current is passed until 1.6 gm of O_2 has been liberated at anode. The amount of silver deposited at cathode would be
(a) 107.88 gm (b) 1.6 gm
(c) 0.8 gm (d) 21.60 gm

5. 1.08 g of pure silver was converted into silver nitrate and its solution was taken in a beaker. It was electrolysed using platinum cathode and silver anode. 0.01 Faraday of electricity was passed using 0.15 volt above the decomposition potential of silver. The silver content of the beaker after the above shall be
(a) 0 g (b) 0.108 g
(c) 1.08 g (d) None of these

6. A current of 2.0 A passed for 5 hours through a molten metal salt deposits 22.2 g of metal (At wt. = 177). The oxidation state of the metal in the metal salt is
(a) +1 (b) +2
(c) +3 (d) +4

7. A 5 ampere current is passed through a solution of zinc sulphate for 40 minutes. Find the amount of zinc deposited at the cathode
(a) 40.65 g (b) 4.065 g
(c) 0.4065 g (d) 65.04 g

8. On passing a current of 1.0 ampere for 16 min and 5 sec through one litre solution of $CuCl_2$, all copper of the solution was deposited at cathode. The strength of $CuCl_2$ solution was (Molar mass of Cu = 63.5, Faraday constant = 96500 C mol^{-1}).
(a) 0.07 M (b) 0.2 N
(c) 0.005 M (d) 0.02 N

9. In a solution of $CuSO_4$ how much time will be required to precipitate 2 g copper by 0.5 ampere current ?
(a) 12157.48 sec (b) 102 sec
(c) 510 sec (d) 642 sec

10. What is the amount of chlorine evolved when 2 amperes of current is passed for 30 minutes in an aqueous solution of NaCl?

(a) 66 g
(b) 1.32 g
(c) 33 g
(d) 99 g

11. When 9.65 coulombs of electricity is passed through a solution of silver nitrate (atomic mass of Ag = 108 g mol^{-1}), the amount of silver deposited is

(a) 16.2 mg
(b) 21.2 mg
(c) 10.8 mg
(d) 6.4 mg

12. The charge required to deposit 9 g of Al from Al^{3+} solution is (At. wt. of Al = 27.0)

(a) 3216.3 C
(b) 96500 C
(c) 9650 C
(d) 32163 C

13. The quantity of electricity needed to deposit 127.08 g of copper is

(a) 1 Faraday
(b) 4 Coulombs
(c) 4 Faraday
(d) 1 Ampere

14. Silver is monovalent and has atomic mass of 108. Copper is divalent and has an atomic mass of 63.6. The same electric current is passed for the same length of time through a silver coulometer and a copper coulometer. If 27.0 g of silver is deposited, then the corresponding amount of copper deposited is

(a) 63.60 g
(b) 31.80 g
(c) 15.90 g
(d) 7.95 g

15. By passing 0.1 Faraday of electricity through fused sodium chloride, the amount of chlorine liberated is

(a) 35.45 g
(b) 70.9 g
(c) 3.545 g
(d) 17.77 g

16. The unit of specific conductivity is

(a) ohm cm^{-1}
(b) ohm cm^{-2}
(c) ohm^{-1} cm
(d) ohm^{-1} cm^{-1}

17. The cell constant of a given cell is 0.47 cm^{-1}. The resistance of a solution placed in this cell is measured to be 31.6 ohm. The conductivity of the solution (in S cm^{-1} where S has usual meaning) is

(a) 0.15
(b) 1.5
(c) 0.015
(d) 150

18. The specific conductivity of N/10 KCl solution at 20°C is 0.212 ohm^{-1} cm^{-1} and the resistance of the cell containing this solution at 20°C is 55 ohm. The cell constant is

(a) 4.616 cm^{-1}
(b) 11.66 cm^{-1}
(c) 2.173 cm^{-1}
(d) 3.324 cm^{-1}

19. The resistance of 1 N solution of acetic acid is 250 ohm, when measured in a cell of cell constant 1.15 cm^{-1}. The equivalent conductance (in ohm^{-1} cm^2 equiv^{-1}) of 1 N acetic acid will be

(a) 4.6
(b) 9.2
(c) 18.4
(d) 0.023

20. The equivalent conductance at infinite dilution of a weak acid such as HF

(a) can be determined by extrapolation of measurements of dilute solutions of HCl, HBr and HI
(b) can be determined by measurement of very dilute HF solutions
(c) can be determined from measurements of dilute solutions of NaF, NaCl and HCl
(d) is an undefined quantity

21. The unit of equivalent conductivity is

(a) ohm cm
(b) ohm^{-1} cm^{+2} (g equivalent)$^{-1}$
(c) ohm cm^2 (g equivalent)
(d) S cm^{-2}

22. The conductivity of a saturated solution of $BaSO_4$ is 3.06×10^{-6} ohm^{-1} cm^{-1} and its equivalent conductance is 1.53 ohm^{-1} cm^2 equiv^{-1}. The K_{sp} for $BaSO_4$ will be

(a) 4×10^{-12}
(b) 2.5×10^{-9}
(c) 2.5×10^{-13}
(d) 4×10^{-6}

23. The resistance of 0.1 N solution of a salt is found to be 2.5×10^3 ohm . The equivalent conductance of the solution is (cell constant = 1.15 cm^{-1})

(a) 4.6
(b) 5.6
(c) 6.6
(d) 7.6

24. Specific conductance of 0.1 M sodium chloride solution is 1.06×10^{-2} ohm^{-1} cm^{-1}. Its molar conductance in ohm^{-1} cm^2 mol^{-1} is

(a) 1.06×10^2
(b) 1.06×10^3
(c) 1.06×10^4
(d) 5.3×10^2

25. Molar conductivity of a solution is 1.26×10^2 Ω^{-1} cm^2 mol^{-1}. Its molarity is 0.01. Its specific conductivity will be

(a) 1.26×10^{-5}
(b) 1.26×10^{-3}
(c) 1.26×10^{-4}
(d) 0.0063

26. Molar ionic conductivities of a two-bivalent electrolytes x^{2+} and y^{2-} are 57 and 73 respectively. The molar conductivity of the solution formed by them will be

(a) 130 S cm^2 mol^{-1}
(b) 65 S cm^2 mol^{-1}
(c) 260 S cm^2 mol^{-1}
(d) 187 S cm^2 mol^{-1}

27. The equivalent conductivity of 0.1 M weak acid is 100 times less than that at infinite dilution. The degree of dissociation of weak acid will be

(a) 100
(b) 10
(c) 0.01
(d) 0.001

28. An electrochemical cell is set up as follows :
Pt (H_2, 1 atm)/0.1 M HCl/0.1 M acetic acid/(H_2, 1 atm) Pt
EMF of this cell will not be zero because

(a) the temperature is constant
(b) the pH of 0.1 M HCl and 0.1 M acetic acid is not the same
(c) acids used in the two compartments are different
(d) EMF of a cell depends on molarities of the acids used

29. Which one of the following reaction occurs at the cathode?

(a) $2OH^- \longrightarrow H_2O + O + 2e^-$
(b) $Ag \longrightarrow Ag^+ + e^-$
(c) $Fe^{2+} \longrightarrow Fe^{3+} + e^-$
(d) $Cu^{2+} + 2e^- \longrightarrow Cu$

30. Which of the following statements is true for an electrochemical cell?

(a) Reduction occurs at H_2 electrode
(b) H_2 is cathode and Cu is anode
(c) H_2 is anode and Cu is cathode
(d) Oxidation occurs at Cu electrode

31. On the basis of the information available from the reaction

$\frac{4}{3}Al + O_2 \longrightarrow \frac{2}{3}Al_2O_3$, $\Delta G = -827\ kJmol^{-1}$ of O_2, the minimum e.m.f. required to carry out electrolysis of Al_2O_3 is ($F = 96500\ C\ mol^{-1}$)

(a) 4.28 V (b) 6.42 V
(c) 8.56 V (d) 2.14 V

32. In the electrochemical reaction

$2Fe^{3+} + Zn \longrightarrow Zn^{2+} + 2Fe^{2+}$,

on increasing the concentration of Fe^{2+}

(a) increases cell emf
(b) increases the current flow
(c) decreases the cell emf
(d) alters the pH of the solution

33. In the cell reaction

$Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$,

$E^o_{cell} = 0.46$ V. By doubling the concentration of Cu^{2+}, E^o_{cell} will become

(a) doubled
(b) halved
(c) increases but less than double
(d) decreases by a small fraction

34. If salt bridge is removed from two half-cells the voltage

(a) drops to zero (b) does not change
(c) increases gradually (d) increases rapidly

35. In a salt bridge KCl is used because

(a) it is an electrolyte
(b) it is good conductor of electricity
(c) the transport number of K^+ and Cl^- ions are nearly same or both have same ionic mobility
(d) it is ionic compound

36. The reference electrode is made by using

(a) $ZnCl_2$ (b) $CuSO_4$
(c) $HgCl_2$ (d) Hg_2Cl_2

37. The standard hydrogen electrode potential is zero, because

(a) there is no potential difference between the electrode and the solution
(b) hydrogen ions acquire electrons from a platinum electrode
(c) it has been measured accurately
(d) it has been defined that way

38. The standard reduction potentials E° for the half reactions are as

$Zn \longrightarrow Zn^{2+} + 2e^-;\ E° = 0.76V$

$Fe \longrightarrow Fe^{2+} + 2e^-;\ E° = 0.41V$

The EMF for the cell reaction will be

(a) –0.3 V (b) 0.35 V
(c) 1.17 V (d) –1.17 V

39. The standard electrode potential (E°) for OCl^- / Cl^- and $Cl^- / \frac{1}{2}Cl_2$ respectively are 0.94 V and –1.36 V. The E° value for $OCl^- / \frac{1}{2}Cl_2$ will be

(a) –0.42 V (b) –2.20 V
(c) 0.52 V (d) 1.04 V

40. The standard reduction potential for Fe^{2+} / Fe and Sn^{2+}/ Sn electrodes are –0.44 and –0.14 volt respectively. For the cell reaction

$Fe^{2+} + Sn \longrightarrow Fe + Sn^{2+}$

the standard emf will be

(a) +0.30 V (b) –0.58 V
(c) +0.58 V (d) –0.30 V

41. The emf of the cell

$Ni / Ni^{2+}(1.0\,M) || Au^{3+}(1.0\,M) / Au$ is [E° for Ni^{2+} / Ni = – 0.25 V; E° for Au^{3+} / Au = 1.5 V]

(a) +1.25 V (b) +1.75 V
(c) –1.25 V (d) –1.75 V

42. An unknown metal M displaces nickel from nickel (II) sulphate solution but does not displace manganese from manganese sulphate solution. Which order represents the correct order of reducing power?

(a) Mn > Ni > M (b) Ni > Mn > M
(c) Mn > M > Ni (d) M > Ni > Mn

43. Electrode potentials ($E°_{red}$) of four elements A, B, C, D are –1.36, –0.32, 0, –1.26 V respectively. The decreasing reactivity order of these elements is

(a) A, D, B and C (b) C, B, D and A
(c) B, D, C and A (d) C, A, D and B

44. Chlorine cannot displace

(a) Fluorine from NaF (b) Iodine from NaI
(c) Bromine from NaBr (d) None of these

45. Standard potentials (E°) for some half-reactions are given below :

(I) $Sn^{4+} + 2e \longrightarrow Sn^{2+};\ E° = +0.15V$

(II) $2Hg^{2+} + 2e \longrightarrow Hg_2^{2+};\ E° = 0.92V$

(III) $PbO_2 + 4H^+ + 2e \longrightarrow Pb^{2+} + 2H_2O;$
$E° = +1.45V$

based on the above, information which one of the following statements is correct?

(a) Sn^{4+} is a stronger oxidising agent than Pb^{4+}
(b) Sn^{2+} is a stronger reducing agent than Hg_2^{2+}
(c) Pb^{2+} is a stronger oxidising agent than Pb^{4+}
(d) Pb^{2+} is a stronger reducing agent than Sn^{2+}

46. The oxidation potentails of A and B are +2.37 and +1.66 V respectively. In chemical reactions

(a) A will be replaced by B
(b) A will replace B
(c) A will not replace B
(d) A and B will not replace each other

47. Electrode potential data are given below :

$$Fe^{+3}(aq) + e^{-} \longrightarrow Fe^{+2}(aq); \quad E° = +0.77\ V$$

$$Al^{3+}(aq) + 3e^{-} \longrightarrow Al(s); \quad E° = -1.66\ V$$

$$Br_2(aq) + 2e^{-} \longrightarrow 2Br^{-}(aq); \quad E° = +1.08 V$$

Based on the data, the reducing power of Fe^{2+}, Al and Br^{-} will increase in the order

(a) $Br^{-} < Fe^{2+} < Al$ (b) $Fe^{2+} < Al < Br^{-}$

(c) $Al < Br^{-} < Fe^{2+}$ (d) $Al < Fe^{2+} < Br^{-}$

48. Choose the correct statement from the following which is related to the electrochemical series

(a) Electrochemical series is not the arrangement of metals and ions according to their reactivity

(b) The metal ions at the top of the electrochemical series are highly electronegative

(c) Strongly electropositive metals can displace weakly electropositive metals from their salt solution

(d) All metals above hydrogen in the series do not displace hydrogen from dilute acids

49. The standard reduction potentials of four elements are given below. Which of the following will be the most suitable reducing agent?

$I = -3.04\ V$ $II = -1.90\ V$

$III = 0\ V$ $IV = 1.90\ V$

(a) III (b) II

(c) I (d) IV

50. The standard reduction potentials at 298K for the following half reactions are given against each

$$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s);\ -0.762\ V$$

$$Cr^{3+}(aq) + 3e \rightleftharpoons Cr(s); -0.740\ V$$

$$2H^{+}(aq) + 2e \rightleftharpoons H_2(g);\ 0.00\ V$$

$$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq);\ 0.770\ V$$

Which is the strongest reducing agent?

(a) Zn (s) (b) Cs (s)

(c) $H_2(g)$ (d) $Fe^{3+}(aq)$

51. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because

(a) Zn acts as oxidizing when reacts with HNO_3

(b) HNO_3 is weaker acid than H_2SO_4 and HCl

(c) In electrochemical series Zn is above hydrogen

(d) NO_3^{-} is reduced in preference to hydronium

52. A smuggler could not carry gold by depositing iron on the gold surface since

(a) gold is denser

(b) iron rusts

(c) gold has higher reduction potential than iron

(d) gold has lower reduction potential than iron

53. The e.m.f. of a Daniell cell at 298 K is E_1

$$Zn\left|\begin{array}{c}ZnSO_4\\(0.01M)\end{array}\right|\left|\begin{array}{c}CuSO_4\\(1.0\,M)\end{array}\right|Cu$$

When the concentration of $ZnSO_4$ is 1.0 M and that of $CuSO_4$ is 0.01 M, the e.m.f. changed to E_2. What is the relationship between E_1 and E_2?

(a) $E_1 < E_2$ (b) $E_1 = E_2$

(c) $E_2 = 0 \neq E_1$ (d) $E_1 > E_2$

54. The metal that cannot displace hydrogen from dilute hydrochloric acid is

(a) aluminium (b) Iron

(c) copper (d) zinc

55. Which reaction is not feasible?

(a) $2KI + Br_2 \longrightarrow 2KBr + I_2$

(b) $2KBr + I_2 \longrightarrow 2KI + Br_2$

(c) $2KBr + Cl_2 \longrightarrow 2KCl + Br_2$

(d) $2H_2O + 2F_2 \longrightarrow 4HF + O_2$

56. Which of the following will form a cell with the highest voltage?

(a) $1M\,Ag^{+}, 1M\,Co^{2+}$ (b) $2\,M\,Ag^{+}, 2\,M\,Co^{2+}$

(c) $0.1M\,Ag^{+}, 2\,M\,Co^{2+}$ (d) $2\,M\,Ag^{+}, 0.1M\,Co^{2+}$

57. E° of a cell $aA + bB \longrightarrow cC + dD$ is

(a) $E + RT\ln\dfrac{[a]^{A}[b]^{B}}{[c]^{C}[d]^{D}}$ (b) $E + \dfrac{RT}{nF}\ln\dfrac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$

(c) $E + \dfrac{RT}{nF}\ln\dfrac{[C]^{c}[d]^{D}}{[A]^{A}[B]^{B}}$ (d) $E + \dfrac{RT}{nF}\ln\dfrac{[a]^{A}[B]^{B}}{[C]^{C}[d]^{D}}$

58. The standard EMF for the cell reaction,

$Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$ is 1.1 volt at 25°C.

The EMF for the cell reaction, when 0.1 M Cu^{2+} and 0.1 M Zn^{2+} solutions are used, at 25°C is

(a) 1.10 V (b) 0.10 V

(c) –1.10 V (d) –0.110 V

59. What is the potential of half-cell consisting of zinc electrode in 0.01 M $ZnSO_4$ solution at 25°C $\left(E^{\circ}_{ox} = 0.763\ V\right)$

(a) 0.8221 V (b) 8.221 V

(c) 0.5282 V (d) 9.282 V

60. The oxidation potential of 0.05 M H_2SO_4 is

(a) -2×0.0591 (b) -0.01×0.0591

(c) -2.321×0.0591 (d) $+1 \times 0.0591$

61. For the cell reaction,

$$Cu^{2+}[C_1(aq)] + Zn(s) \longrightarrow Zn^{2+}(C_2) + Cu(s)$$

of an electrochemical cell, the change in free energy, ΔG at a given temperature is a function of

(a) $\ln(C_1)$

(b) $\ln\left(\frac{C_2}{C_1}\right)$

(c) $\ln(C_1 + C_2)$

(d) $\ln(C_2)$

62. The relationship between standard reduction potential of a cell and equilibrium constant is shown by

(a) $E^o_{cell} = \frac{n}{0.059} \log k_c$

(b) $E^o_{cell} = \frac{0.059}{n} \log k_c$

(c) $E^o_{cell} = 0.059\, n \log k_c$

(d) $E^o_{cell} = \frac{\log k_c}{n}$

63. E° for the cell,

$Zn \mid Zn^{2+}(aq) \mid\mid Cu^{2+}(aq) \mid Cu$ is 1.10 V at 25°C. The equilibrium constant for the cell reaction

$$Zn + Cu^{2+}(aq) \rightleftharpoons Cu + Zn^{2+}(aq)$$

is of the order of

(a) 10^{-37}

(b) 10^{37}

(c) 10^{-17}

(d) 10^{17}

64. The standard EMF of Daniell cell is 1.10 volt. The maximum electrical work obtained from the Daniell cell is

(a) 212.3 kJ

(b) 175.4 kJ

(c) 106.15 kJ

(d) 53.07 kJ

65. The emf of Daniell cell is 1.1 volt. If the value of Faraday is 96500 coulombs per mole, the change in free energy in kJ is

(a) 212.30

(b) –212.30

(c) 106.15

(d) –106.15

66. Pure water does not conduct electricity because it

(a) has low boiling point

(b) is almost unionised

(c) is neutral

(d) is readily decomposed

67. At cathode, the electrolysis of aqueous Na_2SO_4 gives

(a) Na

(b) H_2

(c) SO_3

(d) SO_2

68. At anode in the electrolysis of fused NaCl

(a) Na^+ is oxidized

(b) Cl^- is oxidized

(c) Cl is reduced

(d) Na is reduced

69. In electrolysis of NaCl when Pt electrode is taken then H_2 is liberated at cathode while with Hg cathode, it forms sodium amalgam

(a) Hg is more inert than Pt

(b) More voltage is required to reduce H^+ at Hg than at Pt

(c) Na is dissolved in Hg while it does not dissolve in Pt

(d) Conc. of H^+ ions is larger when Pt electrode is taken

70. Which of the following reaction occurs at the cathode during the charging of lead storage battery?

(a) $Pb^{2+} + 2e^- \longrightarrow Pb$

(b) $Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

(c) $Pb \longrightarrow Pb^{2+} + 2e^-$

(d) $PbSO_4 + 2H_2O \longrightarrow 2PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

71. Reaction that takes place at graphite anode in dry cell is

(a) $Zn^{2+} + 2e^- \longrightarrow Zn(s)$

(b) $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

(c) $Mn^{2+} + 2e^- \longrightarrow Mn(s)$

(d) $Mn(s) \longrightarrow Mn^+ + e^- + 1.5V$

72. Which one of the following cells can convert chemical energy of H_2 and O_2 directly into electrical energy?

(a) Mercury cell

(b) Daniell cell

(c) Fuel cell

(d) Lead storage cell

73. Hydrogen-Oxygen fuel cells are used in space craft to supply

(a) power for heat and light

(b) power for pressure

(c) oxygen

(d) water

74. As lead storage battery is charged

(a) lead dioxide dissolves

(b) sulphuric acid is regenerated

(c) lead electrode becomes coated with lead sulphate

(d) the concentration of sulphuric acid decreases

75. The thermodynamic efficiency of cell is given by

(a) $\Delta H/\Delta G$

(b) $nFE/\Delta G$

(c) $nFE/\Delta H$

(d) nFE

76. The electroplating with chromium is undertaken because

(a) electrolysis of chromium is easier

(b) chromium can form alloys with other metals

(c) chromium gives protective and decorative coating to the base metal

(d) of the high reactivity of metallic chormium

77. Prevention of corrosion of iron by Zn coating is called

(a) galvanization

(b) cathodic protection

(c) electrolysis

(d) photoelectrolysis

78. Which of the following statements is correct?

(a) Oxidation number of oxygen in KO_2 is +1

(b) The specific conductance of an electrolyte solution decreases with increase in dilution

(c) Sn^{2+} oxidises Fe^{3+}

(d) $Zn/ZnSO_4$ is a reference electrode

79. In the electrolytic cell, flow of electrons is from

(a) cathode to anode in solution

(b) cathode to anode through external supply

(c) cathode to anode through internal supply

(d) anode to cathode through internal supply

Exercise-3 | PAST COMPETITION MCQs

1. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because **[CBSE-PMT 2002]**
(a) Zn acts as an oxidising agent when it reacts with HNO_3
(b) HNO_3 is weaker acid than H_2SO_4 and HCl
(c) in electrochemical series, Zn is above hydrogen
(d) NO_3^- is reduced in preference to hydronium ion

2. The efficiency of a fuel cell is given by **[CBSE-PMT 2007]**
(a) $\frac{\Delta G}{\Delta S}$ (b) $\frac{\Delta G}{\Delta H}$ (c) $\frac{\Delta S}{\Delta G}$ (d) $\frac{\Delta H}{\Delta G}$

3. The equilibrium constant of the reaction:
$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$;
E° = 0.46 V at 298 K is **[CBSE-PMT 2007]**
(a) 2.0×10^{10} (b) 4.0×10^{10} (c) 4.0×10^{15} (d) 2.4×10^{10}

4. On the basis of the following E° values, the strongest oxidizing agent is : **[CBSE-PMT 2008]**
$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^-$; E° = – 0.35 V
$Fe^{2+} \rightarrow Fe^{3+} + e^-$; E° = – 0.77 V
(a) $[Fe(CN)_6]^{4-}$ (b) Fe^{2+}
(c) Fe^{3+} (d) $[Fe(CN)_6]^{3-}$

5. Kohlrausch's law states that at : **[CBSE-PMT 2008]**
(a) finite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte.
(b) infinite dilution each ion makes definite contribution to equivalent conductance of an electrolyte depending on the nature of the other ion of the electrolyte.
(c) infinite dilution, each ion makes definite contribution to conductance of an electrolyte whatever be the nature of the other ion of the electrolyte.
(d) infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte.

6. Standard free energies of formation (in kJ/mol) at 298 K are – 237.2, – 394.4 and – 8.2 for $H_2O(l)$, $CO_2(g)$ and pentane (*g*), respectively. The value $E°_{cell}$ for the pentane-oxygen fuel cell is : **[CBSE-PMT 2008]**
(a) 1.968 V (b) 2.0968 V (c) 1.0968 V (d) 0.0968 V

7. Given: **[CBSE-PMT 2009]**
(i) $Cu^{2+} + 2e^- \rightarrow Cu$, $E^o = 0.337$ V
(ii) $Cu^{2+} + e^- \rightarrow Cu^+$, $E^o = 0.153$ V
Electrode potential, E^o for the reaction,
$Cu^+ + e^- \rightarrow Cu$, will be :
(a) 0.90 V (b) 0.30 V (c) 0.38 V (d) 0.52 V

8. Al_2O_3 is reduced by electrolysis at low potentials and high currents. If 4.0×10^4 amperes of current is passed through molten Al_2O_3 for 6 hours, what mass of aluminium is produced? (Assume 100% current efficiency. At. mass of Al = 27 g mol^{-1}) **[CBSE-PMT 2009]**
(a) 8.1×10^4 g (b) 2.4×10^5 g
(c) 1.3×10^4 g (d) 9.0×10^3 g

9. The equivalent conductance of $\frac{M}{32}$ solution of a weak monobasic acid is 8.0 mho cm^2 and at infinite dilution is 400 mho cm^2. The dissociation constant of this acid is: **[CBSE-PMT 2009]**
(a) 1.25×10^{-6} (b) 6.25×10^{-4}
(c) 1.25×10^{-4} (d) 1.25×10^{-5}

10. For the reduction of silver ions with copper metal, the standard cell potential was found to be + 0.46 V at 25°C. The value of standard Gibbs energy, $\Delta G°$ will be (F = 96500 C mol^{-1}) **[CBSE-PMT 2010]**
(a) – 89.0 kJ (b) – 89.0 J (c) – 44.5 kJ (d) – 98.0 kJ

11. An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to: **[CBSE-PMT 2010]**
(a) increase in ionic mobility of ions
(b) 100% ionisation of electrolyte at normal dilution
(c) increase in both i.e. number of ions and ionic mobility of ions
(d) increase in number of ions

12. Which of the following expressions correctly represents the equivalent conductance at infinite dilution of $Al_2(SO_4)_3$, Given that $\overset{\circ}{\Lambda}_{Al^{3+}}$ and $\overset{\circ}{\Lambda}_{SO_4^{2-}}$ are the equivalent conductances at infinite dilution of the respective ions? **[CBSE-PMT 2010]**
(a) $\frac{1}{3}\overset{\circ}{\Lambda}_{Al^{3+}} + \frac{1}{2}\overset{\circ}{\Lambda}_{SO_4^{2-}}$ (b) $2\overset{\circ}{\Lambda}_{Al^{3+}} + 3\overset{\circ}{\Lambda}_{SO_4^{2-}}$
(c) $\overset{\circ}{\Lambda}_{Al^{3+}} + \overset{\circ}{\Lambda}_{SO_4^{2-}}$ (d) $\left(\overset{\circ}{\Lambda}_{Al^{3+}} + \overset{\circ}{\Lambda}_{SO_4^{2-}}\right) \times 6$

13. Consider the following relations for emf of a electrochemical cell: **[CBSE-PMT 2010]**
(i) emf of cell = (Oxidation potential of anode) – (Reduction potential of cathode)
(ii) emf of cell = (Oxidation potential of anode) + (Reduction potential of cathode)
(iii) emf of cell = (Reduction potential of anode) + (Reduction potential of cathode)
(iv) emf of cell = (Oxidation potential of anode) – (Oxidation potential of cathode)
Which of the above relations are correct?
(a) (ii) and (iv) (b) (iii) and (i)
(c) (i) and (ii) (d) (iii) and (iv)

14. Standard electrode potential of three metals X, Y and Z are – 1.2 V, + 0.5 V and – 3.0 V, respectively. The reducing power of these metals will be : **[CBSE-PMT 2011]**
(a) Y > Z > X (b) X > Y > Z (c) Z > X > Y (d) X > Y > Z

15. The electrode potentials for **[CBSE-PMT 2011]**

$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$

and $Cu^+(aq) + e^- \longrightarrow Cu(s)$

are + 0.15 V and + 0.50, respectively. The value of $E^\circ_{Cu^{2+}/Cu}$ will be :

(a) 0.500 V (b) 0.325 V (c) 0.650 V (d) 0.150 V

16. Standard electrode potential for Sn^{4+}/Sn^{2+} couple is + 0.15 V and that for the Cr^{3+}/Cr couple is – 0.74 V. These two couples in their standard state are connected to make a cell. The cell potential will be : **[CBSE-PMT 2011]**

(a) + 1.19 V (b) + 0.89 V (c) + 0.18 V (d) + 1.83 V

17. If the E°_{cell} for a given reaction has a negative value, then which of the following gives the correct relationships for the values of ΔG° and K_{eq} ? **[CBSE-PMT 2011]**

(a) $\Delta G^\circ > 0 ; K_{eq} > 1$ (b) $\Delta G^\circ < 0 ; K_{eq} > 1$

(c) $\Delta G^\circ < 0 ; K_{eq} < 1$ (d) $\Delta G^\circ > 0 ; K_{eq} < 1$

18. A solution contains Fe^{2+}, Fe^{3+} and I^- ions. This solution was treated with iodine at 35°C. E° for Fe^{3+}/Fe^{2+} is + 0.77 V and E° for $I_2/2I^- = 0.536$ V. The favourable redox reaction is :

(a) I_2 will be reduced to I^- **[CBSE-PMT 2011 M]**

(b) There will be no redox reaction

(c) I^- will be oxidised to I_2

(d) Fe^{2+} will be oxidised to Fe^{3+}

19. Limiting molar conductivity of NH_4OH **[CBSE-PMT 2012 S]**

$\left(\text{i.e., } \Lambda^{\circ}_{m(NH_4OH}\right)$ is equal to :

(a) $\Lambda^{\circ}_{m(NH_4Cl)} + \Lambda^{\circ}_{m(NaCl)} - \Lambda^{\circ}_{m(NaOH)}$

(b) $\Lambda^{\circ}_{m(NaOH)} + \Lambda^{\circ}_{m(NaCl)} - \Lambda^{\circ}_{m(NH_4Cl)}$

(c) $\Lambda^{\circ}_{m(NH_4OH)} + \Lambda^{\circ}_{m(NH_4Cl)} - \Lambda^{\circ}_{m(HCl)}$

(d) $\Lambda^{\circ}_{m(NH_4Cl)} + \Lambda^{\circ}_{m(NaOH} - \Lambda^{\circ}_{m(NaCl)}$

20. Standard reduction potentials of the half reactions are given below : **[CBSE-PMT 2012 M]**

$F_2(g) + 2e^- \rightarrow 2F^-(aq);\ E^\circ = +2.85$ V

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq);\ E^\circ = +1.36$ V

$Br_2(l) + 2e^- \rightarrow 2Br^-(aq);\ E^\circ = +1.06$ V

$I_2(s) + 2e^- \rightarrow 2I^-(aq);\ E^\circ = +0.53$ V

The strongest oxidising and reducing agents respectively are :

(a) F_2 and I^- (b) Br_2 and Cl^-

(c) Cl_2 and Br^- (d) Cl_2 and I_2

21. Molar conductivities (Λ°_m) at infinite dilution of NaCl, HCl and CH_3COONa are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively. Λ°_m for CH_3COOH will be : **[CBSE-PMT 2012 M]**

(a) 425.5 S cm^2 mol^{-1} (b) 180.5 S cm^2 mol^{-1}

(c) 290.8 S cm^2 mol^{-1} (d) 390.5 S cm^2 mol^{-1}

22. A hydrogen gas electrode is made by dipping platinum wire in a solution of HCl of pH = 10 and by passing hydrogen gas around the platinum wire at one atm pressure. The oxidation potential of electrode would be ? **[NEET 2013]**

(a) 0.59 V (b) 0.118 V

(c) 1.18 V (d) 0.059 V

23. At 25°C molar conductance of 0.1 molar aqueous solution of ammonium hydroxide is 9.54 ohm^{-1} cm^2mol^{-1} and at infinite dilution its molar conductance is 238 $ohm^{-1}cm^2$ mol^{-1}. The degree or ionisation of ammonium hydroxide at the same concentration and temperature is : **[NEET 2013]**

(a) 20.800% (b) 4.008%

(c) 40.800% (d) 2.080%

24. A button cell used in watches functions as following

$$Zn(s) + Ag_2O(s) + H_2O(l) \rightleftharpoons 2Ag(s) + Zn^{2+}(aq) + 2OH^-(aq)$$

If half cell potentials are :

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s);\ E^o = -0.76$ V

$Ag_2O(s) + H_2O\ (l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq);$ $E^o = 0.34$ V

The cell potential will be : **[NEET 2013]**

(a) 0.42 V (b) 0.84 V

(c) 1.34 V (d) 1.10 V

25. Conductivity (unit Siemen's S) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel then the unit of the constant of proportionality is **[AIEEE 2002]**

(a) $Sm\ mol^{-1}$ (b) $Sm^2\ mol^{-1}$

(c) $S^{-2}m^2\ mol$ (d) $S^2m^2\ mol^{-2}$.

26. EMF of a cell in terms of reduction potential of its left and right electrodes is **[AIEEE 2002]**

(a) $E = E_{left} - E_{right}$ (b) $E = E_{left} + E_{right}$

(c) $E = E_{right} - E_{left}$ (d) $E = -(E_{right} + E_{left})$.

27. If ϕ denotes reduction potential, then which is true? **[AIEEE 2002]**

(a) $E^\circ_{cell} = \phi_{right} - \phi_{left}$ (b) $E^\circ_{cell} = \phi_{left} + \phi_{right}$

(c) $E^\circ_{cell} = \phi_{left} - \phi_{right}$ (d) $E^\circ_{cell} = -(\phi_{left} + \phi_{right})$.

28. What will be the emf for the given cell

$Pt\,|\,H_2\,(P_1)\,|\,H^+\,(aq)\,||\,H_2\,(P_2)\,|\,Pt$ **[AIEEE 2002]**

(a) $\dfrac{RT}{f}\log\dfrac{P_1}{P_2}$ (b) $\dfrac{RT}{2f}\log\dfrac{P_1}{P_2}$

(c) $\dfrac{RT}{f}\log\dfrac{P_2}{P_1}$ (d) None of these.

29. Which of the following reaction is possible at anode? **[AIEEE 2002]**

(a) $2\,Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+$

(b) $F_2 \rightarrow 2F^-$

(c) $(1/2)\,O_2 + 2H^+ \rightarrow H_2O$

(d) None of these.

30. For a cell reaction involving a two-electron change, the standard e.m.f. of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be

(a) 29.5×10^{-2} (b) 10 **[AIEEE 2003]**

(c) 1×10^{10} (d) 1×10^{-10}

31. Standard reduction electrode potentials of three metals A, B & C are respectively + 0.5 V, – 3.0 V & –1.2 V. The reducing powers of these metals are **[AIEEE 2003]**

(a) A > B > C (b) C > B > A

(c) A > C > B (d) B > C > A

32. When during electrolysis of a solution of $AgNO_3$ 9650 coulombs of charge pass through the electroplating bath, the mass of silver deposited on the cathode will be

(a) 10.8 g (b) 21.6 g **[AIEEE 2003]**
(c) 108 g (d) 1.08 g

33. For the redox reaction : **[AIEEE 2003]**

$$Zn(s) + Cu^{2+}(0.1M) \rightarrow Zn^{2+}(1M) + Cu(s)$$

taking place in a cell, E°_{cell} is 1.10 volt. E_{cell} for the cell will be $\left(2.303\frac{RT}{F} = 0.0591\right)$

(a) 1.80 volt (b) 1.07 volt
(c) 0.82 volt (d) 2.14 volt

34. Several blocks of magnesium are fixed to the bottom of a ship to **[AIEEE 2003]**

(a) make the ship lighter
(b) prevent action of water and salt
(c) prevent puncturing by under-sea rocks
(d) keep away the sharks

35. In a hydrogen-oxygen fuel cell, combustion of hydrogen occurs to **[AIEEE 2004]**

(a) produce high purity water
(b) create potential difference between two electrodes
(c) generte heat
(d) remove adsorbed oxygen from electron surfaces

36. Consider the following E° values **[AIEEE 2004]**

$E^{o}_{Fe^{3+}/Fe^{2+}} = +0.77V$; $E^{o}_{Sn^{2+}/Sn} = -0.14V$

Under standard conditions the potential for the reaction

$Sn_{(s)} + 2Fe^{3+}{}_{(aq)} \rightarrow 2Fe^{2+}(aq) + Sn^{2+}(aq)$ is

(a) 0.91 V (b) 1.40 V
(c) 1.68 V (d) 0.63 V

37. The standard e.m.f. of a cell involving one electron change is found to be 0.591 V at 25ºC. The equilibrium constant of the reaction will be
($F = 96{,}500\ C\ mol^{-1}$; $R = 8.314\ JK^{-1}\ mol^{-1}$) **[AIEEE 2004]**

(a) 1.0×10^{10} (b) 1.0×10^{5}
(c) 1.0×10^{1} (d) 1.0×10^{30}

38. The limiting molar conductivities Λ^{o} for NaCl, KBr and KCl are 126, 152 and 150 S cm^2 mol^{-1} respectively. The Λ^{o} for NaBr is **[AIEEE 2004]**

(a) 278 S cm^2 mol^{-1} (b) 176 S cm^2 mol^{-1}
(c) 128 S cm^2 mol^{-1} (d) 302 S cm^2 mol^{-1}

39. The $E^{o}_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are – 0.41, + 1.57, + 0.77 and + 1.97V respectively. For which one of these metals the change in oxidation state from +2 to +3 is easiest?

(a) Fe (b) Mn **[AIEEE 2004]**
(c) Cr (d) Co

40. The highest electrical conductivity of the following aqueous solutions is of **[AIEEE 2005]**

(a) 0.1 M difluoroacetic acid
(b) 0.1 M fluoroacetic acid
(c) 0.1 M chloroacetic acid
(d) 0.1 M acetic acid

41. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (At. Mass = 27 amu; 1 Faraday = 96,500 Coulombs). The cathode reaction is–

$$Al^{3+} + 3e^{-} \rightarrow Al$$

To prepare 5.12 kg of aluminium metal by this method we require **[AIEEE 2005]**

(a) 5.49×10^{1} C of electricity

(b) 5.49×10^{4} C of electricity

(c) 1.83×10^{7} C of electricity

(d) 5.49×10^{7} C of electricity

42.

Electrolyte:	KCl	KNO_3	HCl	NaOAc	NaCl
Λ^{∞} (S cm^2 mol^{-1}) :	149.9	145	426.2	91	126.5

Calculate Λ^{∞}_{HOAC} using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25°C **[AIEEE 2005]**

(a) 217.5 (b) 390.7
(c) 552.7 (d) 517.2

43. The molar conductivities Λ^{o}_{NaOAc} and Λ^{o}_{HCl} at infinite dilution in water at 25ºC are 91.0 and 426.2 S cm^2/mol respectively. To calculate Λ^{o}_{HOAc}, the additional value required is **[AIEEE 2006]**

(a) Λ^{o}_{NaOH} (b) Λ^{o}_{NaCl}

(c) $\Lambda^{o}_{H_2O}$ (d) Λ^{o}_{KCl}

44. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 Ω. The conductivity of this solution is 1.29 S m^{-1}. Resistance of the same cell when filled with 0.2 M of the same solution is 520 Ω. The molar conductivity of 0.02 M solution of electrolyte will be **[AIEEE 2006]**

(a) 1.24×10^{-4} S m^2 mol^{-1} (b) 12.4×10^{-4} S m^2 mol^{-1}
(c) 124×10^{-4} S m^2 mol^{-1} (d) 1240×10^{-4} S m^2 mol^{-1}

45. The equivalent conductances of two strong electrolytes at infinite dilution in H_2O (where ions move freely through a solution) at 25°C are given below : **[AIEEE 2007]**

$$\Lambda^{\circ}_{CH_3COONa} = 91.0\ S\ cm^2/equiv.$$

$$\Lambda^{\circ}_{HCl} = 426.2\ S\ cm^2/equiv.$$

What additional information/ quantity one needs to calculate Λ° of an aqueous solution of acetic acid?

(a) Λ° of chloroacetic acid ($ClCH_2COOH$)
(b) Λ° of NaCl
(c) Λ° of CH_3COOK
(d) the limiting equivalent coductance of $H^{+}(\lambda^{\circ}_{H^{+}})$.

46. The cell, $Zn\,|\,Zn^{2+}(1\text{ M})\,||\,Cu^{2+}(1\text{ M})\,|\,Cu\ (E^\circ_{cell} = 1.10\text{ v})$ was allowed to be completely discharged at 298 K. The relative concentration of Zn^{2+} to Cu^{2+} $\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$ is

[AIEEE 2007]

(a) 9.65×10^4 (b) antilog (24.08)
(c) 37.3 (d) $10^{37.3}$.

47. Given $E^\circ_{Cr^{3+}/Cr} = -0.72$ V, $E^\circ_{Fe^{2+}/Fe} = -0.42$ V. The potential for the cell
$Cr|Cr^{3+}(0.1M)||Fe^{2+}(0.01\text{ M})|Fe$ is **[AIEEE 2008]**
(a) 0.26 V (b) 0.336 V (c) –0.339 (d) 0.26 V

48. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is

$$CH_3OH(l) + 3/2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

At 298 K standard Gibb's energies of formation for $CH_3OH(l)$, $H_2O(l)$ and and $CO_2(g)$ are –166.2 –237.2 and –394.4 $kJ\,mol^{-1}$ respectively. If standard enthalpy of combustion of methonal is – 726 kJ mol^{-1}, efficiency of the fuel cell will be:

[AIEEE 2009]

(a) 87% (b) 90% (c) 97% (d) 80%

49. Given:

$$E^\circ_{Fe^{3+}/Fe} = -0.036\text{V},$$

$$E^\circ_{Fe^{2+}/Fe} = -0.439\text{V}$$

The value of standard electrode potential for the change,

$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$ will be: **[AIEEE 2009]**

(a) 0.385 V (b) 0.770 V (c) –0.270 V (d) –0.072 V

50. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows :

$$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2, \Delta_r G = +966\text{ kJ mol}^{-1}$$

The potential difference needed for electrolytic reduction of Al_2O_3 at 500°C is at least **[AIEEE 2010]**
(a) 4.5 V (b) 3.0 V
(c) 2.5 V (d) 5.0 V

51. The correct order of $E^\circ_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is

[AIEEE 2010]

(a) Mn > Cr > Fe > Co (b) Cr < Fe > Mn > Co
(c) Fe > Mn > Cr > Co (d) Cr > Mn > Fe > Co

52. The reduction potential of hydrogen half-cell will be negative if: **[AIEEE 2011]**
(a) $p(H_2) = 1$ atm and $[H^+] = 2.0$ M
(b) $p(H_2) = 1$ atm and $[H^+] = 1.0$ M
(c) $p(H_2) = 2$ atm and $[H^+] = 1.0$ M
(d) $p(H_2) = 2$ atm and $[H^+] = 2.0$ M

53. Consider the following cell reaction: **[AIEEE 2011]**

$$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l); E^\circ = 1.67V$$

At $[Fe^{2+}] = 10^{-3}$ M, $p(O_2) = 0.1$ atm and pH = 3, the cell potential at 25ºC is
(a) 1.47 V (b) 1.77 V (c) 1.87 V (d) 1.57 V

54. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.3 S m^{-1}. If resistance of the 0.4 M solution of the same electrolyte is 260 Ω, its molar conductivity is : **[AIEEE 2011RS]**
(a) 6.25×10^{-4} S m^2 mol^{-1} (b) 625×10^{-4} S m^2 mol^{-1}
(c) 62.5 S m^2 mol^{-1} (d) 6250 S m^2 mol^{-1}

55. The standard reduction potentials for Zn^{2+}/Zn, Ni^{2+}/Ni and Fe^{2+}/Fe are –0.76, –0.23 and –0.44 V respectively. The reaction $X + Y^{2+} \longrightarrow X^{2+} + Y$ will be spontaneous when : **[AIEEE 2012]**
(a) X = Ni, Y = Fe (b) X = Ni, Y = Zn
(c) X = Fe, Y = Zn (d) X = Zn, Y = Ni

56. Given : $E^\circ_{Cr^{3+}/Cr} = -0.74$ V; $E^\circ_{MnO_4^-/Mn^{2+}} = 1.51$ V

$E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V; $E^\circ_{Cl/Cl^-} = 1.36$ V

Based on the data given above, strongest oxidising agent will be : **[JEE M 2013]**
(a) Cl (b) Cr^{3+}
(c) Mn^{2+} (d) MnO_4^-

57. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^\circ_{M^{3+}/M^{2+}}$ value ?

[JEE M 2013]

(a) Cr(Z = 24) (b) Mn(Z = 25)
(c) Fe(Z = 26) (d) Co(Z = 27)

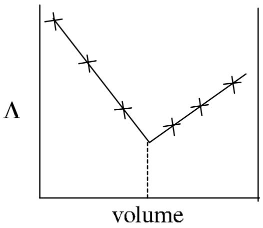
58. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milli ampere current. The time required to liberate 0.01 mol of H_2 gas at the cathode is (1 Faraday = 96500 C mol^{-1})

[IIT-JEE 2008S]

(a) 9.65×10^4 sec (b) 19.3×10^4 sec
(c) 28.95×10^4 sec (d) 38.6×10^4 sec

59. $AgNO_3(aq.)$ was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (Λ) versus the volume of $AgNO_3$ is

[IIT-JEE 2011]



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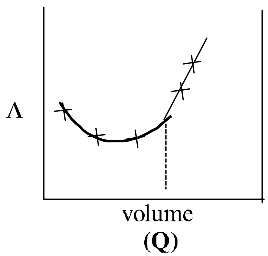

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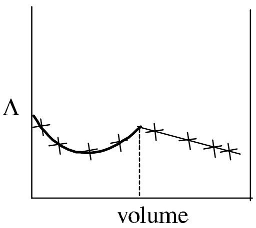
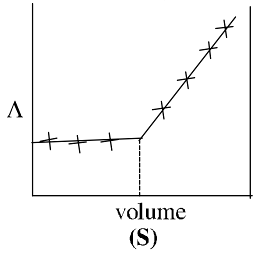


(R)



(S)

(a) (P) (b) (Q)
(c) (R) (d) (S)

Exercise-4 | Applied MCQs

1. Which of the following solutions of KCl will have the highest value of specific conductance?

(a) 1.0 N (b) 0.1 N

(c) 1.0×10^{-2}N (d) 1.0×10^{-3}N

2. Which of the following statements is not correct?

(a) The equivalent conductance of an electrolyte increases on dilution.

(b) The equivalent conductance of an electrolyte decreases on dilution

(c) The degree of ionization of a weak electrolyte is given by $\alpha = \lambda_c/\lambda_0$, where λ_c and λ_0 are equivalent conductances at concentration c and zero respectively

(d) In case of a weak electrolyte on dilution,, specific conductance decreases but its equivalent conductance increases

3. Which of the following statements is wrong ?

(a) Electrolysis of an aqueous sodium hydroxide solution liberates H_2 gas at the cathode and O_2 gas at the anode.

(b) Electrolysis of dil. H_2SO_4 liberates H_2(g) at cathode and O_2 (g) at the anode

(c) $\Delta G° = nFE°$ for a spontaneous reaction

(d) $E = E° - \frac{0.059}{n}\log Q$, Where Q = reaction quotient.

4. In the electrolysis of $CuCl_2$ solution, the mass of the cathode increased by 3.2g. What occured at the copper anode ?

(a) 0.12 litre of Cl_2 was liberated

(b) 0.56 litre of O_2 was liberated

(c) 0.1 mol Cu^{2+} passed into the solution.

(d) 0.05 mol of Cu^{2+} passed into the solution.

5. Copper can be deposited from acidified copper sulphate and alkaline copper cyanide both. If the same current is passed for the definite time, which of the following is correct?

(a) The amount of copper deposited from acidic copper sulphate will be higher

(b) The amount of copper deposited from alkaline copper cyanide will be more.

(c) The same amount of Cu will be deposited

(d) No Cu will be deposited

6. The EMF of the cell Tl/Tl^+ (0.001M) || Cu^{2+} (0.01M) /Cu is 0.83. The cell EMF can be increased by

(a) Increasing the concentration of Tl^+ ions.

(b) Increasing the concentration of Cu^{2+} ions.

(c) Increasing the concentration of Tl^+ and Cu^{2+} ions.

(d) None of these

7. What is the reaction taking place at the anode when an aqueous solution of copper sulphate is electrolysed using Pt–electrodes (inert) ?

(a) $Cu^{2+} + 2e^- \rightarrow Cu$

(b) $2H^+ + 2e^- \rightarrow H_2$

(c) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

(d) $2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$

8. The specific conductance at 298 K of AgCl is 1.826×10^{-6} ohm^{-1}cm^{-1}. The ionic conductances of Ag^+ and Cl^- are 61.92 and 76.34 respectively. What is the solubility of AgCl in water ?

(a) 1.1×10^{-2} g^{-1} (b) 1.9×10^{-3} g L^{-1}

(c) 2.1×10^{-5} g L^{-1} (d) 2.1×10^{-6} g L^{-1}

9. The potential of a hydrogen electrode at pH=10 is

(a) 0.59 V (b) zero volt

(c) –0.59 V (d) 0.059 V

10. Equivalent conductance at infinite dilution, λ° of NH_4Cl, NaOH and NaCl are 128.0, 217.8 and 109.3 ohm^{-1} cm^2 eq^{-1} respectively. The equivalent conductance of 0.01 N NH_4OH is 9.30 ohm^{-1} cm^2 eq^{-1}, then the degree of ionization of NH_4OH at this temperature would be

(a) 0.04 (b) 0.1

(c) 0.39 (d) 0.62

11. What is the standard cell potential E° for an electrochemical cell in which the following reaction takes place spontaneously ?

$Cl_2(g) + 2Br^- \rightarrow Br_2(aq) + 2Cl^- \Delta G° = -50.6$ kJ

(a) 1.2 V (b) 0.53 V

(c) 0.26 V (d) –0.53 V

12. When electric current is passed through acidified water, 112 ml of hydrogen gas at STP collected at the cathode in 965 seconds. The current passed in amperes is

(a) 1.0 (b) 0.5

(c) 0.1 (d) 2.0

13. If the half cell reaction is $A + e^- \rightarrow A^-$ has a large negative reduction potential , it follows that.

(a) A is readily reduced (b) A is ready oxidised

(c) A^- is readily reduced (d) A^- is readily oxidised

14. The electrochemical equivalent of silver is 0.001180 g. When an electric current of 0.5 amp is passed through an aqueous silver nitrate solution for 200 sec., the amount of silver deposited is

(a) 1.1180 g (b) 0.1180 g

(c) 5.590 g (d) 0.5598 g

15. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and M Z^- at 25°C. If the reduction potential of Z > Y > X, then,
(a) Y will oxidize X and not Z
(b) Y will oxidize Z and not X
(c) Y will oxidize both X and Z
(d) Y will reduce both X and Z

16. For the electrochemical cell, $M \mid M^+ \parallel X^- \mid X$,

$E^o M^+ / M = 0.44 V$ and $E^o (X/X^-) = 0.33 V$.
From this data one can deduce that
(a) $M + X \rightarrow M^+ + X^-$ is the spontaneous reaction
(b) $M^+ + X^- \rightarrow M + X$ is the spontaneous reaction
(c) $E_{cell} = 0.77 V$
(d) $E_{cell} = -0.77 V$

17. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below:

$$MnO_4^-(aq.) + 8H^+(aq.) + 5e^- \rightarrow Mn^{2+}(aq.) + 4H_2O(l) \quad E^\circ = 1.51\ V$$

$$Cr_2O_7^{2-}(aq.) + 14H^+(aq.) + 6e^- \rightarrow 2Cr^{3+}(aq.) + 7H_2O(l) \quad E^\circ = 1.38\ V$$

$$Fe^{3+}(aq.) + e^- \rightarrow Fe^{2+}(aq.) \quad E^\circ = 0.77\ V$$

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq.) \quad E^\circ = 1.40\ V$$

Identify the only incorrect statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$
(a) MnO_4^- can be used in aqueous HCl
(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl
(c) MnO_4^- can be used in aqueous H_2SO_4
(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

18. A galvanic cell is constructed as follows. A half-cell consists of a platinum wire immersed in a solution containing 1.0 M of Sn^{2+} and 1.0 M of Sn^{4+}, and another half-cell has a thallium rod immersed in a 1.0 M solution of Tl^+.

Given : $Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq);\ E^\circ = +0.13 V$

and $Tl^+(aq) + e^- \longrightarrow Tl(s);\ E^\circ = -0.34 V$,

what is the cell voltage if the Tl^+ concentration is increased tenfold?
(a) 0.411V (b) 4.101V
(c) 0.492V (d) 0.222V

19. The unit of ionic mobility is
(a) $m^{-2}V^{-1}s^{-1}$ (b) $m^2V^{-1}s^{-1}$
(c) $m^{-2}Vs^{-1}$ (d) $m^2V^{-2}s^{-1}$

20. If ρ is the resistance in ohm of a centimeter cube, generally called the specific resistance of the substance constituting the conductor, the resistance r of the layer containing "a" cubes is given by

(a) $\frac{1}{r} = \frac{1}{\rho} + \frac{1}{\rho} + ...$ (b) $\frac{1}{r} = \frac{1}{\rho a} + \frac{1}{\rho a} + ...$

(c) $r = a / \rho$ (d) $r = \rho + \rho + ...$

21. The mathematical expression for law of independent migration of ions and Ostwald's dilution law are given by

(a) $\Lambda = \Lambda_m^o - BC^{1/2}$ (b) $\Lambda^o = F(U_+ + U_-)$

(c) $\Lambda_m^o = \nu_+\lambda_+ + \nu_-\lambda_-$ (d) $\frac{\Lambda^o}{\Lambda_m} = \frac{1}{\Lambda_m^o} + \frac{\Lambda_m c}{K_a(\Lambda_m^o)^2}$

22. The variation of equivalent conductance of a weak electrolyte with (concentration)$^{1/2}$ is represented as

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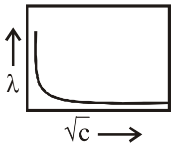

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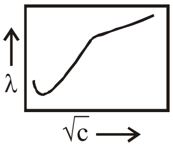

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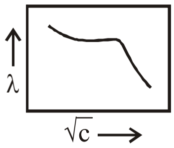

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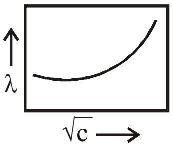
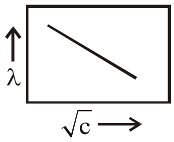


23. The ionic mobility of ions at infinite dilution is related to ionic conductance by
(a) $\Lambda^o = Fk$ (b) $\Lambda^o F = U_+ + U_-$
(c) $\Lambda^o = U_+ + U_-$ (d) $\Lambda^o = F(U_+ + U_-)$

24. The variation of equivalent conductance of strong electrolyte with (concentration)$^{1/2}$ is represented by

(a)


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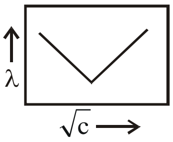

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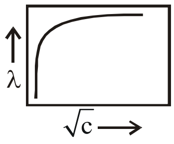
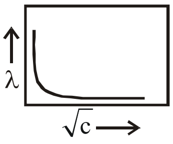
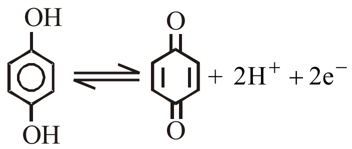


(d)


25. The value of molar conductance of HCl is greater than that of NaCl at a given temperature and concentration because
(a) ionic moblility of HCl is greater than that of NaCl
(b) the dipole moment of NaCl is greater than that of HCl
(c) NaCl is more ionic than HCl
(d) HCl is Bronsted acid and NaCl is a salt of a strong acid and strong base

26. At pH = 2, E^o (quinhydron) = 1.30 V, E(quinhydron) will be



(a) 1.20 V (b) 1.42 V
(c) 1.36 V (d) 1.30 V

27. Consider the following reactions

(i) $Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s),\ E^\circ = -0.40\ V$

(ii) $Ag^+(aq) + e^- \longrightarrow Ag(s),\ E^\circ = 0.80\ V$

For the galvanic cell involving the above reactions. Which of the following is not correct ?

(a) Molar concentration of the cation in the cathodic compartment changes faster than that of the cation in the anodic compartment.

(b) E_{cell} increase when Cd^{2+} solution is diluted.

(c) Twice as many electrons pass through the cadmium electrode as through silver electrode.

(d) E_{cell} decreases when Ag^+ solution is diluted.

28. Conductance of 0.1 M KCl (conductivity = X $Ohm^{-1}cm^{-1}$) filled in a conductivity cell is Y Ohm^{-1}. If the conductance of 0.1 M NaOH filled in the same cell is Z Ohm^{-1}, the molar conductance of NaOH will be

(a) $10^3 \dfrac{XZ}{Y}$ (b) $10^4 \dfrac{XZ}{Y}$

(d) $10 \dfrac{XZ}{Y}$ (d) $0.1 \dfrac{XZ}{Y}$

29. In electrolytic reduction of a nitroarene with 50% current efficiency 20.50 g of the compound is reduced by 2 × 96500 C of electric charge. The molar mass of the compound is

(a) 123.0 g (b) 61.5 g

(c) 10.2 g (d) 20.5 g

30. On electrolysing K_2SO_4 solution using inert electrodes, 1.68 L (STP) of gases was obtained. How many moles of MnO_4^- could be reduced to Mn^{2+} by the same quantity of electricity ?

(a) 0.02 (b) 0.15

(c) 0.20 (d) 0.10

31. The standard reduction potential for Cu^{2+}/Cu is + 0.34. Calculate the reduction potential at pH = 14 for the above couple. (K_{sp} $Cu(OH)_2 = 1 \times 10^{-19}$)

(a) -0.22 V (b) $+0.22$ V

(c) -0.44 V (d) $+0.44$ V

32. A 1.0 M with respect to each of the metal halides AX_3, BX_2, CX_3 and DX_2 is electrolysed using platinum electrodes. If $E^o_{A^{3+}/A} = 1.50$ V, $E^o_{B^2/B} = 0.3$ V, $E^o_{C^{3+}/C} = -0.74$ V, $E^o_{D^2/D} = -2.37$ V. The correct sequence in which the various metals are deposited at the cathode is

(a) A, B, C, D (d) A, B, C

(c) D, C, B, A (b) C, B, A

33. Electrolysis of NaCl solution with inert electrodes for certain period of time gave 600 cm^3 of 1.0 M NaOH in the electrolytic cell. During the same period 31.80 g of copper was deposited in a copper voltmeter in series with the electrolytic cell. What is the percent current efficiency in the electrolytic cell ? (At. wt. of Cu = 63. 6)

(a) 40 (b) 25

(c) 60 (d) 50

34. Absolute ionic mobility is the speed of ion under the electric field of and its dimension

(a) 5 V across a distance of 5 cm, $m^2v^{-1}s^{-1}$

(b) 10 V across a distance of 5 cm, $mv^{-1}s^{-1}$

(c) 5 V across a distance of 10 cm, $m^2v^{-2}s^{-1}$

(d) None of these

35. Given the cell reactions

$MX(s) + e^- \longrightarrow M(s) + X^-$ (aq), $E° = 0.207V$

and $M^+(aq) + e^- \longrightarrow M(s)$, $E° = 0.799$ V

The solubility of MX (s) at 298 K is

(a) 1.10^{-5} mol L^{-1} (b) 1.0×10^{-4} mol L^{-1}

(c) 1.0×10^{-10} mol L^{-1} (d) 1.0×10^{-9} mol L^{-1}

36. Electrolysis is carried out in three cells

(A) 1.0 M $CuSO_4$ Pt electrode

(B) 1.0 M $CuSO_4$ copper electrodes

(C) 1.0 M KCl Pt electrodes

If volume of electrolytic solution is maintained constant in each of the cell, which is correct set of pH changes in (A), (B) and (C) cell respectively ?

(a) decrease in all the three

(b) increase in all the three

(c) decrease, constant, increase

(d) increase, constant, increase

37. The reversible reduction potential of pure water is – 0.414 V under 1 atm H_2 pressure. If the reduction is considered to be $2H^+ + 2e \longrightarrow H_2$. Calculate the $[H^+]$ of pure water

(a) 1.02×10^{-7} (b) 1.02×10^{-9}

(c) 2.01×10^{-7} (d) 2.01×10^{-9}

38. 1. 0 L each of a buffer containing 1 mole NH_3 and 1 mol of NH_4^+ were placed in the cathodic and anodic half-cells and 965 C of electricity was passed. If anodic and cathodic half cells reactions involve oxidation and reduction of water only as

$2H_2O \longrightarrow 4H^+ + O_2 - 4e^-$;

$2H_2O + 2e \longrightarrow H_2 + 2OH^-$

Then pH of

(a) cathodic solution will increase

(b) anodic solution will decrease

(c) both the solutions will remain practically constant

(d) both the solutions will increase

39. The pH of 0.5 L of 1.0 M NaCl after the electrolysis for 965 seconds using 5.0 A current (100% efficiency) is

(a) 1.0 (b) 13.0

(c) 12.7 (d) 1.3

40. The emf of a particular voltaic cell with the cell reaction

$$Hg_2^{2+} + H_2 \rightleftharpoons 2Hg + 2H^+$$

is 0.65 V. The maximum electrical work of this cell when 0.5 g of H_2 is consumed.

(a) -3.12×10^4 J (b) -1.25×10^5 J

(c) 25.0×10^6 J (d) None

41. 48250 C of electricity was required to deposit all the copper present in 0.5 L of $CuSO_4$ solution using inert electrodes. The molarity of solution was (Assume volume constant)

(a) 0.50 M (b) 2.50 M

(c) 0.25 M (d) 1.00 M

42. At 298 K, the conductivity of saturated solution of AgCl in water is 2.6×10^{-6} Scm^{-1}. Its solubility product at 298 K (given λ^∞ (Ag^+) = 63.0 Scm^2 mol^{-1}, λ^∞ (Cl^-) = 67.0 Scm^2 $mol.^{-1}$)

(a) $4.0 \times 10^{-10} M^2$ (b) $4.0 \times 10^{-16} M^2$

(c) $2 \times 10^{-8} M^2$ (d) $2.0 \times 10^{-5} M^2$

43. In acidic medium MnO_2 is an oxidant as

$$MnO_2\ (s) + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$$

If the pH of solution is decreased by one unit, the electrode potential of the half cell Pt : MnO_2, Mn^{2+} will change by

(a) 0.236 V (b) -0.236 V

(c) -0.118 V (d) 0.118 V

44. A lead storage battery containing 5.0 L of (1N) H_2SO_4 solution is operated for 9.65×10^5 s with a steady current of 100 mA. Assuming volume of the solution remaining constant, normality of H_2SO_4 will

(a) remain unchanged (b) increases by 0.20

(c) increase by unity (d) decrease by 0.40

45. The emf of the cell Pt Cl_2 (g) (p_1 atm)/ Cl^- (aq) (1M)/ Cl_2 (g) (p_2 atm) Pt will be positive when

(a) $p_1 = p_2$ (b) $p_1 < p_2$

(c) $p_1 > p_2$ (d) None of these

46. The equilibrium constant for the disproportionation reaction

$$2C\overset{+}{u}\,(aq) \longrightarrow Cu\ (s) + Cu^{2+}(ag)$$

at 25°C ($E^oCu^+/Cu = 0.52V$, $E^oCu^{2+}/Cu = 0.16V$) is

(a) 6×10^4 (d) 6×10^6

(c) 1.2×10^6 (d) 1.2×10^{-6}

47. How long a current of 3 amperes has to be passed through a solution of $AgNO_3$ to coat a metal surface of 80 cm^2 and 0.005 mm thick layer. Density of Ag is 10.5 g cm^{-3}

(a) 125.1 seconds (b) 12.5 seconds

(c) 155.2 seconds (d) 200 seconds

Hints & Solutions

EXERCISE 1

1. Iron ions.
2. No, we cannot use nickel spatula to stir a solution of $CuSO_4$.
7. (*a*) Standard electrode potential = 0.46V
   (*b*) $E_{cell} = 0{\cdot}37\ V$.
8. $2{\cdot}886 \times 10^{-3}$ cm.

17. (a) **18. (d)** **19. (c)** **20. (d)** **21. (c)**
22. (c) **23. (d)** **24. (b)**

EXERCISE 2

1. (c) Electrorefining and electroplating are done by electrolysis.

2. (c) In cell the cathode is of higher reduction potential.

3. (a) Amount of substance deposited

$$= m = \frac{E.\ wt \times Q}{96500};$$

$$107.870 = \frac{107.870}{96500} \times Q;$$

$$\therefore Q = 96500C$$

4. (d) $\frac{W_A}{E_A} = \frac{W_B}{E_B};\ \frac{1.6}{8} = \frac{\text{Wt. of Ag}}{108}$

$\therefore$ Wt. of Ag = 21.6 g

5. (a) $\underset{1F}{Ag^+ + e^-} \longrightarrow \underset{108g}{Ag}$

1 F = 1 mole of electrons = 96500 C
0.01F = 1.08 g Ag; Ag left = 1.08 – 1.08 = 0

6. (c) $m = \frac{E.Wt \times Q}{96500};$

$$\therefore E.wt = \frac{m \times 96500}{Q} = \frac{22.2 \times 96500}{2 \times 5 \times 60 \times 60} = 60.3$$

$$\text{Oxidation state} = \frac{\text{At wt.}}{\text{Eq. wt.}} = \frac{177}{60.3} = 3$$

7. (b) $m = \frac{E \times Q}{96500} = \frac{32.68 \times 5 \times 40 \times 60}{96500} = 4.065\,g$

8. (c) $m = \frac{31.75 \times 1 \times 965}{96500} = 0.3175\,g = \frac{.3175}{63} = 0.005$ moles in one litre. $\therefore$ 0.005 M.

9. (a) $m = \frac{E \times i \times t}{96500};\ 2 = \frac{31.75 \times .5 \times t}{96500},\quad \therefore t = 12157.48$ sec.

10. (b) Apply $m = \frac{E \times i \times t}{96500}$

11. (c) Apply $m = \frac{E \times Q}{96500}$ where Q = coulombs

12. (b) Apply $m = \frac{E \times Q}{96500}$. E. wt of Al $= \frac{27}{3} = 9$.

13. (c) geq of copper to be deposited is $= \frac{127.08}{31.75} = 4$

1F deposits 1 geq, 4F will deposit 4 geq.

14. (d) $\frac{W_A}{E_A} = \frac{W_B}{E_B};\ \frac{27}{108} = \frac{W_{Cu}}{31.8};\quad \therefore W_{Cu} = 7.95g$

15. (c) 0.1 F will liberate 0.1 gev of $Cl_2 = 3.545$ g

16. (d) $Ohm^{-1}\ cm^{-1}$

17. (c) $k = \frac{1}{R} \times \text{Cell constant} = \frac{0.47}{31.6} = 0.01487$

18. (b) Cell constant $= k \times R$

$$= 0.212\ ohm^{-1}\ cm^{-1} \times 55\ ohm$$

$$= 11.66\ cm^{-1}$$

19. (a) $k = \frac{\text{Cell constant}}{R} = \frac{1.15}{250}$

$$\Lambda_{eq} = \frac{1.15}{250} \times \frac{1000}{1} = 4.6$$

20. (c) Kohlrausch Law. Λ_{eq} (NaF)+ Λ_{eq} (HCl)– Λ_{eq} (NaCl) = Λ_{eq} (HF)

21. (b) $Ohm^{-1}\ cm^2\ geq^{-1}$

22. (d) Solubility $= \frac{k \times 1000}{\Lambda_{eq}} = \frac{3.06 \times 10^{-6} \times 1000}{1.53} = 2 \times 10^{-3}$

$$K_{sp} = S^2 = 4 \times 10^{-6}$$

23. (a) Specific conductance = Conductance × Cell constant

$$k = \frac{1}{2.5 \times 10^3} \times 1.15;$$

$$\Lambda_{eq} = \frac{1.15}{2.5 \times 10^3} \times \frac{1000}{0.1} = 4.6$$

24. (a) $\Lambda_m = \frac{k \times 1000}{M} = \frac{1.06 \times 10^{-2} \times 1000}{0.1} = 1.06 \times 10^2$

25. (b) $k = \dfrac{\Lambda_m \times M}{1000} = \dfrac{1.26\times10^{-2}\times0.01}{1000} = 1.26\times10^{-3}$

26. (a) $\Lambda_m^{\infty} = 57+73 = 130\ \text{S cm}^2\text{mol}^{-1}\quad X^{2+}Y^{2-}$

27. (c) Degree of dissociation $= \dfrac{\Lambda_m^c}{\Lambda_m^{\infty}} = \dfrac{\frac{x}{100}}{x} = 0.01$.

28. (b) It is an example of concentration cell, E_{cell} cannot be zero since $[H^+]$ are different (HCl is strong and CH_3COOH weak acid).

29. (d) Reduction occurs at cathode.

30. (c) Consult ECS. Reduction potential of Cu is more than H_2.

31. (d) $\frac{4}{3}Al + O_2 \longrightarrow \frac{2}{3}Al_2O_3;\qquad \Delta G = -827\ \text{kJ mol}^{-1}$

Number of electrons involved is 4 $\left(\frac{2}{3}\times 6 = 4\right)$

$$\Delta G^o = -nFE^o \qquad \text{or} \qquad \frac{827000}{4\times96500} = E^o$$

$$\therefore E^o = 2.14V$$

32. (c) Nernst equation $E_{cell} = E^o_{cell} - \dfrac{RT}{nF}\dfrac{\ln[Fe^{2+}]^2}{[Fe^{3+}]^2}\left[Zn^{2+}\right]$

increasing $[Fe^{2+}]$ will decrease the E_{cell}.

33. (d) Emf will decrease.

34. (a) Salt bridge allows the flow of current by completing circuit. No current will flow and voltage will drop to zero, if salt bridge is removed.

35. (c)

36. (d) Calomel electrode is used as reference electrode.

37. (d) Though it is not zero but has been fixed as zero.

38. (b) $E^o_{cell} = E^o_{red}(Zn) + E^o_{oxi}(Fe) = 0.76 - 0.41 = 0.35V$

39. (a) $OCl^- \longrightarrow Cl^-;\ E^\circ = 0.94\ V\ (I)$

$$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-;\ E^\circ = 1.36\ V\ (II)$$

Add (I)+(II) $OCl^- \longrightarrow \frac{1}{2}Cl_2;\ E^\circ = 0.94 - 1.36 = -0.42\ V$

40. (d) $E^o_{cell} = E^o_{Red}(Fe) + E^o_{oxi}(Sn) = -0.44 + 0.14 = -0.30V$

41. (b) $E^o_{cell} = E^o_{Red}(Au) + E^o_{oxi}(Ni) = 1.5 + 0.25 = 1.75V$

42. (c) Oxidation potential of M is more than Ni and less than Mn. Hence reducing power Mn > M > Ni

43. (a) The greater the oxidation potential greater is reactivity A > D > B > C.

44. (a) Chlorine is less reactive than fluorine.

45. (b) Follow ECS, more the reduction potential, the stronger the oxidising power and vice versa.

46. (b) Follow ECS, A will replace B.

47. (a)

Fe	Al	Br
0.77	–1.66	1.08 E°_{Red}
–0.77	1.66	–1.08 E°_{Oxi}

Hence Reducing power Al > Fe > Br

48. (c) On the basis of ECS strongly electropositive metals can displace less electropositive metals from their salt solutions.

49. (c) I has the highest oxidation potential hence most reducing.

50. (a) Since oxidation potential of Zn is highest hence strongest reducing agent.

51. (d) The reduction potential of NO_3^- ion is more than H^+ ion. (see ECS).

52. (c) Gold having higher E^o_{Red} and oxidises $Fe \longrightarrow Fe^{++}$.

53. (d) Cell reaction $Zn + Cu^{++} \longrightarrow Zn^{++} + Cu$

$$E_1 = E^o_{cell} - \frac{0.059}{2}\log\frac{0.01}{1.0}$$

$$\therefore E_1 = (E^o_{cell} + 0.059)\ V$$

$$E_2 = E^o_{cell} - \frac{0.059}{2}\log\frac{1.0}{0.01}$$

$$\therefore E_2 = (E^o_{cell} - 0.059)\ V \qquad E_1 > E_2.$$

54. (c) Copper is below in ECS hence cannot displace hydrogen from HCl.

$HCl \rightleftharpoons H^+ + Cl^-$

$2H^+ + 2e^- \rightarrow H_2$

$Cu \rightarrow Cu^{++} + 2e^-$

not possible. Hence evolution of H_2 is not possible.

55. (b) I_2 is less reactive than Br_2.

56. (d) Oxidation potential of Co is more than Ag, hence cell reaction will be

$$Co + 2Ag^+ \longrightarrow Co^{2+} + 2Ag$$

$E_{cell} = E^o_{cell} - \dfrac{RT\ln}{nF}\dfrac{[Co^{2+}]}{[Ag^+]^2}$, the lesser the value of the factor $\dfrac{[Co^{2+}]}{[Ag^+]^2}$ greater will be value of E_{cell}. .

57. (b) $E_{cell} = E^o_{cell} - \dfrac{RT}{nF}\ln\dfrac{[C]^c[D]^d}{[A]^a[B]^b}$.

Hence $E^o_{cell} = E_{cell} + \dfrac{RT}{nF}\ln\dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

58. (a) Since concentration of ions is the same hence $E_{cell} = E^o_{cell}$.

59. (a) The Half cell reaction is $Zn^{++} + 2e^- \longrightarrow Zn$.

$$E_{cell} = E^o_{cell} - \frac{0.059}{2}\log\frac{1}{[Zn^{++}]}$$

$$= -0.763 - \frac{0.059}{2}\log\frac{1}{0.01} = -0.822V$$

$$E_{oxi} = 0.822\ V$$

60. (d) $2H^+ + 2e^- \longrightarrow H_2$

$$E_{Red} = E^o_{Red} - \frac{0.059}{n}\log\frac{1}{[H^+]^2};$$

$$E_{Red} = 0 - \frac{0.059}{2}\log\frac{1}{(0.1)^2};\ E_{Red} = -0.059\,V,$$

$E_{oxi} = 0.059$ V.

61. (b) $E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln\frac{C_2}{C_1}$ and $\Delta G = -nFE°_{cell}$

Hence ΔG is a function of $\ln\frac{C_2}{C_1}$.

62. (b) At equilibrium $E_{cell} = 0$. $E^o_{cell} = \frac{0.059}{n}\log K_C$

63. (b) $E^o_{cell} = \frac{0.059}{2}\log K_C$ or $\frac{1.10 \times 2}{0.059} = \log K_C$

$\therefore K_C = 1.9 \times 10^{37}$

64. (a) $\Delta G = -nF\,E°_{cell} = -2 \times 96500 \times 1.1\ J = 212.3$ kJ.

65. (a) ∵ Change in free energy = maximum electrical work done

66. (b) Water is weak electrolyte and remains almost unionised.

67. (b)

	Cathode	Anode
Aqs. soln. of Na_2SO_4	$2Na^+$	SO_4^{--}
Ionisation of $H_2O \rightarrow$	H^+	OH^-

$E°_{Red}$ of H is more hence $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

68. (b) Cl^- is oxidised to Cl_2 at anode.

69. (b) **70. (d)** **71. (b)** **72. (c)**

73. (b) $H_2 - O_2$ fuel cell supply power for pressure.

74. (b) H_2SO_4 regenerated follow text.

75. (c) Thermodynamic efficiency is given by $\frac{-nFE}{\Delta H}$

76. (c)

77. (a) Galvanization

78. (b) Specific conductance decreases with dilution (follow text).

79. (d) In electrolytic cell the flow of electrons is from anode to cathode through internal supply.

EXERCISE 3

1. (d) Zinc gives H_2 gas with dil H_2SO_4/HCl but not with HNO_3 because in HNO_3, NO_3^- ion is reduced and give NH_4NO_3, N_2O, NO and NO_2 (based upon the concentration of HNO_3)

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Zn is on the top position of hydrogen in electrochemical series. So Zn displaces H_2 from dilute H_2SO_4 and HCl with liberation of H_2.

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

2. (b) Efficiency of a fuel cell $(\eta) = \frac{\Delta G}{\Delta H}$

3. (c) As $E^o_{cell} = \frac{0.0591}{n}\log K_c$

$\therefore 0.46 = \frac{0.0591}{2}\log K_c$

$\therefore \log K_c = \frac{2 \times 0.46}{0.0591} = 15.57$

or K_c = Antilog $15.57 = 3.7 \times 10^{15} \approx 4 \times 10^{15}$

4. (c) From the given data we find Fe^{3+} is strongest oxidising agent. More the positive value of E°, more is the tendency to get oxidized. Thus correct option is (c).

5. (d) Kohlrausch's Law states that at infinite dilution, each ion migrates independent of its co-ion and contributes to the total equivalent conductance of an electrolyte a definite share which depends only on its own nature. From this definition we can see that option (d) is the correct answer.

6. (c) Writing the equation for pentane-oxygen fuel cell at respective electrodes and overall reaction, we get

At Anode:

$$\underset{\text{(pentane)}}{C_5H_{12}} + 10H_2O \rightarrow 5CO_2 + 32H^+ + 32e^-$$

At Cathode:

$$\frac{8O_2 + 32H^+ + 32e^- \rightarrow 16H_2O}{\text{Overall}: C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O}$$

Calculation of $\Delta G°$ for the above reaction

$\Delta G° = [5\times(-394.4) + 6\times(-237.2)]$
$- [-8.2]$
$= -1972.0 - 1423.2 + 8.2 = -3387.0$ kJ
$= -3387000$ Joules.

From the equation we find n = 32

Using the relation, $\Delta G° = -\ nFE^o_{cell}$ and substituting various values, we get

$-3387000 = -32 \times 96500 \times E^o_{cell}$ (F = 96500C)

or $E^o_{cell} = \frac{3387000}{32 \times 96500}$

$= \frac{3387000}{3088000}$ or $\frac{3387}{3088}$ V = 1.0968 V

Thus option (c) is correct answer.

7. (d) $Cu^{2+} + 2e^- \rightarrow Cu;\ \Delta G^o = -nE^oF$
$= -2 \times F \times 0.337$
$= -0.674F$ ....(i)

$Cu^+ \rightarrow Cu^{2+} + e^-;\ \Delta G^o = -nE^oF$
$= -1 \times F \times -0.153$
$= 0.153F$ ....(ii)

On adding eqn (i) & (ii)

$Cu^+ + e^- \rightarrow Cu$;

$\Delta G^o = -0.521\,F = -nE^oF$;

Here n = 1 $\quad\therefore E^o = +0.52$ V

8. **(a)** $\because Q = i \times t$

$\therefore Q = 4.0 \times 10^4 \times 6 \times 60 \times 60\ C$

$= 8.64 \times 10^8\ C$

$$\underset{}{Al^{3+}} + \underset{3 \times 96500 C}{3e^-} \longrightarrow \underset{27 g}{Al}$$

[3 × 96500 C liberates = 27 g of Al]

$\therefore$ 96500 C liberates 9 g of Al

8.64×10^8 C liberates $= \dfrac{9}{96500} \times 8.64 \times 10^8$ g Al

$= 8.1 \times 10^4$ g of Al

9. **(d)** Degree of dissociation

$$\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{8.0}{400} = 2 \times 10^{-2}$$

$$K_a = \frac{c\alpha^2}{(1-\alpha)} \approx c\alpha^2 = \frac{1}{32} \times \left(2 \times 10^{-2}\right)^2$$

$$= 1.25 \times 10^{-5}$$

10. **(a)** $Cu + 2\,Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)$

Here, $n = 2$, $\quad E^\circ_{cell} = +0.46\ V$

$\Delta G^\circ = -nE^\circ F$

$= \dfrac{-2 \times 0.46 \times 96500}{1000}\ kJ \simeq -89\ kJ$

11. **(a)** Dilution of strong electrolytes increases ionisation, hence ionic mobility of ions which in turn increases equivalent conductance of the solution.

12. **(c)** Conductivity of an electrolyte depends on the mobility of ions and concentration of ions. The motion of an ionic species in an electric field is retarded by the oppositely charged ions due to their interionic attraction. On dilution, concentration of electrolyte decreases and the retarding influence of oppositely charged ions decreases. Therefore mobility of ions increases.

13. **(a)** Option (ii) and (iv) are correct

14. **(c)** As the value of standard reduction potential decreases the reducing power increases i.e.,

$$\underset{(-3.0)}{Z} > \underset{(-1.2)}{X} > \underset{(+0.5)}{Y}$$

15. **(b)** $Cu^{2+} + 1e^- \rightarrow Cu^+ \quad E_1^o = 0.15V; \Delta G_1^o = -n_1 E_1^o F$

$Cu^+ + 1e^- \rightarrow Cu \quad E_2^o = 0.50V; \Delta G_2^o = -n_2 E_2^o F$

$Cu^{2+} + 2e^- \rightarrow Cu \quad \Delta G^\circ = \Delta G^\circ_1 + \Delta G^\circ_2$

$-nE^\circ F = -1\ n_1\ E_1^\circ\ F + (-1)\ n_2\ E_2^o F$

$-nE^\circ F = -1\ (n_1\ E_1^\circ\ F + n_2\ E_2^o F)$

$$E^\circ = \frac{n_1 E_1^o + n_2 E_2^o}{n} = \frac{0.15 \times 1 + 0.50 \times 1}{2}$$

$E^\circ = 0.325\ V$

16. **(b)** Given $E_{Sn^{+4}/Sn^{+2}} = +0.15\ V$

$E_{Cr^{+3}/Cr} = -0.74\ V$

$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$

$= 0.74 + 0.15$

$= 0.89\ V$

17. **(d)** Standard Gibbs free energy is given as $\Delta G^\circ = -nE^\circ F$

If $E^\circ_{cell} < 0$ i.e., – ve

$\Delta G^\circ > 0$

Further $\Delta G^\circ = -RT \ln K_{eq}$

$\therefore \Delta G^\circ > 0$ and $K_{eq} < 0$

18. **(c)** Given $Fe^{+3}/Fe^{2+} = +0.77\ V$

and $\quad I_2/2I^- = 0.536V$

$2\,(e^- + Fe^{+3} \longrightarrow Fe^{+2}) \qquad E^\circ = 0.77\ V$

$2I^- \longrightarrow I_2 + 2e^- \qquad E^\circ = -0.536\ V$

$2Fe^{+3} + 2I^- \longrightarrow 2Fe^{+2} + I_2$

$E^\circ = E^\circ_{ox} + E^\circ_{red}$

$= 0.77 - 0.536$

$= 0.164\ V$

$\therefore$ Since value of E° is + ve reaction will take place.

19. **(d)** $\overset{o}{\Lambda}_{m(NH_4Cl)} = \overset{o}{\Lambda}_{m_{NH_4^+}} + \overset{o}{\Lambda}_{m_{Cl^-}}$

$\overset{o}{\Lambda}_{m(NaOH)} = \overset{o}{\Lambda}_{m_{Na^+}} + \overset{o}{\Lambda}_{m_{OH^-}}$

$\overset{o}{\Lambda}_{m(NaCl)} = \overset{o}{\Lambda}_{m_{Na^+}} + \overset{o}{\Lambda}_{m_{Cl^-}}$

$\therefore \quad \overset{o}{\Lambda}_{m}\left(NH_4^+\right) + \overset{o}{\Lambda}_{m}\left(OH^-\right)$

$= \overset{o}{\Lambda}_{m}\left(NH_4^+\right) + \overset{o}{\Lambda}_{m}\left(Cl^-\right) + \overset{o}{\Lambda}_{m}\left(Na^+\right)$

$+ \overset{o}{\Lambda}_{m}\left(OH^-\right) - \left[\overset{o}{\Lambda}_{m}\left(Na^+\right) + \overset{o}{\Lambda}_{m}\left(Cl^-\right)\right]$

$\overset{o}{\Lambda}_{m(NH_4OH)} = \overset{o}{\Lambda}_{m(NH_4Cl)} + \overset{o}{\Lambda}_{m(NaOH)} - \overset{o}{\Lambda}_{m(NaCl)}$

20. **(a)** Higher the value of reduction potential higher will be the oxidising power whereas the lower the value of reduction potential higher will be the reducing power.

21. **(d)** $\overset{o}{\Lambda}_{CH_3COOH} = \overset{o}{\Lambda}_{CH_3COONa} + \overset{o}{\Lambda}_{HCl} - \overset{o}{\Lambda}_{NaCl}$

$= 91 + 425.9 - 126.4 = 390.5\ S\ cm^2 mol^{-1}$

22. **(a)** $\underset{1\ atm}{H_2} \longrightarrow \underset{10^{-10}}{2H^+} + 2e^-$

$$E_{H_2/H^+} = 0 - \frac{0.059}{2} \log \frac{\left(10^{-10}\right)^2}{1}$$

$E_{H_2/H^+} = +0.59\ V$

23. (b) $\alpha = \dfrac{\Lambda_M}{\Lambda_M^{\infty}} = \dfrac{9.54}{238} = 0.04008 = 4.008\,\%.$

24. (d) $E^\circ_{Cell} = E^\circ_{OP} + E^\circ_{RP}$
$= 0.76 + 0.314 = 1.10\,V$

25. (b) $S = \dfrac{K\,m^2 mol}{m \times m^3} \quad \therefore K = Sm^2 mol^{-1}$

26. (c) E_{cell} = Reduction potential of cathode (right) - reduction potential of anode (left)
$= E_{right} - E_{left}$.

27. (a) $E_{cell} = E_{right\ (cathode)} - E_{left\ (anode)}$.

28. (d) If $p_1 > p_2$ then $E_{cell} = \dfrac{2.303}{nF} RT \log \dfrac{p_1}{p_2}$

29. (a) $2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+$
O.S. of Cr changes from + 3 to + 6 by loss of electrons. At anode oxidation takes place.

30. (c) The equilibrium constant is related to the standard emf of cell by the expression

$$\log K = E^\circ_{cell} \times \frac{n}{0.059} = 0.295 \times \frac{2}{0.059}$$

$$\log K = \frac{590}{59} = 10 \text{ or } K = 1 \times 10^{10}$$

31. (d)

A	B	C
+0.5C	–3.0V	–1.2V

The higher the negative value of reduction potential, the more is the reducing power. Hence B > C > A.

32. (a) No. of moles of silver $= \dfrac{9650}{96500} = \dfrac{1}{10}$ moles

$\therefore$ Mass of silver deposited $= \dfrac{1}{10} \times 108 = 10.8$ g

33. (b) $E_{cell} = E^\circ_{cell} + \dfrac{0.059}{n} \log \dfrac{[Cu^{+2}]}{[Zn^{+2}]}$

$$= 1.10 + \frac{0.059}{2} \log[0.1] = 1.10 - 0.0295 = 1.07\,V$$

34. (b) Magnesium provides cathodic protection and prevent rusting or corrosion.

35. (b) In $H_2 - O_2$ fuel cell, the combustion of H_2 occurs to create potential difference between the two electrodes

36. (a) $Fe^{3+} + \bar{e} \rightarrow Fe^{2+}, \ \Delta G^\circ = -1 \times F \times 0.77$

$Sn^{2+} + 2\bar{e} \rightarrow Sn(s), \ \Delta G^\circ = -2 \times F(-0.14)$
for

$Sn(s) + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq) + Sn^{2+}(aq)$

$\Delta G = -(-2F \times (-0.14) + 2(-1 \times F \times 0.77) = -1.82F$

$\therefore$ Standard potential for the given reaction

$$= \frac{-1.82F}{-2 \times F} = 0.91V$$

37. (a) $E_{cell} = \dfrac{0.059}{n} \log K_c$

$0.591 = 0.059 \log K_c$ or $10 = \log K_c \therefore K_c = 1 \times 10^{10}$

38. (c) $\Lambda^o NaCl = \lambda^o\left(Na^+\right) + \lambda Cl^-$ ....(i)

$\Lambda^o KBr = \lambda^o\left(K^+\right) + \lambda^o\left(Br^-\right)$ ....(ii)

$\Lambda^o KCl = \lambda^o\left(K^+\right) + \lambda\left(Cl^-\right)$ ....(iii)

(i) + (ii) - (iii)

$\Lambda^o NaBr = \lambda^o\left(Na^+\right) + \lambda^o\left(Br^-\right)$

$= 126 + 152 - 150 = 128 \ S\ cm^2\ mol^{-1}$

39. (c) The given values show that Cr has maximum oxidation potential, therefore its oxidation will be easiest. (Change the sign to get the oxidation values)

40. (a) Thus difluoro acetic acid being strongest acid will furnish maximum number of ions showing highest electrical conductivity. The decreasing acidic strength of the carboxylic acides given is difluoro acetic acid > fluoro acetic acid > chloro acetic acid > acetic acid.

41. (d) 1 mole of e^- = 1F = 96500 C
27g of Al is deposited by 3 × 96500 C
5120 g of Al will be deposited by

$$= \frac{3 \times 96500 \times 5120}{27} = 5.49 \times 10^7 C$$

42. (b) $\Lambda^{\infty}_{HCl} = 426.2$ (i)

$\Lambda^{\infty}_{AcONa} = 91.0$ (ii)

$\Lambda^{\infty}_{NaCl} = 126.5$ (iii)

$$\Lambda^{\infty}_{AcOH} = (i) + (ii) - (iii) = [426.2 + 91.0 - 126.5] = 390.7$$

43. (b) $\Lambda^o_{CH_3COOH}$ is given by the following equation

$$\Lambda^o_{CH_3COOH} = \left(\Lambda^o_{CH_3COONa} + \Lambda^o_{HCl}\right) - \left(\Lambda^o_{NaCl}\right)$$

Hence Λ^o_{NaCl} is required.

44. (a) Conductivity (kappa) $= \dfrac{l}{R.a.}$

cell constant. $\left(\dfrac{l}{a}\right) = \kappa \times R = 1.29 \times 100 = 129$

Again conductivity of 0.02M solution $\kappa = \dfrac{1}{520} \times 129$

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{129}{520} \times \frac{1000}{0.02} = 1.24 \times 10^{-4} S m^{-2} mol^{-1}$$

45. (b) According to Kohlrausch's law, molar conductivity of weak electrolyte acetic acid (CH_3COOH) can be calculated as follows:

$$\Lambda^{\circ}_{CH_3COOH} = \left(\Lambda^{\circ}_{CH_3COONa} + \Lambda^{\circ}_{HCl}\right) - \Lambda^{\circ}_{NaCl}$$

$\therefore$ Value of Λ°_{NaCl} should also be known for calculating value of $\Lambda^{\circ}_{CH_3COOH}$.

46. (d) $E_{cell} = 0$; when cell is completely discharged.

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{2}\log\left(\frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}\right)$$

$$\text{or } 0 = 1.1 - \frac{0.059}{2}\log\left(\frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}\right)$$

$$\log\left(\frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}\right) = \frac{2\times1.1}{0.059} = 37.3$$

$$\therefore \frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]} = 10^{37.3}$$

47. (d) From the given representation of the cell, E_{cell} can be found as follows.

$$E_{cell} = \left(E^{o}_{Fe^{2+}/Fe} - E^{o}_{Cr^{3+}/Cr}\right) - \frac{0.059}{6}\log\frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

[Nernst-Equ.]

$$= -0.42 - (-0.72) - \frac{0.059}{6}\log\frac{(0.1)^2}{(0.01)^3}$$

$$= -0.42 + 0.72 - \frac{0.059}{6}\log\frac{0.1\times0.1}{0.01\times0.01\times0.01}$$

$$= 0.3 - \frac{0.059}{6}\log\frac{10^{-2}}{10^{-6}} = 0.3 - \frac{0.059}{6}\times4$$

$= 0.30 - 0.0393 = 0.26\text{ V}$

Hence option (d) is correct answer.

48. (c) $CH_3OH\,(l) + \frac{3}{2}O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$

$$\Delta G_r = [\Delta G_f(CO_2, g) + 2\Delta G_f(H_2O, \ell)] - \left[\Delta G_f(CH_3OH, \ell) + \frac{3}{2}\Delta G_f(O_2, g)\right]$$

$= -394.4 + 2(-237.2) - (-166.2) - 0$

$= -394.4 - 474.4 + 166.2 = -702.6\text{ kJ}$

$$\%\text{ efficiency} = \frac{702.6}{726}\times100 = 97\%$$

49. (b) Given

$Fe^{3+} + 3e^- \rightarrow Fe$,

$E^{\circ}_{Fe^{3+}/Fe} = -0.036\text{ V}$ ...(i)

$Fe^{2+} + 2e^- \rightarrow Fe$,

$E^{\circ}_{Fe^{2+}/Fe} = -0.439\text{V}$ ...(ii)

we have to calculate

$Fe^{3+} + e^- \rightarrow Fe^{2+}$, $\Delta G = ?$

To obtain this equation subtract equ (ii) from (i) we get

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ ...(iii)

As we know that $\Delta G = -nFE$

Thus for reaction (iii)

$\Delta G = \Delta G_1 - \Delta G_2$

$-nFE^{\circ} = -nFE_1 - (-nFE_2)$

$-nFE^{\circ} = nFE_2 - nFE_1$

$-1FE^{\circ} = 2\times(-0.439) - 3\times(-0.036)$

$-1\,FE^{\circ} = -0.770\text{ F}$

$\therefore E^{\circ} = +0.770\text{V}$

50. (c) $\Delta G = -nFE$

For 1 mol of Al, n = 3

For $\frac{4}{3}$ mol of Al, $n = \frac{4}{3}\times3 = 4$

$$\text{or } E = \frac{\Delta G}{-nF} = \frac{966\times10^3}{-4\times96500} = -2.5\text{ V}$$

$\therefore$ The potential difference needed for the reduction = 2.5 V.

51. (a) The value of $E^{\circ}_{M^{2+}/M}$ for given metal ions are

$E^{\circ}_{Mn^{2+}/Mn} = -1.18\text{ V}$,

$E^{\circ}_{Cr^{2+}/Cr} = -0.9\text{ V}$,

$E^{\circ}_{Fe^{2+}/Fe} = -0.44\text{ V}$ and

$E^{\circ}_{Co^{2+}/Co} = -0.28\text{ V}$.

The correct order of $E^{\circ}_{M^{2+}/M}$ values without considering negative sign would be

$Mn^{2+} > Cr^{2+} > Fe^{2+} > Co^{2+}$.

52. (c) $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

$$E = E^{\circ} - \frac{0.059}{1}\log\frac{[P(H_2)]^{1/2}}{[H^+]}$$

Now if $p_{H_2} = 2$ atm and $[H^+] = 1M$

$$\text{then } E = 0 - \frac{0.059}{1}\log\frac{2^{1/2}}{1} = \frac{-0.059}{2}\log 2$$

53. **(d)** Here $n = 4$, and $[H^+] = 10^{-3}$ (as pH = 3)

Applying Nernst equation

$$E = E^\circ - \frac{0.059}{n}\log\frac{[Fe^{2+}]^2}{[H^+]^4(p_{O_2})}$$

$$= 1.67 - \frac{0.059}{4}\log\frac{(10^{-3})^2}{(10^{-3})^4 \times 0.1}$$

$$= 1.67 - \frac{0.059}{4}\log 10^7 = 1.67 - 0.103 = 1.567$$

54. **(a)** $\kappa = \frac{1}{R} \times \frac{\ell}{A}$

$$1.3 = \frac{1}{50} \times \frac{\ell}{A}$$

$$\frac{\ell}{A} = 65\,m^{-1}$$

$$\Lambda = \frac{\kappa \times 1000}{\text{molarity}}$$

[molarity is in moles/litre but 1000 is used to convert liter into cm^3]

$$= \frac{\left(\frac{1}{260} \times 65\ m^{-1}\right) \times 1000\ cm^3}{0.4\ \text{moles}}$$

$$= \frac{650\ m^{-1}}{260 \times 4\ \text{mol}} \times \frac{1}{1000}\ m^3$$

$= 6.25 \times 10^{-4}\ S\,m^2\,mol^{-1}$

55. **(d)** For a spontaneous reaction ΔG must be –ve

Since $\Delta G = -nFE^\circ$

Hence for ΔG to be -ve ΔE° has to be positive. Which is possible when X = Zn, Y = Ni

$$Zn + Ni^{++} \longrightarrow Zn^{++} + Ni$$

$$E^\circ_{Zn/Zn^{+2}} + E^\circ_{Ni^{2+}/Ni} = 0.76 + (-0.23)$$

$$= +0.53 \text{ (positive)}$$

56. **(d)** Higher the value of standard reduction potential, stronger is the oxidising agent, hence MnO_4^- is the strongest oxidising agent.

57. **(d)** $E^\circ_{Cr^{3+}/Cr^{2+}} = -0.41\ V$

$E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77\ V$

$E^\circ_{Mn^{3+}/Mn^{2+}} = +1.57\ V,$

$E^\circ_{Co^{3+}/Co^{2+}} = +1.97\ V$

58. **(b)** $H_2O \rightleftharpoons H^+ + OH^-$

$$H^+ + e^- \longrightarrow \frac{1}{2}H_2$$

$\therefore$ 0.5 mole of H_2 is liberated by 1 F = 96500 C

0.01 mole of H_2 will be liberated by

$$= \frac{96500}{0.5} \times 0.01 = 1930\,C$$

$$Q = I \times t$$

$$t = \frac{Q}{I} = \frac{1930\ C}{10 \times 10^{-3}\ A} = 19.3 \times 10^4\ \text{sec}$$

59. **(d)** $AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$

Conductivity of the solution is almost compensated due to formation of $KNO_3(aq)$. However, after end point, conductivity increases more rapidly due to addition of excess $AgNO_3$ solution.

EXERCISE 4

1. **(a)** The specific conductance increases with concentration. The number of ions per cm^{-3} increase with increase of concentration.

2. **(a)** The equivalent conductance increase with dilution, since interionic attractions decrease with dilution

3. **(c)** The correct-relation is $\Delta G^\circ = -nFE^\circ$

4. **(d)** The amount. of copper deposited at cathode by reduction of Cu^{2+} ions is $\frac{3.2}{63} = 0.05$ moles. The same amount 0.05 mole of Cu^{2+} must pass into solution from anode by oxidation

5. **(c)** $Cu(CN)_2$ in basic medium forms a complex which maintains the constant supply of Cu^{2++} ions

6. **(b)** The oxidation potential $\propto \frac{1}{\text{Concentration of ions}}$ and reduction potential $\propto$ concentration of ions. The cell voltage can be increased by decreasing the concentration of ions around anode or by increasing the concentration of ions around cathode

7. **(c)** Electrodialysis of aqueous solution of

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

Around anode we have SO_4^{--} and H_2O. The oxidation Potential of $H_2O(1.23V)$ is lower than oxidation potential of $SO_4^{--}(2.0V)$

$$\therefore 2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

8. **(b)** $\Lambda^\infty_m(AgCl) = \lambda^\infty(Ag^+) + \lambda^\infty(Cl^-) = 61.92 + 76.34 = 138.26$

$$\Lambda_m = \frac{k \times 1000}{M} \therefore M = \frac{1.826 \times 10^{-6} \times 1000}{138.26} = 1.32 \times 10^{-5} M$$

Hence solubility $= 1.32 \times 10^{-5} \times 143.5\,g/l$

$= 1.9 \times 10^{-3}\,g/l$

9. **(a)** The equation is $H^+ + e^- \rightleftharpoons 1/2H_2$;

$$E = E^\circ - \frac{0.159}{1}\log\frac{1}{[H^+]}$$

Since

$$pH = 10, [H^+] = 10^{-10}; E = 0 - \frac{0.059}{1}\log\frac{1}{10^{-10}}; E = 0.59$$

10. (a) $\Lambda_{eq}^{\infty}(NH_4OH)=\Lambda_{eq}^{\infty}(NH_4Cl)+\Lambda_{eq}^{\infty}(NaOH)-\Lambda_{eq}^{\infty}(NaCl)$

$=129.8+217.8-109.3=238.3\ ohm^{-1}cm^2eq^{-1}$

$\alpha=\dfrac{\Lambda_{eq}}{\Lambda_{aq}^{\infty}}=\dfrac{9.30}{238.3}=0.04\ \text{or}\ 4\%$

11. (c) $\Delta G^{\circ}=-nFE^{\circ}; E^{\circ}=\dfrac{-\Delta G^{\circ}}{nF};$

$E^{\circ}=\dfrac{-(-50.61kJ)}{2\times96500\times10^{-3}}=0.26V$

12. (a) 112 ml of H_2 at STP $=\dfrac{2\times112g}{22400}$ (Since 22400 ml at STP= M.wt)

Amount deposiled $=\dfrac{Eq.wt\times i\times t}{96500}$

$\therefore\ \dfrac{2\times112}{22400}=\dfrac{1\times965\times i}{96500};$

$i=1$ amp

13. (a) $A+e^{-}\rightarrow A^{-}$ has large negative potential . It means A^{-} is readily oxidised the reaction proceeds towards left hand side

14. (b) The electrochemical equivalent is the amount deposited by one coulomb of electricity

coulomb of electricity $=0.5\times200=100^{\circ}C$

$\therefore$ Amount deposited $=0.001180\times100=0.1180g$

15. (a) The given order of reduction potentials (or tendencies) is Z > Y > X. A spontaneous reaction will have the following characteristics

Z reduced and Y oxidised

Z reduced and X oxidised

Y reduced and X oxidised

Hence, Y will oxidise X and not Z.

16. (b) For, $M^{+}+X^{-}\longrightarrow M+X$, $E_{cell}^{o}=0.44-0.33=0.11V$ is positive, hence reaction is spontaneous.

17. (a) MnO_4^{-} will oxidise Cl^{-} ion according to the equation

$2MnO_4^{-}+16H^{+}+10Cl^{-}\longrightarrow 2Mn^{2+}+8H_2O+5Cl_2\uparrow$

The cell corresponding to this reaction is as follows:

Pt, $Cl_2(1\,atm)|\,Cl^{-}\,||\,MnO_4^{-},Mn^{2+},H^{+}\,|$ Pt

$E_{cell}^{o}=1.51-1.40=0.11\,V$

E_{cell}^{o} being +ve, ΔG° will be -ve and hence the above reaction is feasible. MnO_4^{-} will not only oxidise Fe^{2+} ion but also Cl^{-} ion simultaneously.

18. (a) The reaction is $2Tl(s)+Sn^{4+}\rightarrow 2Tl^{+}+Sn^{2+}$

The cell is $Tl(s)\,|\,Tl^{+}(1.0M)\,||\,Sn^{4+}(1.0M)\,|\,Sn^{2+}(1.0M)$ 1Pt

-0.34 V $\qquad +0.13$V

$E=0.13-(-0.34)-\dfrac{0.0592}{2}\log\dfrac{[Tl^{+}]^2[Sn^{2+}]}{[Sn^{4+}]}$

$=0.47\,V-0.0296\log(10)^2$ [Tl^{+} conc. increases tenfold)

$=0.47-0.0592=0.411V$

19. (b) Unit of ionic mobility is $cm^2\,s^{-1}\,volt^{-1}$

20. (b) Reciprocal of resistance is conductance. We can add the conductance and not resistance. Hence $\dfrac{1}{r}=\dfrac{1}{\rho}+\dfrac{1}{\rho}+.........$

21. (c) At infinite dilution each ion makes a definite contribution towards molar conductance which is given by

$\Lambda_m^{o}=V_{+}\lambda_{+}+V_{-}\lambda_{-}$

22. (a) The equivalent conductance of weak electrolytes increase with dilution ($\sqrt{c}$).

23. (d) The relation between ionic mobility and ionic conductance is $U^{o}=\dfrac{\lambda^{o}}{F}$

Where U^{o} is ionic mobility and λ^{o} ionic conductance

$\therefore\ \Lambda^{o}=F(U_{+}+U_{-})$

24. (a) In case of equivalent conductance of strong electrolyte there is little increase with dilution.

25. (a) The greater the ionic mobility, the greater the molar conductance. The ionic mobility of HCl is greater than that of NaCl.

26. (b) $\Delta E=E^{\circ}-\dfrac{0.059}{2}\log[H^{+}]^2$

$=1.30-\dfrac{0.059}{2}\log(10^{-2})^2$

$=1.418\,V$

27. (c) $Cd(s)+2\,Ag^{+}(aq)\longrightarrow Cd^{2+}(aq)+Ag\,(s),$

$E_{cell}=E_{cell}^{o}-\dfrac{0.059}{2}\log\dfrac{[Cd^{2+}]}{[Ag^{+}]^2}$

28. (b) Conductivity (X) = conductance (c) × cell constant

$\therefore$ Cell constant $=\dfrac{X}{Y}$

Conductivity of NaOH $=\dfrac{X}{Y}.Z$

$\Delta m(NaOH)=\dfrac{X}{Y}.Z\times\dfrac{1000}{0.1}=\dfrac{XZ}{Y}10^4$

29. (a) $ArNO_2+6H^{+}+6e^{-}\longrightarrow ArNH_2+2H_2O$

$W=\dfrac{Ewt\times Q}{96500};20.50=\dfrac{M}{6}\times\dfrac{2\times96500}{96500}\times\dfrac{50}{100}$

$\therefore\quad M=123.0\,g$

30. (a) $K_2SO_4 \rightleftharpoons 2K^+ + SO_4^{2-}$

$$\begin{array}{lll} H_2O & \rightleftharpoons H^+ + & OH^- \\ & +\downarrow 4e^- & -\downarrow 4e^- \\ & 2H_2 & O_2 + 2H_2O \end{array}$$

For $22.4 \times 3\text{ L} \equiv 4e^-$

or $1.68\text{ L at STP} \equiv \dfrac{4 \times 1.68}{22.4 \times 3} e^- = 0.1 \text{ mole } e^-$

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$5e^-$ reduce 1 mole MnO_4^-

0.1 will reduce $= \dfrac{1}{5} \times 0.1 = 0.02$ Moles

31. (a) When pH = 14 $[H^+] = 10^{-14}$ and $[OH^-] = 1$ M

$K_{sp} = [Cu^{2+}][OH^-]^2 = 10^{-19}$

$\therefore \quad [Cu^{2+}] = \dfrac{10^{-19}}{[OH^-]^2} = 10^{-19}$

The half cell reaction

$Cu^{2+} + 2e^- \longrightarrow Cu$

$$E = E^\circ - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]}$$

$$= 0.34 - \frac{0.059}{2} \log \frac{1}{10^{-19}} = -0.22\text{ V}$$

32. (b) The more the reduction potential, the more is the deposition of metals at cathode. Cation having E° value less than – 0.83 V (reduction potential of H_2O) will not deposit from aqueous solution.

33. (c) Moles of NaOH formed $= \dfrac{600 \times 1}{100} = 0.6$

or geq of NaOH = 0.6

geq of Cu deposited $= \dfrac{31.8}{63.6/2} = 1.0$

$\therefore$ Current efficiency $= \dfrac{0.6 \times 100}{1} = 60\ \%$

34. (d) Ionic mobility is the velocity of an ion under a potential gradient of 1Vm^{-1}.

35. (a) $MX(s) + e^- \longrightarrow M(s) + X^-(aq); E^\circ = 0.207\text{V}$ ....(i)

$M^+(aq) + e^- \longrightarrow M(s); \ E^\circ = 0.799\text{ V}$ ......(ii)

From (i) – (ii),

$MX(s) \longrightarrow M_s^+(aq) + X_s^-(aq);$

$E^\circ_{cell} = 0.207 - 0.799 = -0.592\text{ V}$

$MX(s) \rightarrow M_s^+(aq) + X_s^-(aq)$

$K_{sp} = [M^+][X^-] = S \times S = S^2$

$E^\circ_{cell} = \dfrac{0.592}{n} \log K_{sp}$

$-0.592 = \dfrac{0.0591}{1} \log K_{sp}$

$\log K_{sp} = -10, K_{sp} = 10^{-10}$,

Solubility $= \sqrt{K_{sp}} = 1.0 \times 10^{-5}$

36. (c) Anode :

$CuSO_4$ / Pt. $H_2O \longrightarrow 2H^+ + \dfrac{1}{2}O_2 + 2e^-$

$CuSO_4$ / Cu $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

KCl/Pt $2Cl^- \longrightarrow Cl_2(aq) + 2e^-$

Cathode :

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ (pH = decrease)

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ (pH = constant)

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-(aq)$ (pH = increase)

37. (a) $2H^+ + 2e^- \longrightarrow H_2; E^\circ = 0V$

$$E_{H^+/H_2} = E^\circ_{H^+/H_2} - \frac{0.059}{2} \log \frac{1}{[H^+]^2}$$

$-0.414 = 0 + 0.059 \log[H^+]$

$\therefore \quad [H^+] = 1.02 \times 10^{-7}$ M

38. (c) Due to buffer action the pH will remain practically constant.

39. (b) Anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$

Cathode : $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

Moles of OH^- formed $= Z \times i \times t = \dfrac{1 \times 5 \times 965}{96500} = 0.05$

$[OH^-] = \dfrac{0.05}{0.5} = 1 \times 10^{-1}$

$[H^+] = 10^{-13}$ pH = 13

40. (a) $W_{max} = -n.FE;$

$W_{max} = -2 \times 96500 \times 0.65 = -1.25 \times 10^5$ J

0.5g H_2 = 0.25 mole.

Hence $W_{max} = -1.25 \times 10^5 \times 0.25 = -3.12 \times 10^4$ J

41. (a) Moles of Cu^{2+} deposited $= \dfrac{1\times 48250}{2\times 96500} = 0.25$

$\therefore \quad \text{Molarity} = \dfrac{0.25}{0.5} = 0.5$

42. (a) $\Lambda_m\,(AgCl) = 63 + 67 = 130$

$\Lambda_m = \dfrac{\kappa \times 1000}{\text{solubility}}$

$\therefore$ Solubility $S = \dfrac{2.6\times 10^{-3}\times 1000}{130} = 2\times 10^{5}\,\text{mol}^{-1}$

$\therefore \quad K_{sp} = 4\times 10^{10}$

43. (d) $E = E^\circ - \dfrac{0.0592}{2}\log\dfrac{[Mn^{2+}]}{[H^+]^4}$

$= E^\circ - \dfrac{0.0592\times 4}{2}\log\dfrac{[Mn^{2+}]^{1/4}}{[H^+]}$

$= E^\circ - 0.0592\times 2\ (\log[Mn^{2+}]^{1/4} + pH)$

$\Delta E = E_2 - E_1 = 0.0592\times 2\,(pH_1 - pH_2)$

$= 0.188 \times 1V$

44. (d)

$$Pb + SO_4^{--} \longrightarrow PbSO_4 + 2e^-$$

$$PbO_2 + 4H^+ + SO_4^{--} + 2e^- \longrightarrow PbSO_4 + 2H_2O$$

$$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

The reaction indicates that 2 moles of H_2SO_4 corresponds to 2 × 96500 C and 2 mol $H_2SO_4 \equiv 4$ equiv. of H_2SO_4.

2 × 96500 C consumed 4 equiv. of H_2SO_4

and $100\times 10^{-3}\times 9.65\times 10^{5}$ C consumed

$= \dfrac{4\times 100\times 10^{-3}\times 9.65\times 10^{5}}{2\times 96500} = 2$ equiv. H_2SO_4

$\therefore$ Decrease in normality $= \dfrac{2}{5} = 0.40$

45. (b) The cell reaction is

$Cl_2\,(g)\,(P_2\,\text{atm}) \longrightarrow Cl_2\,(aq)\,(P_1\text{atm})$

$E_{cell} = -\dfrac{0.0592}{2}\log\dfrac{P_1}{P_2} = \dfrac{0.0592}{2}\log\dfrac{P_2}{p_1}$

E_{cell} will be positive when $p_2 > p_1$.

46. (c) The reaction

$2\,Cu^+\,(aq) \longrightarrow Cu(s) + Cu^{2+}(aq)$

$E_{cell} = E^\circ_{cell} - \dfrac{0.0592}{1}\log\dfrac{[Cu^{2+}]}{[Cu^+]^2}$

At equilibrium $E_{cell} = 0 \quad \therefore \quad E^\circ_{cell} = 0.0592\log K_c$

or, $\log K_c = \dfrac{0.52 - 0.16}{0.0592} \quad \therefore \quad K_c = 1.2\times 10^{6}$

47. (a) Volume = Area × thickness

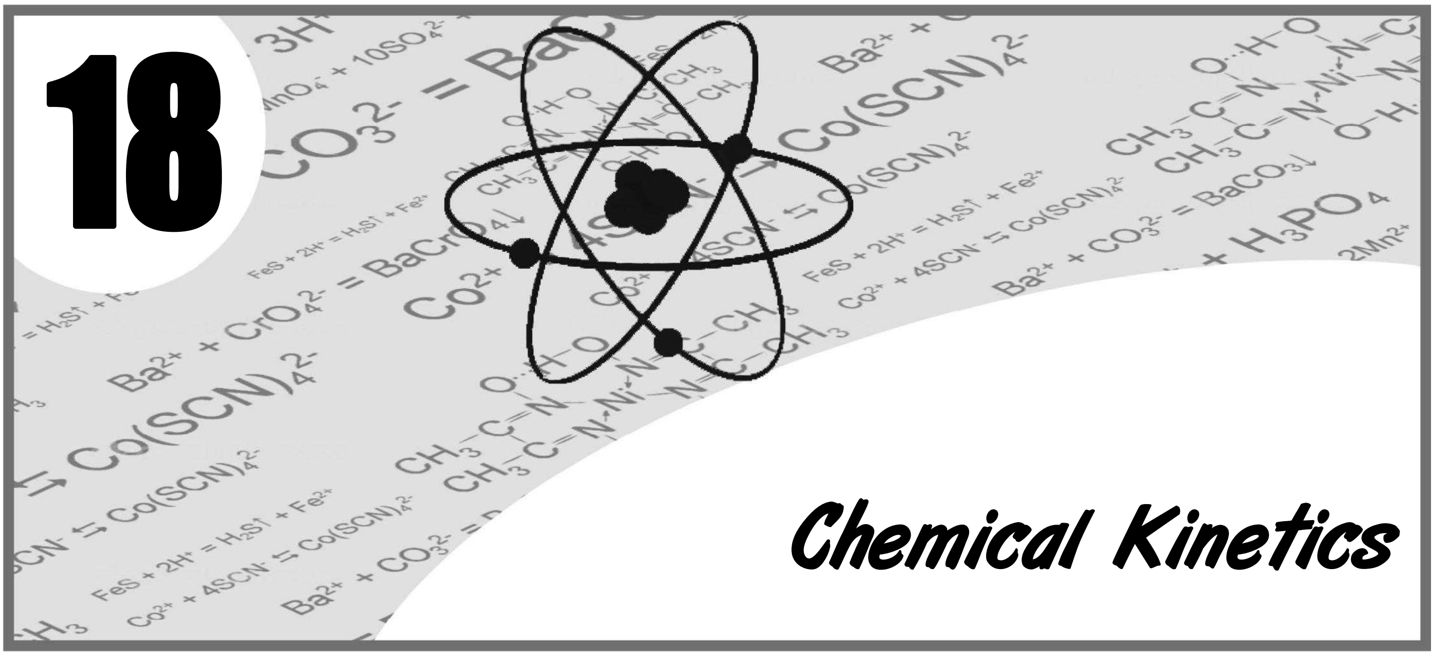
Mass = Volume × density

$\therefore$ Mass of Ag to be deposited

$= \dfrac{80\times 0.005}{10}\times 10.5 = 0.42$ g

Amount deposited $= \dfrac{E.wt\times i\times t}{96500}$

$\therefore \quad 0.42 = \dfrac{108\times 3\times t}{98500} \quad \therefore \quad t = 125.1$ seconds



18

Chemical Kinetics

CHEMICAL KINETICS :

Deals with rate, mechanism and factors affecting the chemical reactions.

RATE OF REACTION :

It is defined as the change in concentration of a reactant or a product in a particular interval of time. The change in concentration of a substance say A is represented by $\Delta[A]$

$\Delta[A]$ = [Final concentration – Initial concentration]

For a reactant : Final concentration < Initial concentration

Thus $\Delta[A]$ will have negative sign

For a product : Final concentration > Initial concentration

Thus $\Delta[A]$ will have positive sign

Average rate in terms of products

$$= \frac{\Delta[A]}{\Delta t} = \frac{\text{Total change in concentration}}{\text{Total change in time}}$$

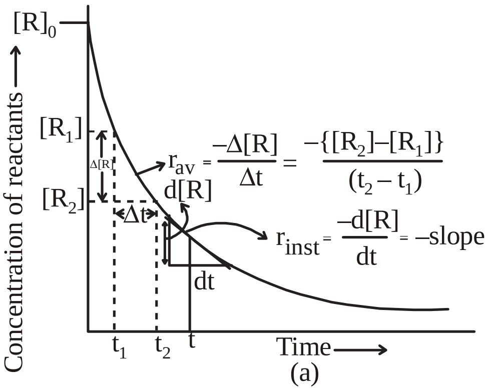
Average rate in terms of reactants $= -\dfrac{\Delta[A]}{\Delta t}$

The negative sign in the expression make the rate positive. Hence rate of a reaction is never negative.

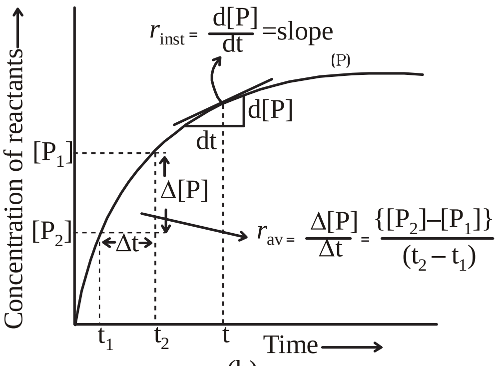
Consider the decomposition of N_2O_5

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

$$\text{Rate} = -\frac{1}{2}.\frac{\Delta N_2O_5}{\Delta t} = \frac{1}{4}\frac{\Delta NO_2}{\Delta t} = \frac{\Delta O_2}{\Delta t}$$



(a)



(b)

Instantaneous and average rate of a reaction

The minus sign indicates the decrease in concentration and plus sign increase in concentration. The above expressions give the **average rate of reaction**.

FEATURES OF THE RATE OF REACTION :

(I) Rate of reaction is proportional to the concentration of the reactants

(II) Rate of a reaction is always a positive quantity

(III) Rate of a reaction is determined by measuring the concentration of a reactant or a product as a function of time

(IV) Property related to concentration is selected e.g. volume, pressure, thermal or electrical conductivity, colour change, pH, etc.

UNITS OF RATE OF REACTION :

Mol L^{-1} $time^{-1}$ and for gaseous reaction atm $time^{-1}$

INSTANTANEOUS RATE :

As the reaction progresses the concentration of reactants keeps on falling. Hence the rate of reaction keeps on falling with time. The rate of reaction at any given instant will be given by the expression $r = \dfrac{dx}{dt} = -\dfrac{1}{2}\dfrac{dN_2O_5}{dt} = \dfrac{1}{4}.\dfrac{dNO_2}{dt} = \dfrac{dO_2}{dt}$

where dx is the infinitesimally small change in the concentration of x in infinitesimally small interval of time dt.

RELATION BETWEEN AVERAGE AND INSTANTANEOUS RATE:

Instantaneous rate = Average rate as Δt approaches to zero

$$\text{Instantaneous rate} = \left(\frac{\Delta x}{\Delta t}\right)_{\Delta t \to 0} = \frac{dx}{dt}$$

FACTORS AFFECTING THE RATE OF REACTION :

(i) ***Nature of the reactants :*** Reactions involving lesser bond rearrangement proceed much faster than those which involve larger bond rearrangement.

(ii) ***Temperature :*** In most cases the rate of reaction in a homogeneous system is approximately doubled or even tripled by an increase in temperature of 10°C.

(iii) ***Concentration of reactants :*** At fixed temperature and in absence of catalyst, the rate increases with increased concentration of reactants.

(iv) ***Surface area :*** The more the surface area, the more is the rate of reaction.

(v) ***Positive catalyst :*** Increases the rate by lowering the energy of activation.

(vi) ***Presence of light :*** Photochemical reactions are influenced by radiations of specific wavelength.

THE RATE CONSTANT :

Consider a reaction $A + B \longrightarrow \text{Products}$.

At a particular temperature rate is given by

$$r = \frac{dx}{dt} \propto C_A.C_B = kC_A.C_B$$

where k is ***rate constant***, ***velocity constant*** *or* ***specific reaction rate***. When $C_A = C_B = 1$ then k= r (rate)

In general rate constant may be defined as the rate of the reaction when the concentration of each of the reactants is unity. It is characteristic of a particular reaction.

FACTORS INFLUENCING RATE CONSTANT :

(a) ***Temperature :*** Variation of rate constant with temperature is given by

Arrhenius equation *:* $k = Ae^{-E_a/RT}$ (i)

A = Constant known as frequency factor

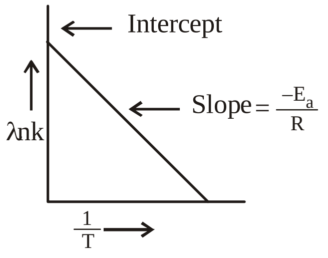
E_a = Energy of activation. Both A and E_a are characteristic of a particular reaction.

$e^{-E_a/RT}$ = known as Boltzmann factor

Taking natural logarithm of (i)

$$\ell nk = \frac{-E_a}{RT} + \log A \qquad \text{(ii)}$$

The plot of ℓnk *vs* $\frac{1}{T}$ gives a straight line



Increase in temperature or decrease in the activation energy will increase the rate of reaction and exponential increase in the rate constant

At temperature T_1 the equation (ii) is

$$\ell nk_1 = \frac{-E_a}{RT_1} + \log A \qquad \text{(iii)}$$

and at temperature T_2

$$\ell nk_2 = \frac{-E_a}{RT_2} + \log A \qquad \text{(iv)}$$

Since *A* is constant for a given reaction

Subtracting (iii) from (iv)

$$\ell nk_2 - \ell nk_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

Knowing the value of slope E_a can be calculated.

(b) ***Catalyst :*** Presence of positive catalyst lowers the energy of acitvation and hence influences the rate constant.

UNITS OF RATE CONSTANT :

Units depend upon the order of a reaction

units = $(\text{Concentration})^{1-n}$. time^{-1}

$$= \mathbf{(Mol\ L^{-1})^{1-n}\ .\ time^{-1}}$$

where n = order of reaction

Units of rate constant for zero order reaction

= $\text{Mol L}^{-1}\ \text{time}^{-1}$

Units of rate constant for first order reaction = time^{-1}

CHARACTERISTICS OF RATE CONSTANT :

(I) The value of k is different for different reactions.

(II) At fixed temperature the value of k is constant.

(III) It is independent of concentration but depends on temperature.

(IV) The larger the value of k the faster is the reaction and vice versa.

THE DIFFERENCE BETWEEN RATE CONSTANT AND RATE OF REACTION :

Rate Constant	Rate of reaction
(a) It is equal to rate of reaction when the concentration of reacting species is unity	(a) It is the change in concentration of reactants or products per unit time.
(b) Units depends on order of reaction = $(\text{Mol L}^{-1})1^{-n}$ time–1 (n = Order of reaction)	(b) Units are $\text{Mol L}^{-1}\ \text{Sec}^{-1}$
(c) It depends upon temperature	(c) It depends upon temperature and concentration

TEMPERATURE COEFFICIENT :

It is the ratio of two rate constants differing by a temperature of 10 °C. Generally the temperatures are 298K & 308 K.

$$\text{Temperature Coefficient} = \frac{\text{Rate constant at 308K}}{\text{Rate constant at 298K}}$$

The value of temperature coefficient is generally 2 and 3. In rare cases the value is 4, 5 etc.

RATE LAW EQUATION :

The mathematical expression, which practically relates the rate of a chemical reaction and concentration of reactants is called rate law equation e.g. for a hypothetical reaction.

$$aA + bB \rightleftharpoons cC + dD$$

Rate $\propto$ $[A]^a [B]^b$. It is law of mass action

Rate $\propto$ $[A]^x [B]^y$ It is rate law.

If rate actually vary according to this equation practically then this is rate law equation. For decomposition of N_2O_5.

$$2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2$$

Rate $\propto [N_2O_5]$ and not Rate $\propto [N_2O_5]^2$

$\therefore$ Rate law equation is, Rate = $k[N_2O_5]$

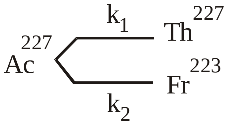
Rate law equation for reversible reaction

$$H_2 + I_2 \underset{k2}{\overset{k1}{\rightleftharpoons}} 2HI$$

$$\text{Rate} = \frac{1}{2}\frac{d[HI]}{dt} = k_1[H_2][I_2] - k_2[HI]^2$$

$$\text{Rate} = \begin{bmatrix}\text{Rate of forward} \\ \text{reaction}\end{bmatrix} - \begin{bmatrix}\text{Rate of backward} \\ \text{reaction}\end{bmatrix}$$

Rate law equation involving side reactions



Rate of fromation of $Th^{227} = k_1[Ac^{227}]$

Rate of formation of $Fr^{223} = k_2[Ac^{227}]$

$\therefore$ Rate = $(k_1 + k_2)[Ac^{227}]$

ORDER OF REACTION :

The sum of all the powers to which the concentration terms are raised in rate law equation is known as the order of a reaction. For a general reaction

$$aA + bB \rightleftharpoons cC + dD$$

The rate law equation is

$$\frac{dx}{dt}(\text{Rate}) = [A]^x[B]^y \ ;$$

Order w.r.t. A is x, Order w.r.t. B is y

Overall order is x + y

FEATURES OF ORDER OF REACTION :

(I) The order of a reaction is experimentally determined quantity.

(II) It cannot be written from balanced chemical equation.

(III) It can be written from the rate law equation.

(IV) It depends upon the molecules undergoing change in concentration.

(V) Order may be zero, whole number, fractional or negative even

(VI) Reaction with order $\geq$ 3 are rare.

RATE DETERMINING STEP :

Some reactions take place in more than one step. Each step has its own rate. The slowest step is called the rate determining step or rate controlling step e.g.

$$2NO_2 + F_2 \longrightarrow 2NO_2F$$

Mechanism

$$NO_2 + F_2 \longrightarrow NO_2F + F \quad (\text{slow})$$

$$NO_2 + F \longrightarrow NO_2F \quad (\text{fast})$$

$$2NO_2 + F_2 \longrightarrow 2NO_2F$$

First step is the rate determining step. **The rate law equation is always written from slow step**.

$\therefore$ The rate law is given as $\text{rate} = k[NO_2][F_2]$

Remember that reaction intermediate are never shown in rate law equation.

MOLECULARITY OF REACTION :

The number of molecules of reactants which take part in a single actual step of the reaction, whether their concentration is appreciably changed or not is known as molecularity of reaction. Molecularity is a theoretical concept and is always a whole number.

$NH_4NO_2 \longrightarrow N_2 + 2H_2O$	Unimolecular
$2HI \longrightarrow H_2 + I_2$	Bimolecular
$2NO + O_2 \longrightarrow 2NO_2$	trimolecular

The reactions with molecularity more than 3 are rare and generally not possible. Such reactions proceed through more than one steps and are termed as complex reactions. Each step has its own molecularity e.g.

$$4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$$

Probable mechanism is

$HBr + O_2 \longrightarrow HOOBr$	Molecularity two
$HOOBr + HBr \longrightarrow 2HOBr$	Molecularity two
$(HOBr + HBr \longrightarrow H_2O + Br_2) \times 2$	Molecularity two
$4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$	Molecularity five

PSEUDO UNIMOLECULAR REACTIONS :

Reactions like hydrolysis of an ester or cane sugar, which though bimolecular and yet following the kinetics of first order are called pseudo unimolecular reactions.

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

$$\frac{dx}{dt} = k[CH_3COOC_2H_5]$$

$$C_{12}H_{22}O_{11} + H_2O \rightleftharpoons C_6H_{12}O_6 + C_6H_{12}O_6$$

$$\frac{dx}{dt} = k[C_{12}H_{22}O_{11}].$$

In above reactions the rate is independent of concentration of H_2O being present in excess. Hence $[H_2O]$ is constant.

DIFFERENCES BETWEEN ORDER AND MOLECULARITY OF REACTION :

	Order of reaction	*Molecularity*
1.	It is experimentally determined quantity	It is a theoretical concept.
2.	It can have integral, fractional or negative values	Always integral values only, never zero or negative
3.	It cannot be obtained from balanced or stoichiometric equation.	It can be obtained.
4.	It tells about the slowest step in the mechanism	It does not tell anything about mechanism
5.	It is sum of the powers of the concentration terms in the rate law equation.	It is the number of reacting species undergoing simultaneous collision in the reaction.
6.	It is changed when one reactant is taken in large excess	It undergoes no change.

KINETIC EQUATIONS OF DIFFERENT ORDERS :

(1) ***First order reaction :*** The reaction rate is determined by one concentration variable term.

$$A \longrightarrow \text{products}$$

$$\frac{dA}{dt} = k[A]$$

Let 'a' moles per unit volume be the initial concentration and x moles have disappeared after time t. Then the concentration left will be (a – x) moles per unit volume.

$$k = \frac{1}{t}.\ln\frac{a}{(a-x)} = \frac{2.303}{t}\log\frac{a}{a-x}$$

This is called the kinetic equation of a first order reaction.
Units of k = $time^{-1}$ eg h^{-1}, m^{-1} or s^{-1}

Half-life period ($t_{1/2}$). The time taken for the completion of half of the reaction is known as half-life period. When $t = t_{1/2}$, $x = a/2$.

$$t_{1/2} = \frac{0.693}{k}$$

The half-life period of the first order reaction is independent of the initial concentration of reacting substances.
The time taken for the completion of any fraction of the reaction is independent of the initial concentration.

First order growth kinetics : It is used in population growth and bacteria multiplication

$$k = \frac{2.303}{t}\log\frac{a+x}{a}$$

where a is initial population and (a + x) population after time t.

(2) ***Second order reaction :*** The reaction rate is determined by the variation of two concentration terms. They are of two types

(a) $2A \longrightarrow \text{Products}$

Rate $\propto [A]^2$

(b) $A + B \longrightarrow \text{Products}$

Rate $\propto [A][B]$

For the (a) type of reaction $k = \frac{1}{t}.\frac{x}{a(a-x)}$

Unit of k = $conc^{-1}$ $time^{-1}$ = $(mol\ L^{-1})^{-1}$ $time^{-1}$ i.e. mol^{-1} L. s^{-1}

When $t = t_{1/2}$, $x = a/2$.

Half-life period $(t_{1/2}) = \frac{1}{k_a}$ $\left(t_{1/2} \propto \frac{1}{a}\right)$

The time taken for the completion of half of the reaction is inversely proportional to the initial concentration of the reactant.

Note: The time taken for the completion of half or any fraction of the reaction is inversely proportional to the initial concentration of the reactant.

(3) ***Third order reaction :*** The reaction rate is determined by the variation of three concentration terms. They are of three types

(a) $3A \longrightarrow \text{Products}$

Rate $\propto [A]^3$

(b) $2A + B \longrightarrow \text{Products}$

Rate $\propto [A]^2[B]$

(c) $A + B + C \longrightarrow \text{Products}$

Rate $\propto [A][B][C]$

Consider the type (a) $k = \frac{x(2a-x)}{2t\,a^2(a-x)^2}$

Unit of k = $(mol\ L^{-1})^{-2}\ s^{-1} = mol^{-2}\ L^2\ s^{-1}$
When t = $t_{1/2}$, x = a/2

Half-life period $(t_{1/2}) = \frac{3}{2ka^2}$ $\quad (\because t_{1/2} \propto \frac{1}{a^2})$

The time taken for the completion of half of the reaction is inversely proportional to the square of the initial concentration of reactants.

Note : The time taken for the completion of any fraction of the reaction is inversely proportional to the square of the initial concentration of reactants.

(4) ***Zero order reaction :*** The reaction rate is independent of the concentration of the reactants.

$$A \longrightarrow \text{Product}$$

$$\text{Rate} = k[A]^0 \text{ or } \frac{dx}{dt} = k \text{ on integration}$$

$x = kt + c$

when $t = 0$, $x = 0$ so $c = 0$

$$\text{Hence } x = kt \text{ or } k = \frac{x}{t}$$

Unit of k = Conc. $\text{time}^{-1} = \text{mol L}^{-1}\,\text{s}^{-1}$

When the reaction is complete, C = 0

$$\therefore E_{\text{completion}} = \frac{C_o}{k}$$

$$\text{For zero order reaction } k = \frac{C_o - C}{t}$$

C_o = initial concentiation

C = conc. at any time t

When $t = t_{1/2}$, $x = a/2$

$$\text{Half life period } (t_{1/2}) = \frac{a}{2k} \; \left(t_{1/2} \propto a\right)$$

The time taken for the completion of half of the reaction is directly proportional to the initial concentration of reactants.

For zero order reaction,

(I) Rate is independent of concentration of reactant (s)

(II) Concentration of reactants do not vary with time

(III) Rate does not vary with time.

(IV) Rate is always equal to rate constant.

(V) $t_{½} < a$

(VI) If we double the amount of reactants then time for completion will be doubled.

HALF-LIFE PERIOD FOR THE n^TH^ ORDER REACTION :

When the order of reaction is n, $t_{1/2}$ is given by

$$t_{1/2} = \frac{1}{k(n-1)}\left[\frac{2^{n-1}-1}{a^{n-1}}\right]$$

$$\therefore t_{1/2} \propto \frac{1}{a^{n-1}}$$

Unit of k = $(\text{conc})^{1-n}.\ \text{time}^{-1}$

FRACTIONAL ORDER REACTIONS :

(I) Reaction between H_2 and D_2.

Rate $= k\,P_{H_2}(P_{D_2})^{1/2}$. Order w.r.t. D_2 is 1/2.

(II) Conversion of para hydrogen to ortho hydrogen at high temperature.

$$\text{Rate} \propto (P_{H_2})^{3/2}$$

$$\therefore \text{Rate} = k(P_{H_2})^{1.5}$$. Order w.r.t. H_2 is 3/2.

NEGATIVE ORDER REACTIONS :

Conversion of ozone into oxygen.

Rate = $K\,[O_3]^2\,[O_2]^{-1}$

Order with respect to oxygen is –1.

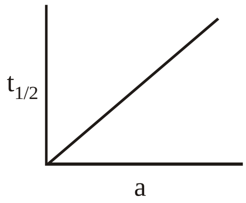
DETERMINATION OF ORDER OF REACTION :

(1) ***Fractional change method :*** The time required to complete a definite fraction of reaction is given by

$t_{1/2} \propto (a)^{1-n}$ where n is order of reaction

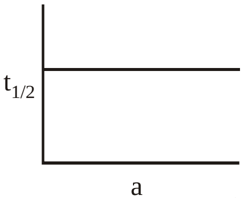
The following graphs are obtained between $t_{1/2}$ and initial concentration 'a'.

I.



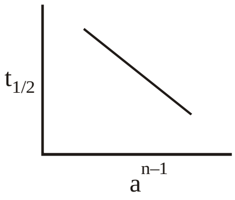
Zero order $t_{1/2} \propto a$

II.



First order $t_{1/2} \propto a^0$

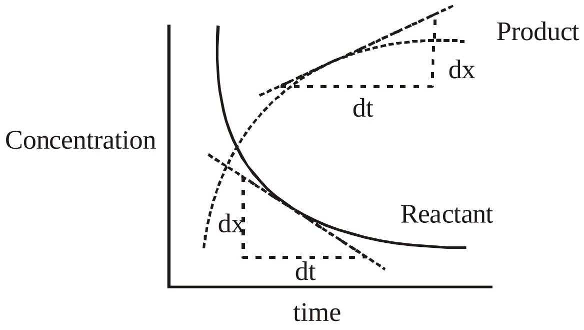
III.



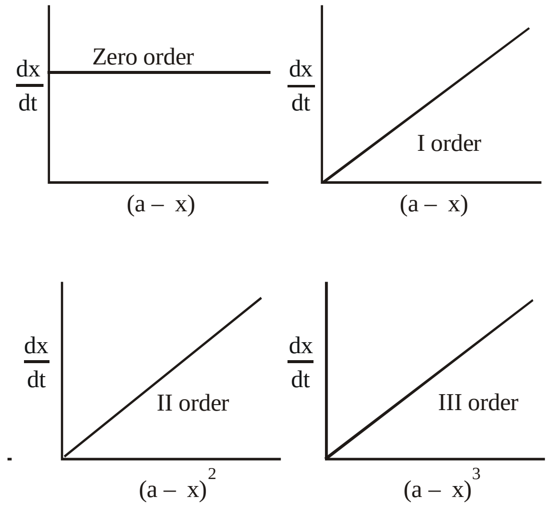
Second & Third Order
where n = 2 & 3

$$t_{1/2} \propto \frac{1}{a} \text{ and } t_{1/2} \propto \frac{1}{a^2}$$

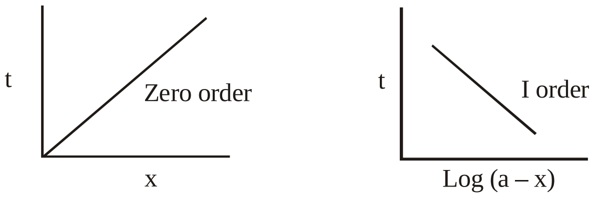
(2) ***Graphical method :*** (a) The graphs between concentration of any reactant Vs. time or concentration of any product Vs. time are plotted. The slope of the tangent to the curve gives the rate of reaction at that time.



The new graphs between $\frac{dx}{dt}$ Vs. $(a-x)$, $(a-x)^2$ or $(a-x)^3$ are plotted.



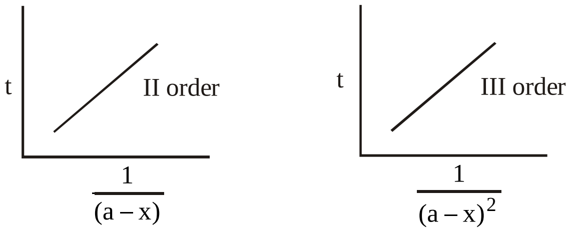
(b) Making use of integrated form of rate expression :



Zero order $t = \frac{x}{k}$

For first order $kt = 2.303 \log \frac{a}{a-x}$

or $t = \frac{2.303}{k} \log a - \frac{2.303}{k} \log(a-x)$



2nd order $kt = \frac{x}{a(a-x)}$; 3rd order $kt = \frac{1}{2} \frac{x(2a-x)}{a^2(a-x)^2}$

$t = \frac{1}{k(a-x)} - \frac{1}{k(a)}$; $t = \frac{1}{2k(a-x)^2} - \frac{1}{2k(a)^2}$

Evaluation of k

For zero order slope $= \frac{1}{k}$

For I order slope $= \frac{-2.303}{k}$; k can be calculated

For II order slope $= \frac{1}{k}$; k can be calculated

For III order slope $= \frac{1}{2k}$; k can be calculated

(3) Use of differential rate equations.

(4) Use of integral rate equations – hit and trial method

(5) Ostwald's isolation method.

Examples of reactions of different order :

(a) Reactions of zero order :

(I) $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl\ (g)$

(II) $2NH_3(g) \xrightarrow[h\nu]{MO} N_2(g) + 3H_2(g)$

(III) $2HI(g) \xrightarrow{Au} H_2(g) + I_2(g)$

(b) Reactions of Ist order :

(I) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

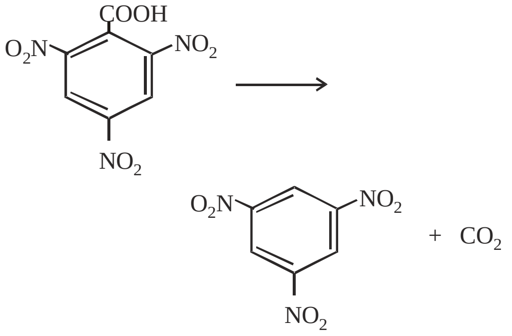
(II) $2H_2O_2 \longrightarrow 2H_2O + O_2$

(III) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

(IV) $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

(V) $(CH_3)_3CO.OC(CH_3)_3 \longrightarrow 2CH_3COCH_3 + C_2H_6$

(VI)



(VII) $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

(VIII) $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

(IX) $\underset{\text{azo isopropane}}{(CH_3)_2CHN = NCH(CH_3)_2} \longrightarrow N_2 + C_6H_{14}$

(c) Reactions of II order :

(I) $2NO_2 + F_2 \longrightarrow 2NO_2F$

(II) $2HI \longrightarrow H_2 + I_2$

III) $2CH_3CHO \longrightarrow 2CH_4 + 2CO$

(IV) $CH_3COOC_2H_5 + NaOH \longrightarrow$

$\cdot CH_3COONa + C_2H_5OH$

(V) $NO + O_3 \longrightarrow NO_2 + O_2$

(VI) $2NO_2 \longrightarrow 2NO + O_2$

(VII) $C_2H_4 + H_2 \longrightarrow C_2H_6$

(VIII) $2N_2O \longrightarrow 2N_2 + O_2$

(IX) $S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$

(d) ***Reactions of III order :***

(I) $2NO + O_2 \longrightarrow 2NO_2$

(II) $2NO + Br_2 \longrightarrow 2NOBr$

(III) $2NO + Cl_2 \longrightarrow 2NOCl$

(IV) $2NO + H_2 \longrightarrow N_2O + H_2O$

(V) $2NO + D_2 \longrightarrow N_2O + D_2O$

(VI) $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

(VII) $Fe^{3+} + 3I^- \longrightarrow FeI_3$

(e) ***Reactions of fractional order :***

(I) $H_2 + Br_2 \longrightarrow 2HBr$

$\text{Rate} = k[H_2][Br_2]^{1/2} \quad \text{Order} = 1.5$

(II) $CO + Cl_2 \longrightarrow COCl_2$

$\text{Rate} = k[CO]^2[Cl_2]^{1/2} \quad \text{Order} = 2.5$

(III) $COCl_2 \longrightarrow CO + Cl_2$

$\text{Rate} = k[COCl_2]^{3/2} \quad \text{Order} = 1.5$

(f) ***Reaction of IV order :***

$4KClO_3 \longrightarrow 3KClO_4 + KCl$

COLLISION THEORY :

Chemical reaction occurs as a result of effective collisions between reacting molecules. For this two things are important.

(I) Proper orientation of reacting molecules.

(II) Possession of certain minimum amount of energy by reacting molecules

THRESHOLD ENERGY :

The minimum amount of energy possessed by the reacting molecules to have effective collisions, resulting in the formation of product, is called threshold energy.

ACTIVATION ENERGY (E_a) :

The excess energy over and above the average potential energy possessed by reacting molecules to have effective collisions resulting in the formation of product is known as activation energy.

Activation Energy = threshold energy – average energy of reactants

For fast reaction the activation energy is low.

For slow reaction the activation energy is high.

COLLISION FREQUENCY (z) :

Total number of collisions which occur among the reacting molecules per second per unit volume is called collision frequency. Its value is given by

$$z = \sqrt{2}\,\pi \bar{v} \sigma^2 n^2$$

$\bar{v}$ = average velocity, σ = molecular diameter in cm.,

n = number of molecules per cc.

RATE OF REACTION FROM COLLISION THEORY :

It is given by

Rate of reaction = f × z

z = collision frequency, f = fraction of effective collisions

$$= \frac{\Delta n}{N} = e^{-E_a/RT}$$

$\therefore$ Rate (k) = $Ze^{-E_a/RT}$

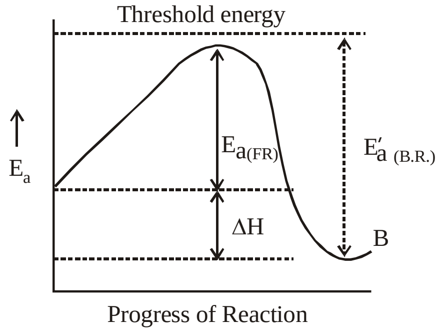
GRAPHICAL REPRESENTATION OF EXOTHERMIC REACTION :

A(Reactant) → B (Product)

$E_{a(F.R.)} + \Delta H = E_{a(B.R.)}$

$\Delta H = -ve$

where F.R. = Forward reaction and B.R. = Backward reaction

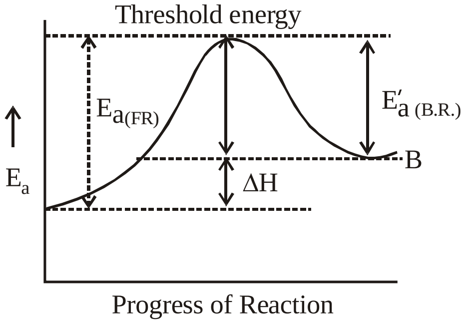


GRAPHICAL REPRESENTATION OF ENDOTHERMIC REACTION :

A(Reactant) → B (Product)

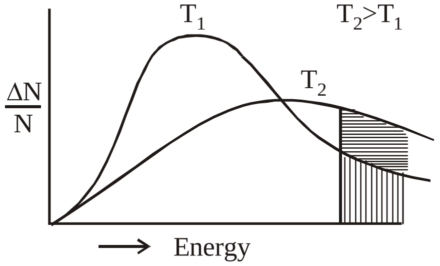
$\Delta H = +ve$

$E_{a(F.R.)} = \Delta H + E'_{a(B.R.)}$



GRAPHICAL REPRESENTATION OF THE EFFECT OF TEMPERATURE ON RATE OF REACTION :

Fraction of the molecules having energy equal to activation energy is shown by shaded portion. The fraction of such molecules become almost double for 10°C rise of temperature and the rate of reaction almost doubles for 10°C rise of temperature.



PHOTOCHEMICAL REACTIONS :

Reactions which take place by the absorption of radiations of suitable wavelength e.g.

$$H_2(g)+Cl_2(g)\xrightarrow{\text{light}}2HCl(g)$$

Photosynthesis of carbohydrates in plants takes place in presence of chlorophyll and sunlight.

$$6CO_2+6H_2O\xrightarrow{\text{light}}C_6H_{12}O_6+6O_2$$

FREE ENEREGY CHANGE IN PHOTOCHEMICAL REACTIONS :

The free energy change of a photochemical reaction may not be negative. In the synthesis of carbohydrates and formation of HCl, ΔG is +ve.

PHOTOSENSITISATION :

Certain molecules absorb light energy and transfer it to another molecule which may undergo a reaction. The process is called photosensitisation and the substance doing so is called photosensitizer e.g. chlorophyll acts as photosensitizer in photosynthesis.

VISION :

The isomerisation of retina by absorbing photon of light in the retina of eye and reconversion to original form by releasing energy is known as vision.

GROTHUS-DRAPER LAW :

Only those rays which are absorbed by the substance are effective in producing a chemical change. A part of light is reflected and transmittted also.

LAW OF PHOTOCHEMICAL EQUIVALENCE OR EINSTEIN'S LAW (STARK-EINSTEIN LAW) :

In a photochemical reaction, one quantum of active light (photon) is absorbed per molecule of the reacting substance which disappears.

QUANTUM EFFICIENCY OR QUANTUM YIELD :

Number of moles reacting per Einstein of the light absorbed. It is expressed as

$$\phi=\frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

$$\phi=\frac{\text{Number of moles reacting in a given time}}{\text{Number of Einsteins absorbed in the same time}}$$

CHEMILUMINESCENE :

Emission of light in a chemical reaction at ordinary temperature is called chemiluminescence.

FLUORESCENCE :

The absorption of energy and instantaneous re-emitting of the energy is called fluorescence.

PHOSPHORESCENCE :

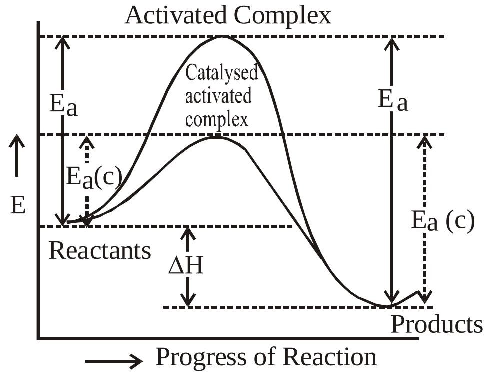
The continuous glow of some substances even after the cutting of source of light is called phosphorescene e.g. ZnS.

BIOLUMINESCENCE :

The phenomenon of chemiluminescence exhibited by certain living organisms is called bioluminescence e.g. light emission by fire flies.

EFFECT OF CATALYST ON REACTION RATES :

A catalysed reaction provides a new pathway or a mechanism by which the potential energy barrier between the reactants and products is lowered. The graphical representation is as follows :



(I) ΔH (enthalpy) of reaction remains the same for catalysed as well as uncatalysed reaction.

(II) Energy of activation is lowered considerably for catalysed forward and backward reactions.

Study of kinetics of some reactions :

(I) Hydrolysis of an ester

$$CH_3COOC_2H_5+H_2O\rightleftharpoons CH_3COOH+C_2H_5OH$$

It is biomolecular and 1 order. The rate constant is given by

$$k=\frac{2.303}{t}\log\frac{V_\infty-v_0}{V_\infty-v_t}$$

Initial conc. of ester $\propto V_\infty-v_0$ and conc. of ester present after time $t\propto V_\infty-v_t$.

(II) Inversion of cane sugar :

$$\underset{\underset{\text{Bimolecular I order}}{\text{Sucrose (d)}}}{C_{12}H_{22}O_{11}} + H_2O \rightleftharpoons \underbrace{\underset{\text{Glucose (d)}}{C_6H_{12}O_6} + \underset{\text{Fructose (l)}}{C_6H_{12}O_6}}_{\text{Laevorotatory}}$$

The change is noted by rotation of plane polarised light in a polarimeter.

$$a \propto r_0 - r_\infty$$

$$(a - x) \propto r_t - r_\infty$$

Hence velocity constant k is given by

$$k = \frac{2.303}{t}\log\frac{(r_0 - r_\infty)}{(r_t - r_\infty)}$$

(III) Saponification of ethyl acetate :

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

Bimolecular II order reaction.

The value of $k = \dfrac{a}{t.a\,(a - x)}$

Miscellaneous Solved Examples

1. The reaction $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ takes place in a closed flask. The concentration of NO_2 increases by 20×10^{-3} moles lit^{-1} in 5 sec.

(a) Calculate the rate of the reaction (b) the rate of change of concentration of N_2O_5.

Sol. (a) Rate of reaction

$$= \frac{1}{4}.\frac{dNO_2}{dt} = \frac{1}{4}.\frac{20\times10^{-3}}{5} = 10^{-3}\text{mol. lit}^{-1}s^{-1}$$

(b) Rate of change of concentration of N_2O_5

$$r = -\frac{1}{2}\frac{dN_2O_5}{dt};\quad 10^{-3} = \frac{1}{2}\frac{dN_2O_5}{dt}$$

$$= 2.0\times10^{-3}\text{mol lit}^{-1}s^{-1}$$

2. A first order reaction is 20% complete in 10 minutes. Calculate (I) the rate constant of the reaction (II) time taken for the reaction to go to 75% completion.

Sol. (I) For Ist order reaction $k = \dfrac{2.303}{t}\log\dfrac{a}{a - x}$

$$k = \frac{2.303}{10}\log\frac{100}{100 - 20} = 0.0223\ \text{min}^{-1}$$

(II) $t = \dfrac{2.303}{0.0223}\log\dfrac{100}{100 - 75} = 62.18$ min

3. The decomposition of $2N_2O_5 \longrightarrow 2N_2O_4 + O_2$ is at 200°C. If the initial pressure is 114 mm Hg and after 25 min. of the reaction the total pressure of gaseous mixture is 133 mm Hg. Calculate the average rate of the reaction in

(a) atm. m^{-1} (b) mol s^{-1}

Sol. $\underset{a-x}{2N_2O_5} \longrightarrow \underset{x}{2N_2O_4} + \underset{x/2}{O_2}$

Pressure due to a moles = 114 mm Hg

Pressure due to $a + \dfrac{x}{2}$ moles =133 mm Hg

Hence pressure due to $\dfrac{x}{2}$ moles

= 133 – 114 = 19 mm Hg

and due to x moles 19 × 2 = 38 mm Hg.

$\therefore$ Pressure due to (a – x) moles = 114 – 38 = 76 mm Hg

Change in pressure 114 – 76 = 38 mm Hg.

Average rate = $\dfrac{38}{25\times760} = 0.002$ atm min^{-1}

Again PV = nRT.

$$\therefore \frac{n}{V} = \frac{0.002}{0.0821\times473\times60} = 8.58\times10^{-7}\ \text{mol lit}^{-1}s^{-1}$$

4. The rate constant of a reaction is given by lnk (sec^{-1}) = 14.34 – (1.25 × 10^4)/T. Calculate (a) the energy of activation (b) the rate constant at 500 K (c) At what temperature will its half-life period be 256 minute.

Sol. (a) Given ln k = 14.34 – (1.25 × 10^4)/T.

Arrhenius equation ln k = ln A – $\dfrac{E_a}{RT}$

Comparing both the equations $\dfrac{E_a}{R} = 1.25\times10^4$

$$\therefore E_a = 1.25\times10^4 R = 1.25\times10^4\times1.987 = 24.83\ \text{kcal mol}^{-1}$$

(b) $\ln k = 14.34 - \dfrac{(1.25\times10^4)}{500}$ $\quad(\because T = 500K)$

$$\therefore k = 2.35\times10^{-5}\ \text{sec}^{-1}$$

(c) $k = \frac{0.693}{256\times 60}$ $\quad \therefore \log\frac{0.693}{256\times 60} = 14.34 - \frac{1.25\times 10^4}{T}$

$\therefore T = 513K$

5. The rate constant of reaction is $1.5\times 10^7 s^{-1}$ at 50°C and $4.5\times 10^7 s^{-1}$ at 100°C. Evaluate Arrhenius parameter and E_a.

Sol. $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\frac{(T_2 - T_1)}{T_1T_2}$

$$\log\frac{4.5\times 10^7}{1.5\times 10^7} = \frac{E_a}{2.303\times 8.314}\frac{(373-323)}{373\times 323}$$

$E_a = 2.2\times 10^4 \text{ J mol}^{-1}$

Again $k = Ae^{-E_a/RT}$

$\therefore 4.5\times 10^7 = Ae^{-2.2\times 10^4/8.314\times 373}$

$\therefore A = 5.42\times 10^{10}$

6. The rate constant for an isomerisatrion reaction $A \to B$ is 4.5×10^{-3} min^{-1}. If the initial concentration of A is 1 M. Calculate the rate of reaction after 1 hour.

Sol. For I order reaction $k = \frac{2.303}{t}\log\frac{a}{a-x}$

$$4.5\times 10^{-3} = \frac{2.303}{60}\log\frac{1}{a-x}$$

$\therefore (a - x) = 0.7634$

Then the rate after 60 minutes = k(a – x)

$= 4.5 \times 10^{-3} \times 0.7634 = 3.4354 \times 10^{-3}$ M min^{-1}

7. The data given below are for the rection NO and Cl_2 to form NOCl at 295 K

[Cl$_2$]	***[NO]***	***Initial rate mol L^{-1} Sec^{-1}***
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

(a) What is the order with respect to NO and Cl_2 in the reaction.

(b) Write rate expression

(c) Calculate the rate constant.

(d) Determine the rate when $[Cl_2]$ = 0.2 M and [NO] = 0.4 M.

Sol. The reaction is $2NO + Cl_2 \longrightarrow 2NOCl$

$\therefore \text{Rate} = k[Cl_2]^m[NO]^n$

$1\times 10^{-3} = [0.05]^m[0.05]^n$ (I)

$3\times 10^{-3} = [0.15]^m[0.05]^n$ (II)

$9\times 10^{-3} = [0.05]^m[0.15]^n$ (III)

Divide II by I,

$$\frac{3\times 10^{-3}}{1\times 10^{-3}} = \frac{[0.15]^m}{[0.05]^m}\frac{[0.05]^n}{[0.05]^n} \quad \therefore 3 = (3)^m \quad \therefore m = 1$$

Order with respect to Cl_2 is 1.

Divide III by I,

$$\frac{9\times 10^{-3}}{1\times 10^{-3}} = \frac{[0.05]^m}{[0.05]^m}\frac{[0.15]^n}{[0.05]^n} \quad \therefore 9 = (3)^n \quad \therefore n = 2$$

Order with respect to NO is 2.

(b) Rate = k $[Cl_2]$ $[NO]^2$

(c) Rate constant, $1\times 10^{-3} = k[0.05][0.05]^2$

$\therefore$ k = 8 lit^2 mol^{-2} sec^{-1}

(d)Rate = k $[Cl_2]$ $[NO]^2$ = 8 [0.2] $[0.4]^2$

= 0.256 mol lit^{-1} time^{-1}

8. In oxidation of oxalic acid when 2 ml of

$(COOH)_2 \longrightarrow CO + CO_2 + H_2O$

solution were withdrawn and titrated against standard solution of $KMnO_4$, the following results were obtained.

Time	***Vol. of KMnO$_4$ (in ml) required for the titration of oxalic acid***
0	22.0
300	17.0
450	15.0
600	13.4

Show that the reaction is of first order.

Sol. $k = \frac{2.303}{300}\log\frac{22}{17} = 8.6\times 10^{-4}$

$$k = \frac{2.303}{450}\log\frac{22}{15} = 8.34\times 10^{-4}$$

Since the value of k is the same hence the reaction is of Ist order.

9. A first order reaction has a specific reaction rate of 2.31×10^{-3} s^{-1}. Calculate $t_{1/2}$.

Sol. $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.31\times 10^{-3}} = 300$ sec

10. Show that the time required for the completion of 3/4th of reaction of Ist order is twice the time required for the completion of 1/2 of the reaction.

Sol. $t_{3/4} = \frac{2.303}{k}\log\frac{1}{(1-3/4)} = \frac{2.303}{k}\log 4$

$$t_{1/2} = \frac{2.303}{k}\log\frac{1}{(1-1/2)} = \frac{2.303}{k}\log 2$$

$$\frac{t_{3/4}}{t_{1/2}} = \frac{\log 4}{\log 2}; \qquad t_{3/4} = 2t_{1/2}$$

11. When the initial concentration is changed from 0.50 to 1.0 mole lit^{-1}, the time of half completion for a certain reaction is found to change from 50 sec. to 25 sec. Calculate the order of reaction.

Sol. $\frac{T_1}{T_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$

$\frac{50}{25} = \left(\frac{1.0}{0.5}\right)^{n-1}$ $2 = (2)^{n-1}$ or $2^1 = (2)^{n-1}$

$\therefore$ 1 = n – 1. Hence n = 1 + 1 = 2. Reaction is of second order.

12. Find the 3/4 th life ($t_{3/4}$) of a first order reaction. The rate constant $k = 7.4 \times 10^{-5}\ \text{sec}^{-1}$

Sol. $t_{\frac{3}{4}} = \frac{2.303}{k} \log \frac{a}{a-x} = \frac{2.303}{k} \log \frac{1}{1-\frac{3}{4}}$

$$t_{\frac{3}{4}} = \frac{2.303}{7.4 \times 10^{-5}} \log 4 = 1.84 \times 10^4\ \text{sec}$$

13. For a reaction it takes 10 min. for the initial concentration of 2.0 mol L^{-1} to become 1.0 mol L^{-1} and another 10 min to become 0.50 mol L^{-1}. Calculate the rate constant of the reaction.

Sol. The time taken for the concentration to fall to half concentration is constant in both the cases. Hence the reaction is of first order

$$\therefore \quad k = \frac{0.693}{t½} = \frac{0.693}{10} = 0.0693\ \text{min}^{-1}$$

14. The rate of reaction $2NO + Cl_2 \rightarrow 2NOCl$ is doubled when concentration of Cl_2 is doubled and it becomes 8 times when concentration of both NO and Cl_2 are doubled. Deduce the order of reaction.

Sol. Rate is doubled when $[Cl_2]$ is doubled

Rate w.r.t. $Cl_2 = k[Cl_2]^1$

Rate becomes 8 times when concentration of both NO and Cl_2 is doubled

$$\text{Rate} = k[Cl_2][NO]^x$$

$$8 = k[2][2]^x$$

$$\therefore x = 2$$

Rate law is $\text{Rate} = K[Cl_2][NO]^2$

Total order 1 + 2 = 3

15. A reaction that is of the first order with respect to reactant A has a rate constant of 6 min^{-1}. If we start with [A] = 5.0 mol L^{-1} when would [A] reach the value of 0.05 mol L^{-1}.

Sol. $k = \frac{2.303}{t} \log \frac{a}{a-x}$

$$6 = \frac{2.303}{t} \log \frac{5.0}{0.05}$$

$$t = \frac{2.303}{6\ \text{min}^{-1}} \log 100 = 46.06\ \text{sec}.$$

16. For the reaction, $2A + B + C \rightarrow A_2B + C$, rate law has been determined to be rate = $k[A][B]^2$. If the rate constant $k = 2.0 \times 10^{-6}\ \text{mol}^{-2}\ L^2\ \text{sec}^{-1}$, what will be initial rate of the reaction with [A] = 0.1 mol L^{-1} and [B] = 0.2 mol L^{-1} and [C] = 0.8 mol L^{-1}.

Sol. For $2A + B + C \rightarrow A_2B + C$

Rate = $k[A][B]^2$

$$= 2.0 \times 10^{-6} \times 0.1 \times [0.2]^2$$

$$= 8.0 \times 10^{-9}\ \text{mol}\ L^{-1}\ s^{-1}$$

17. At some temperature, the rate constant for the decomposition of HI on the surface of gold is 0.08 mol L^{-1} s^{-1}

$$2HI\ (g) \rightarrow H_2\ (g) + I_2\ (g)$$

what is the order of the reaction. How long will it take for the concentration of HI to drop from 1.50 M to 0.30 M.

Sol. From the unit of k, the reaction is of zero order.

$$k = \frac{C_0 - C}{2t}$$

$0.08 = \frac{1.5 - 0.30}{2t}$ or $t = \frac{1.2}{0.08 \times 2}$

$\therefore$ t = 7.5 s

18. The following data were obtained at a certain temperature for the decomposition of ammonia in contact with tungsten

p (mm Hg)	50	100	200
t½	3.64	1.82	0.90

Find the order of the reaction.

Sol. $\frac{(t½)_1}{(t½)_2} = \left(\frac{a_1}{a_2}\right)^{n-1}$ or $\frac{3.64}{1.82} = \left(\frac{100}{50}\right)^{n-1}$

$2 = (2)^{n-1}$ or $n - 1 = 1$

$\therefore$ n = 2

Exercise-1 | NCERT Based Questions

Very Short/Short Answer Questions

1 Hydrolysis of ethyl acetate with KOH is a second order reaction while with HCl, it is first order reaction., Why ?

2. A reaction, P + Q $\longrightarrow$ products, has rate law equation, rate = k $[P]^{1/3}$ $[Q]^3$. Suggest the suitable changes in initial concentration of P and Q so as to make the initial rate 16 times.

3. For the homogeneous decomposition of N_2O_5 into NO_2 and O_2

$$N_2O_5\,(g) \longrightarrow 4NO_2\,(g) + O_2\,(g)$$

$$\text{Rate} = -\frac{1}{2}\,\frac{d\,[N_2O_5]}{dt} = k\,[N_2O_5]$$

Find out the order of reaction with respect to N_2O_5.

4. Give an expression for time required to complete the n^{th} fraction of a first order reaction.

5. For the reaction, 2A + 2B $\longrightarrow$ Products, on doubling the [A] and keeping the [B] constant, the reaction rate increases by four times. On doubling the [B] and keeping the [A] constant, the reaction rate increases by two times. Write the rate law.

6. The reaction, $2NO(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$ and

$$2CO\,(g) + O_2\,(g) \longrightarrow 2CO_2\,(g)$$

look to be similar. Let the former is faster than the latter at the same temperature. Explain why.

7. In general, it is observed that the rate of a chemical reaction doubles with every 10° rise in temperature. If this generalisation holds good for the reaction in the temperature range 295 K to 305 K, then what would be the value of activation energy for this reaction ? (R = 8·314 $JK^{-1}\,mol^{-1}$).

8. The catalytic decomposition of hydrogen peroxide was studied by titrating it at different intervals with $KMnO_4$. Calculate the rate constant from the following data, assuming the reaction to be of first order:

t (sec)	0	600	1200
$KMnO_4$ (mL)	22·8	13·8	8·2

9. The decomposition of N_2O_5 in CCl_4 solution follows the first order rate law. The concentrations of N_2O_5 measured at different time internals are given below: Find the rate constant for decomposition.

Time in seconds (t)	0	80	160	410	600	1130	1720
$[N_2O_5]$ in mol/L	5.5	5.0	4.8	4.0	3.4	2.4	1.6

10. Nitrogen pentoxide decomposes according to equation:

$$2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$$

This first order reaction was allowed to proceed at 40°C and the data below were collected:

$[N_2O_5]$(M)	Time(min)
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

(a) Calculate the rate constant. Include units with your answer.

(b) What will be the concentration of N_2O_5 after 100 minutes?

(c) Calculate the initial rate of reaction.

11. (a) A reaction is first order in A and second order in B.

(i) Write differential rate equation.

(ii) How is rate affected when concentration of B is tripled?

(iii) How is rate affected when concentration of both A and B is doubled?

(b) What is molecularity of a reaction?

12. (a) For a reaction A + B → P, the rate law is given by,

$$r = k[A]^{1/2}[B]^2$$

What is the order of this reaction?

(b) A first order reaction is found to have a rate constant $k = 5.5 \times 10^{-14}\,s^{-1}$, Find the half life of the reaction.

Long Answer Questions

13. The Arrhenius equation is $k = k_\infty$ exp. ($-E_a/RT$). The energy of activation, E_a for two reactions X and Y are 100 kJ mol^{-1} and 125 kJ mol^{-1} respectively. At 227 °C, the rate constant k_x and k_y are equal. Draw systematic plots of log *k* versus 1/T, covering a temperature range below and above 227 °C.

14. (a) With the help of a labelled diagram explain the role of activated complex in a reaction.

(b) A first order reaction is 15% completed in 20 minutes. How long will it take complete 60% of the reaction?

15. (a) What is the physical significance of energy of activation? Explain with diagram

(b) In general, it is observed that the rate of a chemical reaction doubles with every 10 degree rise in temperature. If the generalization holds good for the reaction in the temperature range of 295 K to 305 K, what would be the value of activation energy for this reaction? [R = 8.314 J mol^{-1} K^{-1}]

16. (a) A reaction is second order in A and first order in B.

(i) Write the differential rate equation.

(ii) How is the rate affected on increasing the concentration of A three times?

(iii) How is the rate affected when the concentration of both A and B are doubled?

(b) A first order reaction takes 40 minutes for 30% decomposition. Calculate $t_{1/2}$ for this reaction.
(Given log 1.428 = 0.1548)

17. (a) For a first order reaction, show that time required for 99% copletion is twice the time required for the completion of 90% of reaction.

(b) Rate constant '*k*' of a reaction varies with temperature 'T' according to the equation:

$$\log k = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$$

Where E_a is the activation energy. When a graph is plotted for log *k* Vs. $\frac{1}{T}$, a straight line with a slope of – 4250 K is obtained. Calculate 'E_a' for the reaction. ($R = 8.314\ JK^{-1}mol^{-1}$)

Multiple Choice Questions

18. The rate of a reaction does not depend upon
(a) Temperature (b) Concentration
(c) Catalyst (d) None of these

19. Which of the following statements is incorrect?
(a) Activation energy for the forward reaction equals activation energy for the reverse reaction
(b) For a reversible reaction, an increase in temperature increases the reaction rate for both the forward and the backward reaction
(c) The larger the initial reactant concentration for a second order reaction, the shorter its half-life.
(d) When Δt is infinitesimally small, the average rate equals the instantaneous rate

20. Order of reaction can be
(a) 0 (b) fraction
(c) whole number (d) integer, fraction, zero

21. The rate of reaction between two reactants A and B decreases by a factor of 4 if the concentration of reactant B is doubled. The order of this reaction with respect to reactant B is:
(a) 2 (b) –2
(c) 1 (d) –1

22. The rate of reaction between A and B increases by a factor of 100, when the concentration of A is increased 10 folds, the order of reaction with respect to A is
(a) 10 (b) 1
(c) 4 (d) 2

23. For the reaction $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$, the rate law is rate $= k[H_2][Br_2]^{1/2}$. Which of the following statement is true about this reaction
(a) The reaction is a second order one
(b) Molecularity of the reaction is 3/2
(c) The unit of k is s^{-1}
(d) Molecularity of the reaction is 2

24. The following data are for the decomposition of ammonium nitrite in aqueous solution :

Vol. of N_2 in cc	Time (min)
6.25	10
9.00	15
11.40	20
13.65	25
35.65	Infinity

The order of rection is :
(a) zero (b) one
(c) two (d) three

Exercise-2 | CONCEPTUAL MCQs

1. In the reversible reaction

$$2\,NO_2 \xrightleftharpoons[k_2]{k_1} N_2O_4,$$

the rate of disappearance of NO_2 is equal to

(a) $\frac{2k_1}{k_2}[NO_2]^2$

(b) $2k_1[NO_2]^2 - 2k_2[N_2O_4]$

(c) $2k_1[NO_2]^2 - k_2[N_2O_4]$

(d) $(2k_1 - k_2)\,[NO_2]$

2. The rate of the reaction intermediates can be determined by the study of
(a) catalyst effects
(b) concentration of the reactants
(c) temperature effects
(d) solvent effects

3. $3A \longrightarrow 2B$, rate of reaction, $\frac{+d[B]}{dt}$ is equal to

(a) $-\frac{3}{2}\frac{d[A]}{dt}$ (b) $-\frac{2}{3}\frac{d[A]}{dt}$

(c) $-\frac{1}{3}\frac{d[A]}{dt}$ (d) $+2\frac{d[A]}{dt}$

4. Consider the chemical reaction,

$N_2\ (g) + 3H_2\ (g) \longrightarrow 2NH_3\ (g)$. The rate of this reaction can be expressed in terms of time derivative of concentration of N_2 (g), H_2 (g) or NH_3 (g). Identify the correct relationship amongst the rate expressions

(a) $\text{Rate} = \frac{-d[N_2]}{dt} = \frac{-1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

(b) $\text{Rate} = \frac{-d[N_2]}{dt} = -3\frac{d[H_2]}{dt} = 2\frac{d[NH_3]}{dt}$

(c) $\text{Rate} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

(d) $\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{d[H_2]}{dt} = \frac{d[NH_3]}{dt}$

5. The rate of a gaseous reaction is given by the expression k(A)(B). If the volume of the reaction vessel is suddenly reduced to 1/4 of the initial vol. the reaction rate relative to the original rate will be

(a) $\frac{1}{16}$ (b) $\frac{1}{8}$

(c) 8 (d) 16

6. The units for the rate constant of first order reaction is

(a) s^{-1} (b) $mol\,L^{-1}\,s^{-1}$

(c) $mol\,s^{-1}$ (d) $L\,mol^{-1}\,s^{-1}$

7. The rate constant of reaction depends upon

(a) temperature (b) pressure

(c) volume (d) All the these

8. The rate constant of a reaction is 10.8×10^{-5} $mol\,dm^{-3}\,s^{-1}$. The order of the reaction is

(a) zero (b) 1

(c) 2 (d) 3

9. If concentration of reactants is increased by 'x', then k becomes

(a) $\ln\frac{k}{x}$ (b) $\frac{k}{x}$

(c) $k+x$ (d) k

10. Rate constant in the case of first order reaction is

(a) inversely proportional to the concentration units

(b) independent of concentration units

(c) directly proportional to the concentration units

(d) inversely proportional to the square of the concentration units

11. The Arrhenius equation expressing the effect of temperature on the rate constant of the reaction is

(a) $k = e^{-E_a/RT}$ (b) $k = \frac{E_a}{RT}$

(c) $k = \log_e \frac{E_a}{RT}$ (d) $k = Ae^{-E_a/RT}$

12. For the following homogeneous reaction,

$A + B \xrightarrow{k} C$

the unit of rate constant is

(a) sec^{-1} (b) $sec^{-1}\,mol\,L^{-1}$

(c) $sec^{-1}\,mol^{-1}\,L$ (d) $sec^{-1}\,mol^{-2}\,L^2$

13. In Arrhenius plot, intercept is equal to

(a) $-\frac{E_a}{R}$ (b) ln A

(c) ln k (b) $\log_{10}a$

14. A chemical reaction was carried out at 300 K and 280 K. The rate constants were found to be k_1 and k_2 respectively. then

(a) $k_1 = 4k_1$ (b) $k_2 = 2k_1$

(c) $k_2 = 0.25\,k_1$ (d) $k_2 = 0.5\,k_1$

15. The decomposition of a substance follows first order kinetics. Its concentration is reduced to 1/8th of its initial value in 24 minutes. The rate constant of the decomposition process is

(a) $1/24\,min^{-1}$ (b) $\frac{0.692}{24}\,min^{-1}$

(c) $\frac{2.303}{24}\log\left(\frac{1}{8}\right)min^{-1}$ (d) $\frac{2.303}{24}\log\left(\frac{8}{1}\right)min^{-1}$

16. The rate of chemical reaction is doubled for every 10°C rise in temperature because of

(a) increase in the activation energy

(b) decrease in the activation energy

(c) increase in the number of molecular collisions

(d) increase in the number of activated molecules

17. The temperature coefficient of most of the reactions lies between

(a) 1 and 3 (b) 2 and 3

(c) 1 and 4 (d) 2 and 4

18. The velocity of a reaction is doubled for every 10°C rise in temp. If the temp. is raised to 50°C the reaction velocity increases by about

(a) 12 times (b) 16 times

(c) 32 times (d) 50 times

19. For the reaction $A \longrightarrow B$, the rate law expression is : rate = k [A]. Which of the following statements is incorrect?

(a) The reaction follows first order kinetics

(b) The $t_{1/2}$ of reaction depends on initial concentration of reactants

(c) k is constant for the reaction at a constant temperature

(d) The rate law provides a simple way of predicting the conc. of reactants and products at any time after the start of the reaction.

20. For a reaction of type $A + B \longrightarrow \text{products}$, it is observed that doubling concentration of A causes the reaction rate to be four times, but doubling amount of B does not affect the rate. The rate equation is

(a) Rate = k [A] [B] (b) $\text{Rate} = \frac{k}{4}[A]^2$

(c) $\text{Rate} = k\,[A]^2\,[B]$ (d) $\text{Rate} = k\,[A]^2\,[B]^2$

21. Select the rate law that corresponds to the data shown for the following reaction $A + B \longrightarrow C$

Expt. No.	*(A)*	*(B)*	*Initial Rate*
1	0.012	0.035	0.10
2	0.024	0.070	0.80
3	0.024	0.035	0.10
4	0.012	0.070	0.80

(a) Rate = $k[B]^3$ (b) Rate = $k[B]^4$
(c) Rate = $k[A][B]^3$ (d) Rate = $k[A]^2[B]^2$

22. The chemical reaction $2O_3 \longrightarrow 3O_2$ proceeds as follows :

$O_3 \xrightarrow{\text{Fast}} O_2 + O$; $O + O_3 \xrightarrow{\text{Slow}} 2O_2$ the rate law expression should be

(a) $r = k[O_3]^2$ (b) $r = k[O_3]^2[O_2]^{-1}$
(c) $r = k^3[O_3][O_2]^2$ (d) $r = [O_3][O_2]^2$

23. For the reaction $2H_2O_2 \longrightarrow 2H_2O + O_2$, $r = k[H_2O_2]$. It is

(a) zero order reaction (b) first order reaction
(c) second order reaction (d) third order reaction

24. If the rate of the reaction is equal to the rate constant, the order of the reaction is

(a) 1 (b) 2
(c) 3 (d) 0

25. For the reaction $A + B \longrightarrow C$, it is found that doubling the concentration of A increases the rate 4 times, and doubling the concentration of B doubles the reaction rate. What is the overall order of the reaction?

(a) 3/2 (b) 4
(c) 1 (d) 3

26. For a first-order reaction, the half life period is independent of

(a) initial concentration
(b) cube root of initial concentration
(c) first power of final concentration
(d) square root of final concentration

27. For a first order reaction, the plot of log K against 1/T is a straight line. The slope of the line is equal to

(a) $-\frac{E_a}{R}$ (b) $-\frac{2.303}{E_a R}$
(c) $-\frac{E_a}{2.303}$ (d) $\frac{-E_a}{2.303R}$

28. For a first order reaction, a plot of log (a – x) against time is a straight line with a negative slope equal to

(a) $\frac{-k}{2.303}$ (b) $-2.303k$
(c) $\frac{2.303}{k}$ (d) $-\frac{E_a}{2.303R}$

29. A first order reaction does not depend upon

(a) volume (b) pressure
(c) temperature (d) All of these

30. $2A \longrightarrow B + C$, would be a zero order reaction when

(a) the rate of reaction is proportional to square of conc. of A
(b) the rate of reaction remains same at any conc. of A
(c) the rate remains unchanged at any conc. of B and C
(d) the rate of reaction doubles if conc. of B is increased to double

31. Which of the following is correct for a first order reaction?

(a) $t_{1/2} \propto a$ (b) $t_{1/2} \propto 1/a$
(c) $t_{1/2} \propto a^0$ (d) $t_{1/2} \propto 1/a^2$

32. Order of reaction is decided by

(a) temperature
(b) mechanism of reaction as well as relative concentration of reactants
(c) molecularity
(d) pressure

33. Half-life of a reaction is found to be inversely proportional to the cube of initial concentration. The order of reaction is

(a) 4 (b) 3
(c) 5 (d) 2

34. The reaction $L \longrightarrow M$ is started with 10.0 g of L. After 30 and 90 minutes 5.0 g and 1.25 g of L respectively are left. The order of the reaction is

(a) 0 (b) 1
(c) 2 (d) 3

35. If initial concentration is reduced to 1/4th in a zero order reaction, the time taken for half the rection to complete

(a) remains same (b) becomes 4 times
(c) becomes one-fourth (d) doubles

36. A first order reaction is half-completed in 45 minutes. How long does it need for 99.9% of the reaction to be completed?

(a) 20 hours (b) 10 hours
(c) $7\frac{1}{2}$ hours (d) 5 hours

37. A reaction which is of first order w.r.t. reactant A, has a rate constant 6 min^{-1}. If we start with [A] = 0.5 mol L^{-1}, when would [A] reach the value of 0.05 mol L^{-1}

(a) 0.384 min (b) 0.15 min
(c) 3 min (d) 3.84 min

38. The rate constant for the reaction

$2N_2O_5 \longrightarrow 4NO_2 + O_2$, is 3.0×10^{-5} sec^{-1}. If the rate is 2.40×10^{-5} mol litre^{-1} sec^{-1}, then the concentration of N_2O_5 (in mol litre^{-1}) is

(a) 1.4 (b) 1.2
(c) 0.04 (d) 0.8

39. The reaction,

$$N_2O_5\ (\text{In } CCl_4) \longrightarrow 2NO_2 + \frac{1}{2}O_2\ (g)$$

is first order in N_2O_5 with rate constant $6.2 \times 10^{-4}\ s^{-1}$. What is the value of rate of reaction when $[N_2O_5] = 1.25\ mol\ L^{-1}$?

(a) $7.75 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$ (b) $6.35 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}$
(c) $5.15 \times 10^{-5}\ mol\ L^{-1}\ s^{-1}$ (d) $3.85 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$

40. The time taken for 90% of a first order reaction to complete is approximately

(a) 1.1 times that of half-life
(b) 2.2 times that of half-life
(c) 3.3 times that of half-life
(d) 4.4 times that of half-life

41. The rate of a certain reaction at different time intervals are as follows

Time	*Rate*
0 sec.	$1.8 \times 10^{-2}\ mol\ l^{-1}\ s^{-1}$
10sec.	$1.82 \times 10^{-2}\ mol\ l^{-1}\ s^{-1}$
20 sec.	$1.79 \times 10^{-2}\ mol\ l^{-1}\ s^{-1}$

The reaction is of

(a) zero order (b) first order
(c) second order (d) third order

42. A substance initial concentration (a) reacts according to zero order kinetics. What will be the time for the reaction to go to completion

(a) $\frac{a}{k}$ (b) $\frac{k}{a}$

(c) $\frac{a}{2k}$ (d) $\frac{2k}{a}$

43. The hypothetical reaction $A_2 + B_2 \longrightarrow 2AB$; follows the following mechanism $A_2 \xrightarrow{\text{Fast}} A + A$, $A + B_2 \xrightarrow{\text{Slow}} AB + B$, $A + B \xrightarrow{\text{Fast}} AB$.

The order of the overall reaction is

(a) 0 (b) 1
(c) 2 (d) 3/2

44. The reaction

$2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2$ is

(a) bimolecular and of second order
(b) unimolecular and of first order
(c) bimolecular and of first order
(d) bimolecular and of zero order

45. The given reaction

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

is an example of

(a) first order reaction (b) second order reaction
(c) third order reaction (d) None of these

46. Collision theory is applicable to

(a) first order reactions (b) zero order reactions
(c) bimolecular reactions (d) intra-molecular reactions

47. According to the collision theory of reaction rates, the rate of reaction increases with temperature due to

(a) greater number of collision
(b) higher velocity of reacting molecules
(c) greater number of molecules having the activation energy
(d) decrease in the activation energy

48. Which of the following has been used to explain the subject of chemical kinetics

(a) Collision theory of bimolecular reactions
(b) The activated complex theory
(c) Arrhenius equation
(d) All of these

49. Which of the following statements is incorrect?

(a) Activation energy for the forward reaction equals to activation energy for the reverse reaction
(b) For a reversible reaction, an increase in temperature increases the reaction rate for both the forward and the backward reaction
(c) The larger the initial reactant concentration for a second order reaction, the shorter is its half-life.
(d) When Δt is infinitesimally small, the average rate equals the instantaneous rate

50. Activation energy of a chemical reaction can be determined by

(a) evaluating rate constant at standard temperature
(b) evaluating velocities of reaction at two different temperatures
(c) evaluating rate constants at two different temperatures
(d) changing concentration of reactants

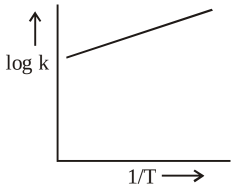
51. A catalyst increases rate of reaction by

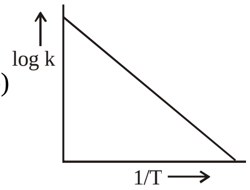
(a) decreasing enthalpy
(b) decreasing internal energy
(c) decreasing activation energy
(d) increasing activation energy

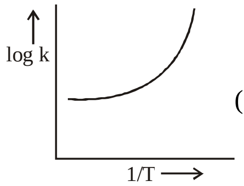
52. The activation energy for a simple chemical reaction $A \rightarrow B$ is E_a in forward direction. The activation energy for reverse reaction

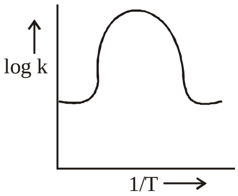
(a) is always less than E_a
(b) can be less than or more than E_a
(c) is always double of E_a
(d) is negative of E_a

53. A graph plotted between log k Vs 1/T for calculating activation energy is shown by

(a) 

(b) 

(c) 

(d) 

54. Activation energy of the reaction is
(a) the energy released during the reaction
(b) the energy evolved when activated complex is formed
(c) minimum amount of energy needed to overcome the potential barrier
(d) the energy needed to form one mole of the product

55. The activation energy for a hypothetical reaction, A $\rightarrow$ Product, is 12.49 kcal/mole. If temperature is raised from 295 to 305, the rate of reaction increased by
(a) 60% (b) 100%
(c) 50% (d) 20%

56. In a reaction, the threshold energy is equal to
(a) activation energy + normal energy of reactants
(b) activation energy - normal energy of reactants
(c) normal energy of reactants - activation energy
(d) average kinetic energy of molecules of reactants

57. When two reactants A and B are mixed to give products C and D, the reaction quotient, 'Q', at the initial stages of the reaction
(a) is zero (b) decreases with time
(c) is independent of time (d) increases with time

58. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation, k = A . e^{-E_a} Activation energy (E_a) of the reaction can be calculated by plotting
(a) k vs. $\frac{1}{\log T}$ (b) log k vs $\frac{1}{T}$
(c) log k vs. $\frac{1}{\log T}$ (d) k vs. T

59. The reaction $A \rightarrow B$ follows first order kinetics. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1 hour. What is the time taken for conversion of 0.9 mole of A to produce 0.675 mole of B?
(a) 0.5 hour (b) 0.25 hour
(c) 2 hours (d) 1 hour

60. According to the adsorption theory of catalysis, the speed of the reaction increases because
(a) in the process of adsorption, the activation energy of the molecules becomes large
(b) adsorption produces heat which increases the speed of the reaction
(c) adsorption lowers the activation energy of the reaction
(d) the concentration of product molecules at the active centres of the catalyst becomes high due to adsorption.

Exercise-3 | PAST COMPETITION MCQs

1. The reaction of hydrogen and iodine monochloride is given as: **[CBSE-PMT 2007]**

$$H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$$

The reaction is of first order with respect to $H_2(g)$ and ICI(g), following mechanisms were proposed.

Mechanism A:

$$H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$$

Mechanism B:

$$H_2(g) + ICl(g) \longrightarrow HI(g); \text{slow}$$
$$HI(g) + ICl(g) \longrightarrow HCl(g) + I_2(g); \text{fast}$$

Which of the above mechanism(s) can be consistent with the given information about the reaction?
(a) A and B both (b) neither A nor B
(c) A only (d) B only

2. In a first-order reaction A $\rightarrow$ B, if k is rate constant and inital concentration of the reactant A is 0.5 M, then the half-life is **[CBSE-PMT 2007]**
(a) $\frac{\log 2}{k}$ (b) $\frac{\log 2}{k\sqrt{0.5}}$ (c) $\frac{\ln 2}{k}$ (d) $\frac{0.693}{0.5k}$

3. If 60% of a first order reaction was completed in 60 minutes, 50% of the same reaction would be completed in aproximately **[CBSE-PMT 2007]**
(a) 45 minutes (b) 60 minutes
(c) 40 minutes (d) 50 minutes

4. The rate constants k_1 and k_2 for two different reactions are $10^{16} . e^{-2000/T}$ and $10^{15} . e^{-1000/T}$, respectively. The temperature at which $k_1 = k_2$ is : **[CBSE-PMT 2008]**
(a) 1000 K (b) $\frac{2000}{2.303}$K (c) 2000 K (d) $\frac{1000}{2.303}$K

5. The bromination of acetone that occurs in acid solution is represented by this equation.

$$CH_3COCH_3\,(aq) + Br_2\,(aq)$$
$$\rightarrow CH_3COCH_2Br\,(aq) + H^+\,(aq) + Br^-\,(aq)$$

These kinetic data were obtained for given reaction concentrations.

Initial Concentrations, M			Initial rate, disappearance of Br_2, Ms^{-1}
$[CH_3COCH_3]$	$[Br_2]$	$[H^+]$	
0.30	0.05	0.05	5.7×10^{-5}
0.30	0.10	0.05	5.7×10^{-5}
0.30	0.10	0.10	1.2×10^{-4}
0.40	0.05	0.20	3.1×10^{-4}

Based on given data, the rate equations is: **[CBSE-PMT 2008]**

(a) Rate = $k[CH_3COCH_3][H^+]$
(b) Rate = $k[CH_3COCH_3][Br_2]$
(c) Rate = $k[CH_3COCH_3][Br_2][H^+]^2$
(d) Rate = $k[CH_3COCH_3][Br_2][H^+]$

6. For the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$, **[CBSE-PMT 2009]**

$\frac{d[NH_3]}{dt} = 2 \times 10^{-4}$ mol L^{-1} s^{-1}, the value of $\frac{-d[H_2]}{dt}$ would be :

(a) 4×10^{-4} mol L^{-1} s^{-1} (b) 6×10^{-4} mol L^{-1} s^{-1}
(c) 1×10^{-4} mol L^{-1} s^{-1} (d) 3×10^{-4} mol L^{-1} s^{-1}

7. In the reaction **[CBSE-PMT 2009]**

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(l) + 3H_2O(l)$$

The rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as following:

(a) $\frac{d[Br_2]}{dt} = -\frac{5}{3}\frac{d[Br^-]}{dt}$ (b) $\frac{d[Br_2]}{dt} = \frac{5}{3}\frac{d[Br^-]}{dt}$

(c) $\frac{d[Br_2]}{dt} = \frac{3}{5}\frac{d[Br^-]}{dt}$ (d) $\frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$

8. Half life period of a first-order reaction is 1386 seconds. The specific rate constant of the reaction is : **[CBSE-PMT 2009]**

(a) 0.5×10^{-2} s^{-1} (b) 0.5×10^{-3} s^{-1}
(c) 5.0×10^{-2} s^{-1} (d) 5.0×10^{-3} s^{-1}

9. For the reaction A + B $\longrightarrow$ products, it is observed that: **[CBSE-PMT 2009]**

(1) On doubling the initial concentration of A only, the rate of reaction is also doubled and
(2) On doubling the initial concentrations of both A and B, there is a change by a factor of 8 in the rate of the reaction.

The rate of this reaction is given by:

(a) rate = $k[A][B]^2$ (b) rate = $k[A]^2[B]^2$
(c) rate = $k[A][B]$ (d) rate = $k[A]^2[B]$

10. For the reaction [$N_2O_5(g) \longrightarrow 2NO_2(g) + 1/2\ O_2(g)$] the value of rate of disappearance of N_2O_5 is given as 6.25×10^{-3} mol $L^{-1}s^{-1}$. The rate of formation of NO_2 and O_2 is given respectively as : **[CBSE-PMT 2010]**

(a) 6.25×10^{-3} mol $L^{-1}s^{-1}$ and 6.25×10^{-3} mol $L^{-1}s^{-1}$
(b) 1.25×10^{-2} mol $L^{-1}s^{-1}$ and 3.125×10^{-3} mol $L^{-1}s^{-1}$
(c) 6.25×10^{-3} mol $L^{-1}s^{-1}$ and 3.125×10^{-3} mol $L^{-1}s^{-1}$
(d) 1.25×10^{-2} mol $L^{-1}s^{-1}$ and 6.25×10^{-3} mol $L^{-1}s^{-1}$

11. For an endothermic reaction, energy of activation is E_a and enthalpy of reaction of ΔH (both of these in kJ/mol). Minimum value of E_a will be. **[CBSE-PMT 2010]**

(a) less than ΔH (b) equal to ΔH
(c) more than ΔH (d) equal to zero

12. During the kinetic study of the reaction, 2A + B $\rightarrow$ C + D, following results were obtained:

Run	[A](mol L^{-1})	[B](mol L^{-1})	Initial rate of formation of D (mol L^{-1} min^{-1})
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Based on the above data which one of the following is correct? **[CBSE-PMT 2010]**

(a) rate = $k[A]^2[B]$ (b) rate = $k[A][B]$
(c) rate = $k[A]^2[B]^2$ (d) rate = $k[A][B]^2$

13. The rate of the reaction $2NO + Cl_2 \longrightarrow 2NOCl$ is given by the rate equation rate = k $[NO]^2[Cl_2]$ **[CBSE-PMT 2010]**
The value of the rate constant can be increased by:

(a) increasing the concentration of NO.
(b) increasing the temperature.
(c) increasing the concentration of the Cl_2
(d) doing all of these

14. Which one of the following statements for the order of a reaction is incorrect ? **[CBSE-PMT 2011]**

(a) Order can be determined only experimentally.
(b) Order is not influenced by stoichiometric coefficient of the reactants.
(c) Order of reaction is sum of power to the concentration terms of reactants to express the rate of reaction.
(d) Order of reaction is always whole number.

15. The rate of the reaction $2N_2O_5 \rightarrow 4NO_2 + 2O_2$ can be written in three ways : **[CBSE-PMT 2011 M]**

$$\frac{-d[N_2O_5]}{dt} = k[N_2O_5]$$

$$\frac{d[NO_2]}{dt} = k'[N_2O_5]$$

$$\frac{d[O_2]}{dt} = k''[N_2O_5]$$

The relationship between k and k' and between k and k'' are :

(a) $k' = 2k$; $k' = k$ (b) $k' = 2k$; $k'' = k/2$
(c) $k' = 2k$; $k'' = 2k$ (d) $k' = k$; $k'' = k$

16. The unit of rate constant for a zero order reaction is **[CBSE-PMT 2011 M]**

(a) mol L^{-1} s^{-1} (b) L mol^{-1} s^{-1}

(c) L^2 mol^{-2} s^{-1} (d) s^{-1}

17. In a zero-order reaction for every 10° rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C, the rate of the reaction will become : **[CBSE-PMT 2012 S]**

(a) 256 times (b) 512 times (c) 64 times (d) 128 times

18. Activation energy (E_a) and rate constants (k_1 and k_2) of a chemical reaction at two different temperatures (T_1 and T_2) are related by : **[CBSE-PMT 2012 M]**

(a) $\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$ (b) $\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$

(c) $\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2}+\frac{1}{T_1}\right)$ (d) $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$

19. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20°C to 35°C? (R = 8.314 J mol^{-1} K^{-1}) **[NEET 2013]**

(a) 269 kJ mol^{-1} (b) 34.7 kJ mol^{-1}

(c) 15.1 kJ mol^{-1} (d) 342 kJ mol^{-1}

20. The formation of gas at the surface of tungsten due to adsorption is the reaction of order **[AIEEE 2002]**

(a) 0 (b) 1

(c) 2 (d) insufficient data.

21. Units of rate constant of first and zero order reactions in terms of molarity (M) unit are respectively **[AIEEE 2002]**

(a) sec^{-1}, $Msec^{-1}$ (b) sec^{-1}, M

(c) $Msec^{-1}$, sec^{-1} (d) M, sec^{-1}.

22. For the reaction $A + 2B \rightarrow C$, rate is given by $R = [A][B]^2$ then the order of the reaction is **[AIEEE 2002]**

(a) 3 (b) 6

(c) 5 (d) 7.

23. The differential rate law for the reaction **[AIEEE 2002]**

$H_2 + I_2 \rightarrow 2HI$ is

(a) $-\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = -\frac{d[HI]}{dt}$

(b) $\frac{d[H_2]}{dt} = \frac{d[I_2]}{dt} = \frac{1}{2}\frac{d[HI]}{dt}$

(c) $\frac{1}{2}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[I_2]}{dt} = -\frac{d[HI]}{dt}$

(d) $-2\frac{d[H_2]}{dt} = -2\frac{d[I_2]}{dt} = \frac{d[HI]}{dt}$

24. The integrated rate equation is **[AIEEE 2002]**

$Rt = \log C_0 - \log C_t$.

The straight line graph is obtained by plotting

(a) time Vs $\log C_t$ (b) $\frac{1}{\text{time}}$ Vs C_t

(c) time Vs C_t (d) $\frac{1}{\text{time}}$ Vs $\frac{1}{C_t}$

25. In respect of the equation $k = Ae^{-E_a/RT}$ in chemical kinetics, which one of the following statements is correct ? **[AIEEE 2003]**

(a) A is adsorption factor

(b) E_a is energy of activation

(c) R is Rydberg's constant

(d) k is equilibrium constant

26. The rate law for a reaction between the substances A and B is given by **[AIEEE 2003]**

Rate = k $[A]^n$ $[B]^m$

On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as

(a) (m + n) (b) (n – m)

(c) $2^{(n-m)}$ (d) $\frac{1}{2^{(m+n)}}$

27. For the reaction system :

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO, the rate of reaction will **[AIEEE 2003]**

(a) diminish to one-eighth of its initial value

(b) increase to eight times of its initial value

(c) increase to four times of its initial value

(d) diminish to one-fourth of its initial value

28. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is **[AIEEE 2004]**

(a) 7.5 minutes (b) 15 minutes

(c) 30 minutes (d) 60 minutes

29. The rate equation for the reaction $2A + B \rightarrow C$ is found to be : rate = k[A][B]. The correct statement in relation to this reaction is that the **[AIEEE 2004]**

(a) rate of formation of C is twice the rate of disappearance of A

(b) $t_{1/2}$ is a constant

(c) unit of k must be s^{-1}

(d) value of k is independent of the initial concentrations of A and B

30. Consider an endothermic reaction $X \rightarrow Y$ with the activation energies E_b and E_f for the backward and forward reactions, respectively. In general **[AIEEE 2005]**

(a) there is no definite relation between E_b and E_f

(b) $E_b = E_f$

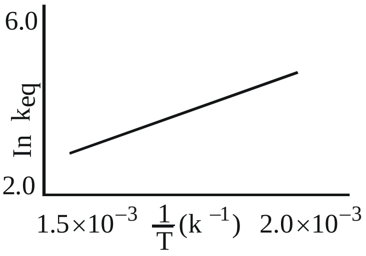
(c) $E_b > E_f$

(d) $E_b < E_f$

31. A reaction involving two different reactants can never be **[AIEEE 2005]**

(a) bimolecular reaction
(b) second order reaction
(c) first order reaction
(d) unimolecular reaction

32. A schematic plot of $\ln k_{eq}$ versus inverse of temperature for a reaction is shown below **[AIEEE 2005]**



The reaction must be
(a) highly spontaneous at ordinary temperature
(b) one with negligible enthalpy change
(c) endothermic
(d) exothermic

33. $t_{1/4}$ can be taken as the time taken for the concentration of a reactant to drop to $\frac{3}{4}$ of its initial value. If the rate constant for a first order reaction is K, the $t_{1/4}$ can be written as **[AIEEE 2005]**

(a) 0.75/k (b) 0.69/k
(c) 0.29/k (d) 0.10/k

34. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will **[AIEEE 2006]**

(a) increase by a factor of 4
(b) double
(c) remain unchanged
(d) triple

35. Rate of a reaction can be expressed by Arrhenius equation as : **[AIEEE 2006]**

$$k = A\,e^{-E/RT}$$

In this equation, E represents

(a) the total energy of the reacting molecules at a temperature, T

(b) the fraction of molecules with energy greater than the activation energy of the reaction

(c) the energy above which all the colliding molecules will react

(d) the energy below which colliding molecules will not react

36. The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr :

$$NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$$

$$NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$$

If the second step is the rate determining step, the order of the reaction with respect to NO(g) is **[AIEEE 2006]**

(a) 3 (b) 2
(c) 1 (d) 0

37. The energies of activation for forward and reverse reactions for $A_2 + B_2 \rightleftharpoons 2AB$ are 180 kJ mol^{-1} and 200 kJ mol^{-1} respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol^{-1}. The enthalpy change of the reaction ($A_2 + B_2 \rightarrow 2AB$) in the presence of a catalyst will be (in kJ mol^{-1}) **[AIEEE 2007]**

(a) 20 (b) 300 (c) 120 (d) 280

38. Consider the reaction, $2A + B \rightarrow$ products. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is **[AIEEE 2007]**

(a) s^{-1} (b) L mol^{-1} s^{-1}
(c) no unit (d) mol L^{-1} s^{-1}.

39. A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial velocity is ten times the permissible value, after how many days will it be safe to enter the room? **[AIEEE 2007]**

(a) 100 days (b) 1000 days
(c) 300 days (d) 10 days.

40. For a reaction $\frac{1}{2}A \rightarrow 2B$, rate of disappearance of 'A' is related to the rate of appearance of 'B' by the expression **[AIEEE 2008]**

(a) $-\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$ (b) $-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$

(c) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$ (d) $-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$

41. The half life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301) **[AIEEE 2009]**

(a) 23.03 minutes (b) 46.06 minutes
(c) 460.6 minutes (d) 230.03 minutes

42. The time for half life period of a certain reaction $A \longrightarrow$ Products is 1 hour. When the initial concentration of the reactant 'A', is 2.0 mol L^{-1}, how much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1} if it is a zero order reaction ? **[AIEEE 2010]**

(a) 4 h (b) 0.5 h (c) 0.25 h (d) 1 h

43. Consider the reaction :

$$Cl_2(aq) + H_2S(aq) \rightarrow S(s) + 2H^+(aq) + 2Cl^-(aq)$$

The rate equation for this reaction is

rate = $k[Cl_2][H_2S]$

Which of these mechanisms is/are consistent with this rate equation? **[AIEEE 2010]**

A. $Cl_2 + H_2S \rightarrow H^+ + Cl^- + Cl^+ + HS^-$ (slow)

$Cl^+ + HS^- \rightarrow H^+ + Cl^- + S$ (fast)

B. $H_2S \rightleftharpoons H^+ + HS^-$ (fast equilibrium)

$Cl_2 + HS^- \rightarrow 2Cl^- + H^+ + S$ (Slow)

(a) B only (b) Both A and B

(c) Neither A nor B (d) A only

44. A reactant (A) froms two products : **[AIEEE 2011RS]**

$A \xrightarrow{k_1} B$, Activation Energy Ea_1

$A \xrightarrow{k_2} C$, Activation Energy Ea_2

If $Ea_2 = 2\,Ea_1$, then k_1 and k_2 are related as :

(a) $k_2 = k_1 e^{Ea_1/RT}$ (b) $k_2 = k_1 e^{Ea_2/RT}$

(c) $k_1 = Ak_2 e^{Ea_1/RT}$ (d) $k_1 = 2k_2 e^{Ea_2/RT}$

45. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about : **[AIEEE 2011]**

(a) 10 times (b) 24 times (c) 32 times (d) 64 times

46. For a first order reaction (A) → products the concentration of A changes from 0.1 M to 0.025 M in 40 minutes.

The rate of reaction when the concentration of A is 0.01 M is : **[AIEEE 2012]**

(a) 1.73×10^{-5} M/min (b) 3.47×10^{-4} M/min

(c) 3.47×10^{-5} M/min (d) 1.73×10^{-4} M/min

47. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be : ($R = 8.314\ JK^{-1}\ mol^{-1}$ and $\log 2 = 0.301$) **[JEE Main 2013]**

(a) 53.6 kJ mol^{-1} (b) 48.6 kJ mol^{-1}

(c) 58.5 kJ mol^{-1} (d) 60.5 kJ mol^{-1}

48. Consider a reaction $aG + bH \rightarrow$ Products. When concentration of both the reactants *G* and *H* is doubled, the rate increases by eight times. However, when concentration of *G* is doubled keeping the concentration of *H* fixed, the rate is doubled. The overall order of the reaction is **[IIT-JEE 2007]**

(a) 0 (b) 1

(c) 2 (d) 3

49. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio (k_1/k_0) of the rate constant for first order (k_1) and zero order (k_0) of the reaction is **[IIT-JEE 2008]**

(a) 0.5 $mol^{-1}\ dm^3$ (b) 1.0 mol dm^{-3}

(c) 1.5 mol dm^{-3} (d) 2.0 $mol^{-1}\ dm^3$

50. For a first order reaction A→P, the temperature (T) dependent rate constant (*k*) was found to follow the equation $\log k = -(2000)\frac{1}{T} + 6.0$. The pre-exponential factor A and the activation energy E_a, respectively, are **[IIT-JEE 2009]**

(a) $1.0 \times 10^6\ s^{-1}$ and 9.2 kJ mol^{-1}

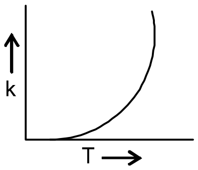
(b) 6.0 s^{-1} and 16.6 kJ mol^{-1}

(c) $1.0 \times 10^6\ s^{-1}$ and 16.6 kJ mol^{-1}

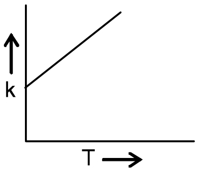
(d) $1.0 \times 10^6\ s^{-1}$ and 38.3 kJ mol^{-1}

51. Plots showing the variation of the rate constant (*k*) with temperature (*T*) are given below. The plot that follows Arrhenius equation is **[IIT-JEE 2010]**

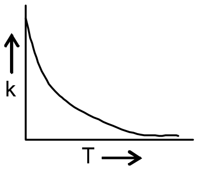
(a)



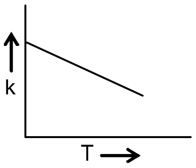
(b)



(c)



(d)



Exercise-4 | Applied MCQs

1. Two substances R and S decompose in solution independently, both following first order kinetics. The rate constant of R is twice that of S. In an experiment, the solution initially contained 0.5 millimoles of R and 0.25 millimoles of S. The molarities of R and S will be equal just at the end of time equal to

(a) twice the half life of R (b) twice the half life of S
(c) the half life of S (d) the half life of R

2. For a reaction, the rate constant at particular temperature has a value of 2.0×10^{-3} mol $lit^{-1}s^{-1}$. The order of the reaction is

(a) –1 (b) 0
(c) 1 (d) 2

3. For the gas phase decomposition $A \rightarrow 2B$, the rate constant is 6.93×10^{-3} min^{-1} at 300 K. The percentage of a remaining at the end of 300 minutes is

(a) 75 (b) 50
(c) 25 (d) 12.5

4. For a first order reaction $t_{0.75}$ is 1368 seconds, therefore, the specific rate constant in sec^{-1} is

(a) 10^{-3} (b) 10^{-2}
(c) 10^{-9} (d) 10^{-5}

5. Consider the following reactions at 300 K

$X \xrightarrow{\qquad} Y$ (uncatalysed reaction)

$X \xrightarrow{\text{catalyst}} Y$ (catalysed reaction)

The energy of activation is lowered by 0.314 KJ mol^{-1} for the catalysed reaction. The rate of reaction is

(a) 38 times
(b) 15 times
(c) 25 times
(d) 22 times that of uncatalysed reaction.

6. For a reaction $A \rightarrow B$, the rate increases by a factor of 2.25 when the concentration of A is increased by 1.5. What is the order of the reaction?

(a) 3 (b) 0
(c) 2 (d) 1

7. The reactions rate $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ was measured $\frac{d[NH_3]}{dt} = 2 \times 10^{-4}$ mol sec^{-1}. The rates of reactions expressed in terms of N_2 and H_2 are

	Rate in terms of N_2. ($mol\ L^{-1}sec^{-1}$)	**Rate in terms of H_2 ($mol\ L^{-1}sec^{-1}$)**
(a)	2×10^{-4}	2×10^{-4}
(b)	3×10^{-4}	1×10^{-4}
(c)	1×10^{-4}	3×10^{-4}
(d)	2×10^{-1}	2×10^{-3}

8. The rate constant , the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are 3×10^{-4} s^{-1},104.4kJ /mol and 6×10^{14} s^{-1} respectively. The value of the rate constant as $T \rightarrow \infty$ is

(a) 2.0×10^{18} s^{-1} (b) 6.0×10^{14} s^{-1}
(c) Infinity (d) 3.6×10^{30} s^{-1}

9. A substance 'A' decomposes in solution following first order kinetics. Flask I contains l L of a 1M solution of A and flask II contains 100 ml of a 0.6 M solution. After 8 hours the concentration of A in flask I has become 0.25. What will be the time taken for concentration of A in flask II to become 0.3M ?

(a) 0.4 h
(b) 2.4 h
(c) 4.0 h
(d) Can't be calculated since rate constant is not given

10. A reaction rate constant is given by $k = 1.2 \times 10^{14} e^{-25000/RT} sec^{-1}$. It means

(a) log k versus log T will give a straight line with a slope as –25000
(b) log k versus T will give a straight line with slope as 25000
(c) log k versus log 1/T will give a straight line with slope as –25000
(d) log k versus 1/T will give a straight line

11. Consider a general chemical change 2A + 3B → products. The rate with respect to A is r_1 and that with respect to B is r_2. The rates r_1 and r_2 are related as

(a) $3r_1 = 2r_2$ (b) $r_1 = r_2$
(c) $2r_1 = 3r_2$ (d) $r_1^2 = 2r_2^2$

12. In case of first order reaction,the ratio of the time required for 99.9% completion to 50% completion is

(a) 2 (b) 5
(c) 10 (d) None of these

13. For the exothermic reaction $A + B \rightarrow C + D, \Delta H$ is the heat of reaction and E_a is the energy of activation. The energy of activation for the formation of A + B will be

(a) E_a (b) ΔH
(c) $E_a + \Delta H$ (d) $\Delta H - E_a$

14. The following statement(s) is (are) correct :

(i) A plot of log k_p versus 1/T is linear

(ii) A plot of log [X] versus time is linear for a first order reaction, X → P

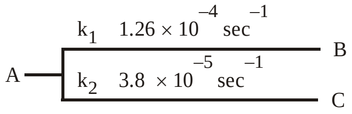
(iii) A plot of log p versus 1/T is linear at constant volume

(iv) A plot of p versus 1/V is linear at constant temperature

(a) (i) only (b) (ii) only

(c) (i) & (iv) (d) (i), (ii) & (iv)

15. The decomposition of A follows two parallel first order reactions



The percentage distribution of B and C are

(a) 90 % B and 10 % C

(b) 80 % B and 20 % C

(c) 60 % B and 40 % C

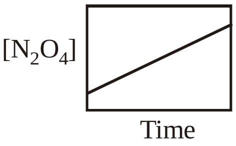
(d) 76.83 of B and 23.17 % C

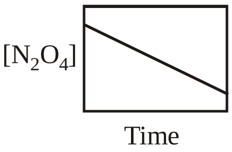
16. In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2 x 10^4 sec. The rate constant of reaction in sec^{-1} is:

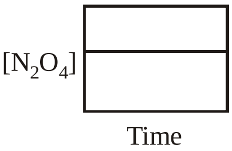
(a) 2×10^4 (b) 3.45×10^{-5}

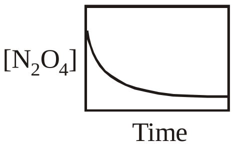
(c) 1.386×10^{-4} (d) 2×10^{-4}

17. Which of the following graphs best describes the rate at which N_2O_4 decomposes to NO_2 if the reaction is first-order in N_2O_4?

(a)


(b)


(c)


(d)


18. The rate constant for a zero-order reaction is

(a) $k = \frac{C_0}{2t}$ (b) $k = \frac{C_0 - C_t}{t}$

(c) $k = \ln\frac{C_0 - C_t}{2t}$ (d) $k = \frac{C_0}{2t}$

19. The rate expression for the reaction A(g) + B(g)→C(g) is rate $= kC_A^2 C_B^{1/2}$. What changes in the initial concentrations of A and B will cause the rate of reaction to increase by a factor of eight?

(a) $C_A \times 2; C_B \times 2$ (b) $C_A \times 2; C_B \times 4$

(c) $C_A \times 1; C_B \times 4$ (d) $C_A \times 4; C_B \times 1$

20. For a reaction following first-order kinetics, which of the following statements are correct?

(a) The time taken for the completion of 50% of the reaction is twice of $t_{1/2}$

(b) A plot of the reciprocal of the concentration of the reactants against time gives a straight line.

(c) The degree of dissociation is equal to $1 - e^{-kt}$.

(d) A plot of $[A]_0/[A]$ versus time gives a straight line.

21. An endothermic reaction has a positive internal energy change ΔU. In such a case, what is the minimum value that the activation energy can have ?

(a) ΔU (b) ΔU = ΔH + ΔnRT

(c) ΔU=ΔH–ΔnRT (d) $\Delta U = E_a + RT$

22. At 400 K the half-life of a sample of a gaseous compound initially at 56.0 kP_a is 340 s. When the pressure is 28.0 kP_a, the half-life is 170s. The order of the reaction is

(a) 0 (b) 2

(c) 1 (d) ½

23. Consider the reaction mechanism

$$A_2 \rightleftharpoons 2A \text{ (fast)}$$
$$A + B \rightarrow P \text{ (slow)}$$

where A is the intermediate. The rate for the reaction is

(a) $k_2[A][B]$ (b) $k_2k^{1/2}[A_2]^{1/2}[B]$

(c) $k_2k^{1/2}[A][B]$ (d) $k_2k^{1/2}[A]^2[B]$

24. $N_2O_2(g) \rightarrow 2NO(g)$ is a first-order reaction in terms of the concentration of $N_2O_2(g)$. Which of the following is valid, $[N_2O_2]$ being constant ?

(a) $[NO] = [N_2O_2]_0 e^{-kt}$ (b) $[NO] = [N_2O_2]_0 (1-e^{-kt})$

(c) $[NO] = [N_2O_2]_0 (e^{-kt}-1)$ (d) $[NO] = [N_2O_2]_0 (1-e^{-kt})$

25. The reaction A(g) + 2B(g) → C(g) + D(g) is an elementary process. In an experiment involving this reaction, the initial partial pressures of A and B are $p_A = 0.60$ atm and $p_B = 0.80$ atm respectively. When $p_C = 0.20$ atm, the rate of the reaction relative to the initial rate is

(a) 1/6 (b) 1/12

(c) 1/36 (d) 1/18

26. In acidic medium the rate of reaction between BrO_3^- and Br^- ion is given by the expression

$$\frac{d(BrO_3^-)}{dt} = k[BrO_3^-][Br^-][H^+]^2$$

Which of the following is correct ?

(a) Doubling the concentration of H^+ ions will increase the reaction rate by 4 times.

(b) Rate constant of overall reaction is 4 sec^{-1}.

(c) Rate of reaction is independent of the conc. of acid

(d) The change in pH of the solution will not affect the rate.

27. The rate constant of the reaction increases by

(a) carrying out the reaction for longer period

(b) increasing the temperature

(c) increasing the conc. of reactants

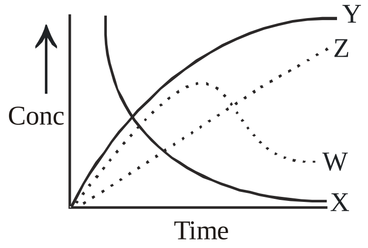
(d) None is correct.

28. The activation energy of the reaction A $\longrightarrow$ X is 12.49 kcal mol^{-1}. If temperature is raised to 305 K from 295 K, the reaction rate increases by

(a) ≈ 50 % (b) ≈ 60 %

(c) ≈ 100 % (d) unpredictable.

29. For the reaction A + B $\longrightarrow$ C + D. The variation of the concentration of the products is given by the curve



(a) Z (b) Y

(c) W (d) X

30. A gaseous reaction

$$X_2(g) \longrightarrow Y + \frac{1}{2}Z(g)$$

There is increase in pressure from 100 mm Hg to 120 mm Hg in 5 minutes. The rate of disappearance of X_2 is

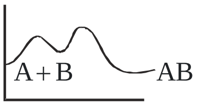
(a) 8 mm Hg min^{-1} (b) 2 mm Hg min^{-1}

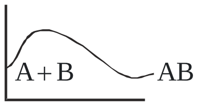
(c) 16 mm Hg min^{-1} (d) 4 mm Hg min^{-1}

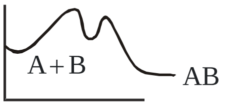
31. For an exothermic chemical process occuring in two steps as

(i) $A + B \longrightarrow X$ (slow) (ii) $X \longrightarrow AB$ (fast)

The progress of the reaction can be best described by

(a)


(b)


(c)


(d) None of these

32. The rate of certain reaction increases by 2.3 times when the temperature is raised from 300 K to 310 k. If k is the rate constant at 300 K then rate constant at 310 k will be

(a) $3\ k^2$ (b) 2.3 k

(c) 2 k (d) k

33. The half life period for catalytic decomposition of AB_3 at 50 mm Hg is 4 hrs and at 100 mm Hg it is 2 hrs. The order of reaction is

(a) 1 (b) 3

(c) 2 (d) 0

34. For a zero order reaction, the plot of conc. Vs time is linear with

(a) –ve slope and non zero intercept

(b) +ve slope and zero intercept

(c) –ve slope and zero intercept

(d) + ve slope and non zero intercept

35. The half life decomposition of gaseous CH_3CHO at constant temperature but at initial pressure of 364 mm and 170 mm of Hg were 410 sec, and 880 sec respectively. The order of the reaction is

(a) 1.0 (b) 3.0

(c) 2.0 (d) 1.5

36. The racemisation of α - pinene is first order reaction. In the gas the specific reaction rate was found to be 2.2×10^{-5} mm Hg^{-1} at 457.6 K and 3.07×10^{-3} mm Hg^{-1} at 510.1 K. The energy of activation is

(a) $K(510.1-457.6)\ln(3.07\times10^{-3}/2.2\times10^{-5})$

(b) 3.048×10^{-3}

(c) $\ln 2.2\times10^{-5}\times457.6$ k cal.

(d) $(510.1\times457.6/52.5)\,R\ln(307)/2.2)$ cal.

37. The half life of the first order reaction

$$CH_3.CHO\ (g) \longrightarrow CH_4\ (g) + CO\ (g)$$

If initial pressure of CH_3CHO (g) is 80 mm Hg and the total pressure at the end of 20 minutes is 120 mm Hg

(a) 80 min (b) 120 min

(c) 20 min (d) 40 min

38. A drop of a solution (volume = 0.05 ml) contains 6×10^{-7} mol of H^+. If rate of disappearnace of H^+ is 6.0×10^{5} mol $lit^{-1}\ s^{-1}$, how long will it take for the H^+ in the drop to disappear ?

(a) 2.0×10^{-2} s (b) 2.0×10^{-8} s

(c) 8.0×10^{-8} s (d) 6.0×10^{-6} s

39. The rate constant for two parallel reactions were found to be $1.0\times10^{-2}\ dm^3\ mol^{-1}s^{-1}$ and $3.0\times10^{-2}\ dm^3\ mol^{-1}s^{-1}$. If the corressponding energies of activation of the parallel reactions are 60.0 kJ mol^{-1} and 70.0 kJ mol^{-1} respectively what is the apparent overall energy of activation

(a) 130.0 kJ mol^{-1} (b) 65.0 kJ mol^{-1}

(c) 67.5 kJ mol^{-1} (d) 100.0 kJ mol^{-1}

Hints & Solutions

EXERCISE 1

2. Increase the concentration of P to eight times and that of Q to two times.

3. The order of reaction with respect to N_2O_5 is one.

4. $t_{1/n} = \frac{2\times303}{k}\log\left(\frac{1}{1-1/n\div}\right)$

5. Rate = $k\,[A]^2\,[B]$.

7. $E_a = 51{\cdot}86$ kJ mol^{-1}.

8. $k = 8{\cdot}455 \times 10^{-4}\ s^{-1}$.

9. $k(\text{at } 410\ s) = 0.77 \times 10^{-4} s^{-1}$.

18. **(d)** **19.** **(a)** **20.** **(d)** **21.** **(b)** **22.** **(d)**

23. **(d)** **24.** **(b)**

EXERCISE 2

1. **(b)** $2\,NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$,

For forward reaction rate = $-\frac{1}{2}\frac{dNO_2}{dt} = \frac{dN_2O_4}{dt}$

$= k_1[NO_2]^2$

For backward reaction

Rate = $-\frac{dN_2O_4}{dt} = \frac{1}{2}\frac{dNO_2}{dt} = k_2[N_2O_4]$.

Rate of disappearance of NO_2 = (Rate of disapperance of NO_2 – Rate of appearence of NO_2)

$= 2k_1[NO_2]^2 - 2k_2[N_2O_4]$.

2. **(b)** By concentration of reactants.

3. **(b)** $3A \to 2B$

Rate of reaction $-\frac{1}{3}\frac{dA}{dt} = \frac{1}{2}\frac{dB}{dt}$ or $-\frac{2}{3}\frac{dA}{dt} = \frac{dB}{dt}$

4. **(a)** $N_2\,(g) + 3H_2\,(g) \longrightarrow 2NH_3\,(g)$

Rate = $-\frac{dN_2}{dt} = -\frac{1}{3}\frac{dH_2}{dt} = \frac{1}{2}\frac{dNH_3}{dt}$

5. **(d)** If volume is reduced to 1/4th concentration will be increased 4 times hence reaction rate will increase by 16. Rate = k[A][B].

New rate = k[4A][4B] = 16k[A][B]

6. **(a)** Remember units of rate constant =(Mol L^{-1})$^{1-n}$. time^{-1}. For 1st order n = 1 ∴ units = time^{-1}.

7. **(a)** Rate constant depends upon temperature see Arrhenius equation.

8. **(a)** mol dm^{-3} s^{-1} units are for zero order.

9 **(d)** Rate constant does not change with concentration.

10. **(b)** k = time^{-1} for 1st order. It is independent of concentration terms.

11. **(d)** $k = Ae^{-E_a/RT}$

12. **(c)** k = (mol lit^{-1})$^{1-n}$ time^{-1}. For given reaction n = 2.

∴ k = mol^{-1} lit sec^{-1}

13. **(b)** $\ln k = \ln A - \frac{E_a}{RT}$, intercept is ln A.

14. **(c)** The rate constant doubles for 10° C rise in temperature.

For 20° C rise, the rate constant will be 4 times

∴ $k_1 = 4k_2$ or $k_2 = 0.25\,K_1$

15. **(d)** $k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{24}\log\frac{1}{\frac{1}{8}} = \frac{2.303}{24}\log 8$

16. **(d)** With temperature the number of activated molecules increase.

17. **(b)** Between 2 and 3.

18. **(c)** There are 5 tens hence $(2)^5 = 32$.

19. **(b)** For 1st order rection $t_{1/2}$ independent of initial concentration.

20. **(c)** Let the rate law equation be $r = k[A]^x[B]^y$................(1)

when A = 2A, $4r = k[2A]^x[B]^y$........................(2)

Divide(2) by (1) $\frac{4r}{r} = \frac{k[2A]^x[B]^y}{k[A]^x[B]^y}$

∴ $4 = (2)^x$, Hence $x = 2$

when B = 2B, $r = k[A]^x\,[2B]^y$........................(3)

∴ 1 = Divide (3) by (1) $\frac{r}{r} = \frac{k[A]^x[2B]^y}{k[A]^x[B]^y}\,(2)^y$ ∴ $y = 0$

∴ Rate $= k[A]^2[B]^0$

21. (a) Let the rate law be $r = k[A]^x[B]^y$

Divide (3) by (1) $\frac{0.10}{0.10} = \frac{[0.024]^x[0.035]^y}{[0.012]^x[0.035]^y}$

$\therefore 1 = [2]^x, x = 0$

Divide (2) by (3) $\frac{0.80}{0.10} = \frac{[0.024]^x[0.070]^y}{[0.024]^x[0.035]^y}$

$\therefore 8 = (2)^y, y = 3$

Hence rate equation, $R = k[A]^0[B]^3 = k[B]^3$

22. (b) $O_3 \xrightarrow{\text{Fast}} O_2 + O;\ O + O_3 \xrightarrow{\text{Slow}} 2O_2$

$k = \frac{[O_2][O]}{[O_3]}$ (I), Rate = $k'[O_3][O]$ put [O] from (I)

$r = \frac{k'[O_3]k[O_3]}{[O_2]} = k[O_3]^2[O_2]^{-1}$

Note intermediates are never represented in rate law equation.

23. (b) 1st order reaction.

24. (d) Rate = $k[A]^0$

$\therefore$ Rate = k for zero order.

25. (d) Order with respect to A is 2 and B is 1.

$\therefore$ Order of reaction = 2+1 = 3

26. (a) $t_{1/2}$ for 1st order is independent of initial concentration.

27. (d) $k = Ae^{-E_a/RT}$ $\log k = \log A - \frac{E_a}{2.303R}\cdot\frac{1}{T}$

Equation of straight line slope = $\frac{-E_a}{2.303R}$.

28. (a) $t = \frac{2.303}{k}\log\frac{a}{a-x}$

or $t = \frac{2.303}{k}\log a - \frac{2.303}{k}\log(a-x)$

29. (d) Order of reaction is independent of given factors.

30. (b) For zero order the rate does not change with concentration.

31. (c) $t_{1/2} \propto a^o$. $t_{1/2}$ is independent of initial concentration.

32. (b) The order of a chemical reaction is given by concentration of reactants appearing in the lowest step.

33. (a) $t_{1/2} \propto a^{1-n}$ $t_{1/2} \propto \frac{1}{a^3}$ hence n = 4.

34. (b) After every 30 minutes the amount is reduced to $\frac{1}{2}$ therefore $t_{1/2}$ is 30 minutes. In 90 minutes the amount is reduced to $\frac{1}{8}$ i.e. $\frac{1}{2^n}$. Here n = 3. True for 1st order reaction.

35. (c) $t = \frac{a}{k}$ for zero order, $t = \frac{1}{4k}$ and $t_1 = \frac{1}{2k}$, $\therefore t_1 = 2t$

36. (c) $k = \frac{0.693}{45}$ further $t = \frac{2.303}{0.693}\times 45 \log\frac{100}{100-99.9}$

$= \frac{2.303\times 45\times 3}{0.693} = 7\frac{1}{2}$ hours.

37. (a) $t = \frac{2.303}{k}\log\frac{a}{a-x} = \frac{2.303}{6}\log\frac{0.5}{0.05} = 0.384\,\text{min}$.

38. (d) Rate = $k[N_2O_5]$;

$2.4\times 10^{-5} = 3.0\times 10^{-5}[N_2O_5]$

$\therefore [N_2O_5] = 0.8$

39. (a) Rate = $k[N_2O_5]$

$= 6.2\times 10^{-4}\times 1.25 = 7.75\times 10^{-4}\ \text{mol L}^{-1}\text{s}^{-1}$

40. (c) $t_{90\%} = \frac{2.303}{k}\log\frac{100}{100-90}$ (I)

$t_{50\%} = \frac{2.303}{k}\log\frac{100}{100-50}$ (II)

Dividing $\frac{t_{90\%}}{t_{50\%}} = \frac{\log 10}{\log 2}$ $\therefore t_{90\%} = 3.3t_{50\%}$

41. (a) Since rate is constant throughout. It is zero order.

42. (a) For zero order reaction $t_{\text{completion}} = a/k$.

43. (d) $A_2 + B_2 \longrightarrow 2AB$; $A_2 \longrightarrow A + A$ (Fast);

$A + B_2 \longrightarrow AB + B$ (Slow)

Rate law = $k[A][B_2]$ put value of [A] from Ist reaction since A is intermediate $\sqrt{k[A_2]} = A$

$\therefore$ Rate law equation = $K\sqrt{k[A_2]}[B_2]$

$\therefore$ Order = $\frac{1}{2} + 1 = \frac{3}{2}$

44. (c) It is bimolecular first order reaction since Rate $\propto [N_2O_5]$

45. (c) Third order

46. (c) Applicable to bimolecular reactions.

47. (a)

48. (d) All the statements are correct (see text).

49. (a) $E_{a(F.R.)} \neq E_{a(B.R.)}$ E_a can be calculated.

50. (c) $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \frac{(T_2 - T_1)}{T_1 T_2}$; E_a can be calculated.

51. (c) Activation energy is lowered in presence of +ve catalyst.

52. (b) Since the nature of reaction (i.e. exothermic or endothermic) not given therefore E_a for reverse reaction can be more or less.

53. (b) In accordance with Arrhenius equation.

54. (c) Statement (c) see text.

55. (b) For 10°C rise of temperature the rate is almost doubled.

56. (a) Threshold Energy = Energy of activation + Internal energy

57. (d) $Q = \frac{[C][D]}{[A][B]} = \frac{[\text{Products}]}{[\text{Reactants}]}$; Q = increases with time

58. (b) $k = Ae^{-E_a/RT}$ $\log k = \log A - \frac{E_a}{2.303R}.\frac{1}{T}$

Plot of log k Vs. $\frac{1}{T}$

Straight line Slope = $\frac{-E_a}{2.303R}$

59. (d)

		A →	B
t =	0	0.8	0
t =	1	0.8 – 0.6	0.06
t =	0	0.9	0
t =	?	0.9 – 0.675	0.675

1st order $t = \frac{2.303}{k} \log \frac{a}{a-x}$

$1 = \frac{2.303}{k} \log \frac{0.8}{0.2}$ $\quad k = \frac{2.303}{1} \log 4$

$k = 2.303 \times 0.6020$

$$t = \frac{2.303}{2.303 \times 0.6020} \log \frac{0.9}{0.675} = \frac{2.303 \times 0.6020}{2.303 \times 0.6020} = 1 \text{ hr.}$$

Second Approach

In first case $\frac{a}{a-x} = \frac{0.8}{0.2} = 4$

In second case $\frac{a}{a-x} = \frac{0.9}{0.225} = 4$

Since the ratio is the same, hence time will be same. Therefore 1 hr.

60. (c) Adsorption lowers the activation energy.

EXERCISE 3

1. (d) As the slowest step is the rate determining step thus the mechanism B will be more consistent with the given information also because it involve one molecule of H_2 and one molecule of ICl it can expressed as

$r = k[H_2][ICl]$

Which shows that the reaction is first order w.r.t. both H_2 & ICl.

2. (c) For a first order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

when $t = t_{½}$

$$k = \frac{2.303}{t_{½}} \log \frac{a}{a - a/2}$$

$$\text{or } t_{½} = \frac{2.303}{k} \log 2 = \frac{\ln 2}{k}$$

3. (a) For a first order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

when $t = 60$ and $x = 60\%$

$$k = \frac{2.303}{60} \log \frac{100}{100-60} = \frac{2.303}{60} \log \frac{100}{40}$$

Now,

$$t_{\frac{1}{2}} = \frac{2.303}{0.0153} \log \frac{100}{100-50} = \frac{2.303}{0.0153} \times \log 2$$

$$= \frac{2.303}{0.0153} \times 0.3010 = 45.31 \text{ min}.$$

4. (d) Given, $k_1 = 10^{16}.e^{-\frac{2000}{T}}$

and $k_2 = 10^{15}.e^{-\frac{1000}{T}}$

when k_1 and k_2 are equal at any temperature T, we have

$$10^{16}.e^{-\frac{2000}{T}} = 10^{15}.e^{-\frac{1000}{T}}$$

$$\text{or } 10\times10^{15}.e^{-\frac{2000}{T}} = 10^{15}.e^{-\frac{1000}{T}}$$

$$\text{or } 10.e^{-\frac{2000}{T}} = e^{-\frac{1000}{T}}$$

$$\text{or } \ln 10 - \frac{2000}{T} = -\frac{1000}{T}$$

$$\text{or } \ln 10 = \frac{2000}{T} - \frac{1000}{T}$$

$$\text{or } 2.303 \log 10 = \frac{1000}{T}$$

$$\text{or } 2.303\times1\times T = 1000 \qquad [\therefore \log 10 = 1]$$

$$\text{or } T = \frac{1000}{2.303}\text{K}$$

5. **(a)** Rewriting the given data for the reaction

$$CH_3COCH_3(aq) + Br_2(aq) \xrightarrow{H^+} CH_3COCH_2Br(aq) + H^+(aq) + Br^-(aq)$$

S. No.	Initial concentration of CH_3COCH_3 in M	Initial concentration of Br_2 in M	Initial concentration of H^+ in M	Rate of disappearance of Br_2 in Ms^{-1} i.e. $-\frac{d}{dt}[Br_2]$ or $\frac{dx}{dt}$
1	0.30	0.05	0.05	5.7×10^{-5}
2	0.30	0.10	0.05	5.7×10^{-5}
3	0.30	0.10	0.10	1.2×10^{-4}
4	0.40	0.05	0.20	3.1×10^{-4}

Actually this reaction is autocatalyzed and involves complex calculation for concentration terms.

We can look at the above results in a simple way to find the dependence of reaction rate (i.e., rate of disappearance of Br_2).

From data (1) and (2) in which concentration of CH_3COCH_3 and H^+ remain unchanged and only the concentration of Br_2 is doubled, there is no change in rate of reaction. It means the rate of reaction is **independent of concentration of Br_2.**

Again from (2) and (3) in which ($CH_3CO\ CH_3$) and (Br_2) remain constant but H^+ increases from 0.05 M to 0.10 i.e. doubled, the rate of reaction changes from 5.7×10^{-5} to 1.2×10^{-4} (or 12×10^{-5}), thus it also becomes almost doubled. It shows that rate of reaction is directly proportional to $[H^+]$. From (3) and (4), the rate should have doubled due to increase in conc of $[H^+]$ from 0.10 M to 0.20 M but the rate has changed from 1.2×10^{-4} to 3.1×10^{-4}. This is due to change in concentration of CH_3COCH_3 from 0.30 M to 0.40 M. Thus the rate is directly proportional to $[CH_3\ COCH_3]$. We now get

$$\text{rate} = k\,[CH_3COCH_3]^1[Br_2]^0[H^+]^1$$
$$= k\,[CH_3COCH_3][H^+].$$

6. **(d)** Rate of disappearance of H_2 = rate of formation of NH_3.

$$-\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$$

$$\Rightarrow \frac{-d[H_2]}{dt} = \frac{3}{2}\frac{d[NH_3]}{dt} = \frac{3}{2}\times2\times10^{-4}$$

$$= 3\times10^{-4}\,\text{mol L}^{-1}\text{s}^{-1}$$

7. **(d)** Rate of disappearance of Br^-

= rate of appearance of Br_2

$$\Rightarrow -\frac{1}{5}\frac{d[Br^-]}{dt} = \frac{1}{3}\frac{d[Br_2]}{dt}$$

$$\Rightarrow \frac{1}{3}\frac{d[Br_2]}{dt} = -\frac{1}{5}\frac{d[Br^-]}{dt}$$

$$\Rightarrow \frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$$

8. **(b)** For a first order reaction

$$t_{1/2} = \frac{0.693}{k};\; k = \frac{0.693}{1386} = 0.5 \times 10^{-3}\text{s}^{-1}$$

9. **(a)** When concentration A is doubled, rate is doubled. Hence order with respect to A is one.

When concentrations of both A and B are doubled, rate increases by 8 times hence order with respect to B is 2.

$\therefore$ rate = $k\,[A]^1\,[B]^2$

Total order = 1 + 2 = 3

10. **(b)** $N_2O_5\,(g) \longrightarrow 2NO_2(g) + 1/2\ O_2\,(g)$

$$-\frac{d}{dt}[N_2O_5] = +\frac{1}{2}\frac{d}{dt}[NO_2] = 2\frac{d}{dt}[O_2]$$

$$\frac{d}{dt}[NO_2] = 1.25\times10^{-2}\ \text{mol L}^{-1}\text{s}^{-1}\text{ and}$$

$$\frac{d}{dt}[O_2] = 3.125\times10^{-3}\ \text{mol L}^{-1}\text{s}^{-1}$$

11. **(b)**

12. (d) In case of (II) and (III), keeping concentration of [A] constant, when the concentration of [B] is doubled, the rate quadruples. Hence it is second order with respect to B. In case of I & IV Keeping the concentration of [B] constant. when the concentration of [A] is increased four times, rate also increases four times. Hence, the order with respect to A is one. hence

$$\text{Rate} = k\,[A]\,[B]^2$$

13. (b) $2\,NO\,(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$

Rate = $k\,[NO]^2\,[Cl]$

The value of rate constant can be increased by increasing the temperature.

$\therefore$ **Correct choice : (b)**

14. (d) order of reaction may be zero, whole number or fractional.

15. (b) Rate of disappearance of reactant = Rate of appearance of products

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\frac{1}{2}k[N_2O_5] = \frac{1}{4}k'[N_2O_5] = k''[N_2O_5]$$

$$\frac{k}{2} = \frac{k'}{4} = k''$$

$$k' = 2k,\ \ k'' = \frac{k}{2}$$

16. (a) Rate = $k[A]^{\circ}$

Unit of k = $mol\ L^{-1}\ sec^{-1}$

17. (b) $\dfrac{r_{100^\circ C}}{r_{10^\circ C}} = 2^{\left(\frac{T_2-T_1}{10}\right)} = 2^{\left(\frac{100-10}{10}\right)} = 2^9 = 512$ (where 2 is temperature coefficient of reaction)

18. (b, d)

According to Arrhenius equation

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$= -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\frac{k_1}{K_2} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

19. (b) $\log\dfrac{k_2}{k_1} = \dfrac{E_a}{2.303R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

$$\log 2 = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{293} - \frac{1}{308}\right]$$

$$0.3 = \frac{E_a}{2.303 \times 8.314} \times \frac{15}{293 \times 308}$$

$$E_a = \frac{0.3 \times 2.303 \times 8.314 \times 293 \times 308}{15}.$$

$= 34673\ J\ mole^{-1}$

$= 34.7\ J\ mole^{-1}$

20. (a) It is zero order reaction

21. (a) $k = (mol\ L^{-1})^{1-n}\ sec^{-1}$, n = 0, 1.

22. (a) Order is the sum of the power of the concentrations terms in rate law expression.

$\therefore$ Order of reaction = 1+2 = 3

23. (d)

24. (a)

25. (b) In equation $k = Ae^{-E_a/RT}$; A = Frequency factor k = velocity constant, R = gas constant and E_a = energy of activation

26. (c) $Rate_1 = k\,[A]^n\,[B]^m$; $Rate_2 = k\,[2A]^n\,[½B]^m$

$$\therefore \frac{Rate_2}{Rate_1} = \frac{k[2A]^n[½B]^m}{k[A]^n[B]^m}$$

$$= [2]^n\,[½]^m = 2^n.2^{-m} = 2^{n-m}$$

27. (b) $r = k\,[O_2][NO]^2$. When the volume is reduced to 1/2, The conc. will double

$\therefore$ New rate = $k\,[2O_2][2NO]^2 = 8\,k\,[O_2][NO]^2$

The new rate increases by eight times.

28. (d) The $t_{1/2}$ is 15 minutes. To fall the concentration from 0.1 to 0.025 we need two half lives i.e., 30 minutes.

29. (d) The velocity constant depends on temperature only. It is independent of concentration of reactants.

30. (d) Enthalpy of reaction (ΔH) = $E_{a\,(f)} - E_{a\,(b)}$

for an endothermic reaction ΔH = +ve hence for ΔH to be positive

$E_{a\,(b)} < E_{a\,(f)}$

31. (d) The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction. Thus the reaction involving two different reactant can never be unimolecular.

32. (d) The graphs show that reaction is exothermic.

$$\log k = \frac{-\Delta H}{RT} + I$$

For exothermic reaction $\Delta H < 0$ or

$\therefore$ log k Vs $\frac{1}{T}$ would be negative straight line with positive slope.

33. (c) $t_{1/4} = \frac{2.303}{k}\log\frac{1}{3/4} = \frac{2.303}{k}\log\frac{4}{3}$

$$= \frac{2.303}{k}(\log 4 - \log 3) = \frac{2.303}{k}(2\log 2 - \log 3)$$

$$= \frac{2.303}{k}(2 \times 0.301 - 0.4771) = \frac{0.29}{k}$$

34. (a) Since the reaction is 2nd order w.r.t Co. Thus, rate law is given as.

$r = k[CO]^2$

Let initial concentration of CO is a i.e. [CO] = a

$\therefore r_1 = k(a)^2 = ka^2$

when concentration becomes doubled, i.e.[CO] = 2a

$\therefore r_2 \, k(2a)^2 = 4ka^2$ $\qquad \therefore \; r_2 = 4r_1$

So, the rate of reaction becomes 4 times.

35. (c) In Arrhenius equation $K = A\,e^{-E/RT}$, E is the energy of activation, which is required by the colliding molecules to react resulting in the formation of products.

36. (b) (i) $NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$

(ii) $NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$

Rate law equation = $k[NOBr_2][NO]$

But $NOBr_2$ is intermediate and must not appear in the rate law equation

from Ist step $K_C = \frac{[NOBr_2]}{[NO][Br_2]}$

$\therefore [NOBr_2] = K_C[NO][Br_2]$

$\therefore$ Rate law equation = $K \cdot K_C [NO]^2 [Br_2]$

hence order by reaction is 2 w.r.t. No.

37. (a) Presence of catalyst does not affect enthalpy change of reaction $\Delta H_R = E_f - E_b = 180 - 200 = -20$ kJ/mol

38. (b) Since doubling the concentration of *B* does not change half life, the reaction is of 1st order w.r.t. *B*.

Order of reaction with respect to *A* = 1 because rate of reaction doubles when concentration of A is doubled keeping concentration of *B* constant.

$\therefore$ Order of reaction = 1 + 1 = 2 and units of second order reaction are L mol^{-1} sec^{-1}.

39. (a) Since initial velocity is ten times the permissible value $\therefore A_0 = 10A$

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{30}$$

$$t_{1/2} = \frac{2.303}{\lambda}\log\frac{A_0}{A} = \frac{2.303}{0.693/30}\log\frac{10A}{A}$$

$$= \frac{2.303 \times 30}{0.693} \times \log 10 = 100 \text{ days.}$$

40. (b) The rates of reactions for the reaction

$$\frac{1}{2}A \longrightarrow 2B$$

can be written either as

$$-2\frac{d}{dt}[A] \text{ with respect to 'A'}$$

or $\qquad \frac{1}{2}\frac{d}{dt}[B]$ with respect to 'B'

From the above, we have

$$-2\frac{d}{dt}[A] = \frac{1}{2}\frac{d}{dt}[B]$$

or $\quad -\frac{d}{dt}[A] = \frac{1}{4}\frac{d}{dt}[B]$

i.e., correct answer is (b)

41. (b) For first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{6.93}$$

$$k = \frac{2.303}{t}\log\frac{100}{100-99}$$

$$\frac{0.693}{6.93} = \frac{2.303}{t}\log\frac{100}{1}$$

$$\frac{0.693}{6.93} = \frac{2.303 \times 2}{t}$$

$t = 46.06$ min

42. (c) For the reaction

A $\to$ Product

given $t_{1/2} = 1$ hour

for a zero order reaction

$$t_{1/2} = \frac{[A_0]}{2k}$$

or $k = \frac{[A_0]}{2t_{1/2}} = \frac{2}{2 \times 1} = 1 \text{ mol lit}^{-1}\text{ hr}^{-1}$

Further for a zero order reaction

$$k=\frac{dx}{dt}=\frac{\text{change in concentration}}{\text{time}}$$

$$1=\frac{0.50-0.25}{\text{time}}$$

$\therefore$ time = 0.25 hr.

43. (d) Since the slow step is the rate determining step hence if we consider option (A) we find

$$\text{Rate}=k[Cl_2][H_2S]$$

Now if we consider option (B) we find

$$\text{Rate}=k[Cl_2]\left[HS^-\right] \quad \text{...(i)}$$

For equation,

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$K=\frac{\left[H^+\right]\left[HS^-\right]}{H_2S}$$

or $$\left[HS^-\right]=\frac{K[H_2S]}{H^+}$$

Substituting this value in equation (i) we find

$$\text{Rate}=k[Cl_2]K\frac{[H_2S]}{H^+}=k'\frac{[Cl_2][H_2S]}{\left[H^+\right]}$$

Thus slow step should involve 1 molecule of Cl_2 and 1 molecule of H_2S.

hence only , mechanism (A) is consistent with the given rate equation.

44. (c) $$k_1=A_1e^{-E_{a_1}/RT} \quad \text{.........(i)}$$

$$k_2=A_2e^{-E_{a_2}/RT} \quad \text{........(ii)}$$

On dividing eqn (i) from eqn. (ii)

$$\frac{k_1}{k_2}=\frac{A_1}{A_2}(E_{a_2}-E_{a_1})/RT \quad \text{........(iii)}$$

Given $E_{a_2}=2E_{a_1}$

On substituting this value in eqn. (iii)

$$k_1=k_2A\times e^{E_{a_1}/RT}$$

45. (c) Since for every 10ºC rise in temperature rate doubles for 50ºC rise in temperature increase in reaction rate $=2^5=32$ times

46. (b) For a first order reaction

$$k=\frac{2.303}{t}\log\frac{a}{a-x}=\frac{2.303}{40}\log\frac{0.1}{0.025}$$

$$=\frac{2.303}{40}\log 4=\frac{2.303\times 0.6020}{40}$$

$$=3.47\times 10^{-2}\ \text{min}^{-1}$$

Rate = k[A] = $3.47\times 10^{-2}\times 0.01$

= 3.47×10^{-4} M/min

47. (a) Activation energy can be calculated from the equation

$$\frac{\log k_2}{\log k_1}=\frac{-E_a}{2.303R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

Given $\frac{k_2}{k_1}=2$; $T_2=310$ K; $T_1=300$ K

$$=\log 2=\frac{-E_a}{2.303\times 8.314}\left(\frac{1}{310}-\frac{1}{300}\right)$$

E_a = 53598.6 J/mol = 53.6 kJ/mol.

48. (d) Overall order = sum of orders w.r.t each reactant.

Let the order be x and y for G and H respectively

Exp.No.	[G]mole litre^{-1}	[H]mole litre^{-1}	rate(mole litre^{-}time^{-1})
1	a	b	r
2	$2a$	$2b$	$8r$
3	$2a$	b	$2r$

$\because$ For (1) and (3), the rate is doubled when conc. of G is doubled keeping that of H constant i.e.,

rate $\propto$ [G] $\therefore x=1$

From (2) and (3), y = 2

$\therefore$ Overall order is 3.

49. (a) The values of rate constants k_0, k_1 for zero order and first order reaction, respectively, are given by the following equation:

$$k_0=\frac{A_0}{2\times t_{1/2}}$$ [where A_0 = initial concentration, and $t_{1/2}$ = half-life period]

and $$k_1=\frac{0.693}{t_{1/2}}$$

Substituting various given values, we get

$$k_0=\frac{1.386\,\text{mol litre}^{-1}}{2\times 20\ \text{sec}} \quad \text{... (i)}$$

and $k_1 = \frac{0.693}{40\,\text{sec}}$ ... (ii)

Dividing (ii) by (i), we get

$$\frac{k_1}{k_0} = \frac{0.693}{40} \times \frac{2\times 20}{1.386\ \text{mol dm}^{-3}} = \frac{0.693}{1.386} = 0.5$$

= $0.5\ \text{mol}^{-1}\ \text{dm}^3$

Thus the correct answer is (a).

50. **(d)** $\log k = \log A - \frac{E_a}{2.303RT}$ …(1)

Also given $\log k = 6.0 - (2000)\frac{1}{T}$ …(2)

On comparing equations, (1) and (2)

$\log A = 6.0 \Rightarrow A = 10^6\ \text{s}^{-1}$

and $\frac{E_a}{2.303\,R} = 2000$;

$\Rightarrow E_a = 2000 \times 2.303 \times 8.314 = 38.29\ \text{kJ mol}^{-1}$

51. **(a)** As per Arrhenius equation $(k = Ae^{-E_a/RT})$, the rate constant increases exponentially with temperature.

EXERCISE 4

1. **(a)**

Substance R	Substance S	
2k	k	rate constant
$t_{½}$	$2\,t_{½}$	Half life period

$T = n \times t_{1/2}$ where n = number of half life period

Amount of R left = $\frac{0.5}{(2)^{T/t_{½}}}$;

Amount of S left = $\frac{0.25}{(2)^{T/2t_{½}}}$

Equating both $\frac{0.5}{0.25} = \frac{(2)^{T/t_{1/2}}}{(2)^{T/2t_{1/2}}}$ or $2 = (2)^{T/t_{1/2}}$

$\therefore T = 2t_{1/2}$. $2t_{1/2}$ is half life of S and twice the half - life of R

2. **(c)** Units of k = $(\text{Mol lit}^{-1})\ \text{time}^{-1}$; Hence n = 1 order

3. **(d)** For first order $t_{½} = \frac{0.693}{6.93\times10^{-3}} = 100$ min; $300 = 100 \times n$

Percentage left = $\frac{100}{(2)^3} = 12.5\%$

4. **(a)** $k = \frac{2.303}{1386}\log\frac{100}{100-75}$ On solving we get . $k = 10^{-3}$

5. **(c)** $k_{uncat} = A\ \overline{e}^{E_{uncat}/RT}$ .... (i)

$k_{cat} = A\ \overline{e}^{E_{cat}/RT}$ .... (ii)

Let the E_a for uncatalysed reaction be A then for catalysed reaction it will be $(A - 8.314\times10^3)$ cal/mole

Dividing (ii) by (i),

$$\frac{k_{cat}}{k_{uncat}} = \frac{\overline{e}^{(A-8.314\times10^3)/RT}}{\overline{e}^{A/RT}} = e^{8.314\times10^3/RT}$$

$\frac{k_{cat}}{k_{uncat}} = e^{3.33} = 28$ (take log then antilog)

6. **(c)** Let the rate law equation be

$r = k[A]^x$ ....(i)

$2.25\times r = k[1.5A]^x$ ....(ii)

Divide (ii) by (i) $2.25 = (1.5)^x$ $\therefore$ x = 2 ; Second order

7. **(c)** $N_2 + 3H_2 \rightleftharpoons 2NH_3$;Rate is given by any of the expressions

$$\frac{-d[N_2]}{dt} = -\frac{1d[H_2]}{3dt} = \frac{1}{2}\frac{d(NH_3]}{dt}$$

Rate of disappearance of $N_2 = \frac{1}{2}$ the rate of formation of $NH_3 = 1\times10^{-4}$

Rate of disappearance of H_2 =3/2 the rate of formation of $NH_3 = 3\times10^{-4}$

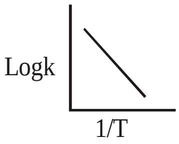
8. **(b)** $k = Ae^{-E_a/Rt}$ When $T\to\infty$ Then k = A

9. **(c)** The concentration of A remains 1/4 th in 8 hours. Therefore $1/(2)^n$, n = 2

and $E_{½}$ is $8 = n\times t_{½}$; $t_{½} = 4$; In 4 hours 0.6 will become 0.3

10. **(c)** $k = 1.2\times10^{14}e^{-25000/RT}\ \text{sec}^{-1}$ or

$\log k = \log 1.2\times10^{14} - \frac{25000}{R}.\frac{1}{T}$



Equation of straight line

slope = $-\frac{2500}{R}$

11. (a) For the change 2A + 3B → products

$$-\frac{1}{2}\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt}, \quad \frac{1}{2}r_1 = \frac{1}{3}r_2; \quad 3r_1 = 2r_2$$

12. (c) $$t_{99.9\%} = \frac{2.303}{k}\log\frac{100}{100-99.9}$$

$$= \frac{2.303}{k}\log\frac{100}{0.1} = \frac{2.303}{k}\log 1000 = \frac{2.303}{k}\times 3$$

$$t_{50.0\%} = \frac{2.303}{k}\log\frac{100}{100-50}$$

$$= \frac{2.303}{k}\log 2 = \frac{2.303}{k}\times 0.3010$$

$$\frac{t_{99.9\%}}{t_{50.0\%}} = \frac{2.303\times 3}{k}\times\frac{k}{2.303\times 0.3010} = \frac{3}{0.3} = 10$$

$$t_{99.9\%} = 10\times t_{50.0\%}$$

13. (c) For the exothermic reaction the energy of products is always less than the reactants. If E_a is the energy of activation for the forward reaction, the energy of activation for backward reaction is $E_a + \Delta H$

14. (d) The relevant expressions are as follows.

Choice (A) $\quad \log K_p = -\frac{\Delta H}{R}\frac{1}{T} + I$

Choice (B) $\quad \log [X] = \log [X]_0 + kt$

Choice (C) $\quad$ P/T = constant (V constant)

Choice (D) $\quad$ PV = constant (T constant)

15. (d) For two parallel reactions

$$k_{\text{average}} = k_1 + k_2 = 1.26\times 10^{-4} + 3.8\times 10^{-5}$$

$$= 1.64\times 10^{-4}\ \text{sec}^{-1}$$

The fractional yield of B = $\frac{k_B}{k_{av}} = \frac{1.26\times 10^{-4}}{1.64\times 10^{-4}}$

$0.7683 = 76.83\ \%$

The fractional yield of C = $\frac{k_C}{k_{av}} = \frac{3.8\times 10^{-5}}{1.64\times 10^{-4}}$

$= 0.2317 = 23.17\ \%$

16. (c) $$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t} = \frac{2.303}{2\times 10^4}\log\frac{800}{50} = 1.386\times 10^4\,s^{-1}$$

17. (d) $N_2O_4 \rightleftharpoons 2NO_2$. Decomposition of N_2O_4 is first order and its concentration will will decrease with time.

18. (b) For zero order

$$k = \frac{C_o - C_t}{t}$$

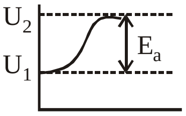
19. (b) $$\text{Rate} = kC_A^2 C_B^{1/2}$$

$$\text{Rate} = k[2C_A]^2[4C_B]^{1/2} = 4\times 2[C_A]^2[C_B]^{1/2}$$

20. (c) $$k = \frac{1}{t}\ln\frac{a}{a-x} \quad \text{or} \quad \ln\frac{a}{a-x} = kt$$

$$\ln\frac{a-x}{a} = -kt \quad \text{or} \quad a - x = a\,e^{-kt}$$

$$\therefore x = a(1-e^{-kt}) \quad \text{or} \quad \frac{x}{a} = (1-e^{-kt})$$

21. (a) 

$\Delta U = U_2 - U_1 = +ve$

22. (a) For zero order reaction the $t_{1/2} \propto a$.

23. (b) $A_2 \rightleftharpoons 2A$ (fast) ....(i)

$A + B \xrightarrow{K_2} P(\text{slow})$ ....(ii)

Rate law = $k_2[A][B]$

But A is intermediate

$$\therefore \text{from } k = \frac{[A]^2}{[A_2]} \therefore [A] = k^{1/2}[A_2]^{1/2}$$

put in rate law equation

$$\text{Rate law} = k_2 k^{1/2}[A_2]^{1/2}[B]$$

24. (d)

25. (a) $$A(g) + 2B(g) \longrightarrow C(g) + D(g)$$

$\text{Rate} = k[A][B]^2 = k(0.60)(0.80)^2$ ....(i)

when p_c = 0.20 atm p_A is reduced to 0.40 and p_B = 0.40 (See stoichiometric representation)

Rate = $k[0.40]\,[0.40]^2$..............................(ii)

$$\therefore \text{(ii) divide by (i)} = \frac{0.40\times 0.40\times 0.40}{0.60\times 0.80\times 0.80} = \frac{1}{6}$$

26. (a) The rate law equation contains $[H^+]^2$, term. The rate will change with change in pH and new rate will be $[2]^2$ = 4 times the old rate

27. (b) $\log k = \log A - \dfrac{E_a}{2.303} \cdot \dfrac{1}{T}$

The value of k increases with the increase of temperature.

28. (c) Generally the rate of reactions is doubled by 10°C rise in temperature i.e. the increase is $\approx$ 100 %.

29. (b) The curve Y shows the increase in concentration of products with time.

30. (a) The increase in pressure shows the increase in conc. of Z.

Rate of appearance of Z = $\dfrac{120-100}{5} = 4 \text{ mm Hg min}^{-1}$

Rate of disappearance of X_2 = 2 × rate of appearance of

$Z = 2 \times 4 \text{ mm Hg min}^{-1} = 8 \text{ mm Hg min}^{-1}$

31. (c) A dip in the curve shows the formation of X (reaction taking place in two steps). Since the reaction is exothermic E_a of X must be less.

32. (b) Temperature coefficient = $\dfrac{K_{310}}{K_{300}} = 2.3$

$K_{310} = 2.3\, K_{300}$

33. (c) $t_{1/2} \propto \dfrac{1}{(p)^{n-1}}$ where n is the order of reaction

$$\frac{2}{4} = \left(\frac{50}{100}\right)^{n-1} \quad \text{or} \quad \frac{1}{2} = \left(\frac{1}{2}\right)^{n-1}$$

$\therefore\ n = 2$

34. (a) For zero order reaction $k = \dfrac{C_0 - C}{t}$ or $C = C_0 - kt$

The equation has negative slope and non zero intercept.

35. (c) $\dfrac{t_{1/2}(1)}{t_{1/2}(2)} = \left[\dfrac{p(2)}{p(1)}\right]^{n-1}$,

$\dfrac{880}{410} = \left[\dfrac{364}{170}\right]^{n-1}$;

$[2.14]^1 = [2.1]^{n-1}$

36. (d) $\ln \dfrac{k_2}{k_1} = \dfrac{E_a}{R} \dfrac{(T_2 - T_1)}{T_2 \times T_1}$

$\ln \dfrac{3.07 \times 10^{-3}}{2.2 \times 10^{-5}} = \dfrac{E_a}{R} \dfrac{(510.1 - 457.6)}{510.1 \times 457.6}$

$\therefore E_a = (510.1 \times 457.6) / 52.5 \times R \ln 307/2.2$ cal.

37. (c)

$$\begin{array}{llll} & CH_3CHO(g) \longrightarrow & CH_4\ (g) + & CO\ (g) \\ \text{When } t = 0 & p^0 & 0 & 0 \\ \text{When } t = t & p^0 - p & p & p \end{array}$$

$\therefore\ p^0 - p + p + p = 120$ mm Hg

or, $p^0 + p = 120$ mm Hg;

$p = 120 - 80 = 40$ mm Hg

$k = \dfrac{1}{t} \ln \dfrac{p^0}{p^0 - p} = \dfrac{1}{20} \ln \dfrac{80}{80-40} = \dfrac{1}{20} \ln 2$

Again, $t_{1/2} = \dfrac{\ell n 2}{k}$

$\therefore\ t_{1/2} = \dfrac{\ln 2}{\ln 2} \times 20 = 20$ min.

38. (b) $[H^+] = \dfrac{6 \times 10^{-7}}{0.05 \times 10^{-3}} = 1.2 \times 10^{-2}$ M

Rate $r = \dfrac{\Delta X}{\Delta t}$; $\Delta t = \dfrac{\Delta X}{r} = \dfrac{1.2 \times 10^{-2}\text{ M}}{6 \times 10^5 \text{ M s}^{-1}}$

$\therefore T = 2 \times 10^{-8}$ s

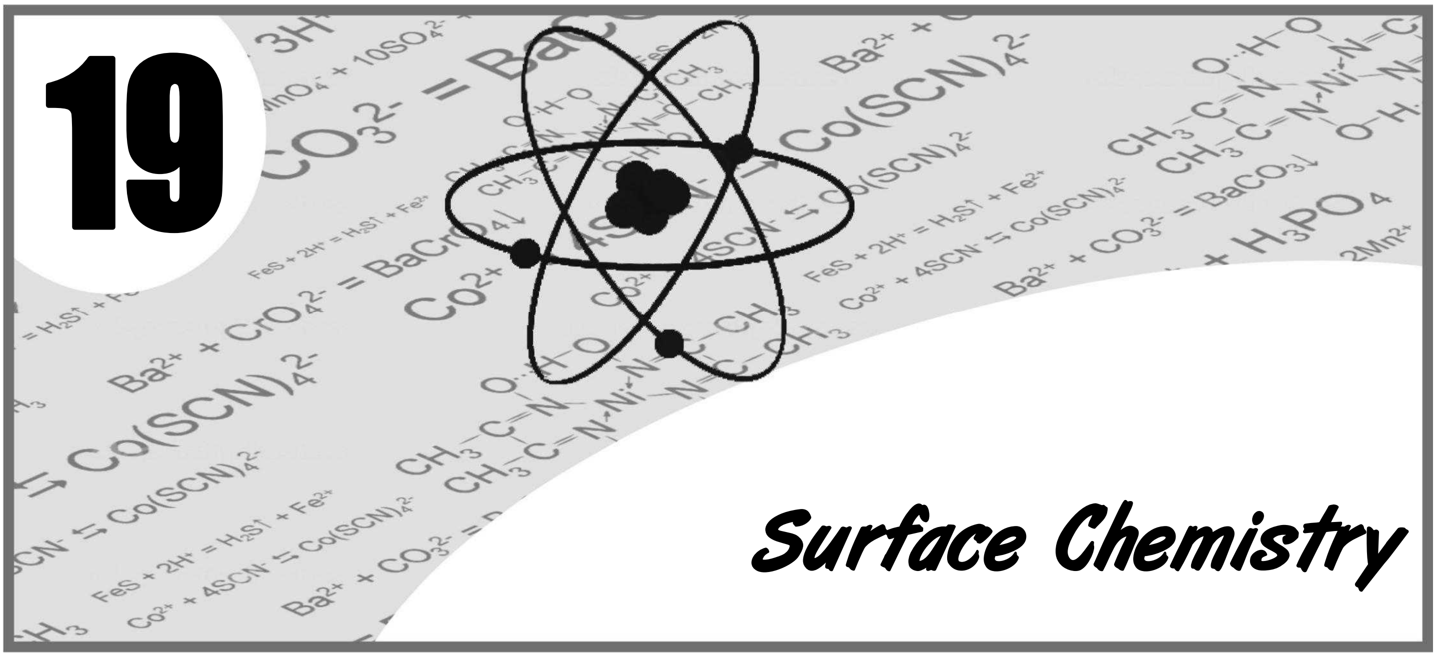
39. (c) $E_a = \dfrac{k_2 E_2 + k_1 E_1}{k_2 + k_1}$

$= \dfrac{1.0 \times 10^{-2} \times 60 + 3.0 \times 10^{-2} \times 70}{1.0 \times 10^{-2} + 3.0 \times 10^{-2}}$

$E_a = 67.5 \text{ kJ mol}^{-1}$

19

Surface Chemistry



Thomas Graham divided the solids into two types.

CRYSTALLOIDS :

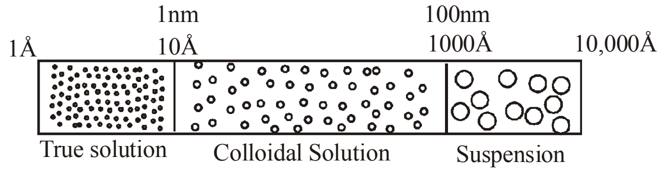
The substances whose solution readily diffuse through a parchment membrane eg sugars, salts, acid and base.

COLLOIDS :

The substance whose solution diffused at very slow rate through a parchment membrane eg glue, gelatin, gum arabic etc.

Later on it was found that crystalloids and colloids differed only in their size of particles. They can be interconverted, hence colloidal is a state.

On the basis of the size of particles we have



COLLOIDAL SYSTEM :

Finely divided particles of any substance with diameters lying between 10Å - 2000Å dispersed in any medium constitute a colloidal system. It is heterogenous system consisting of two phases.

DISPERSED PHASE :

Discontinuous phase of the colloidal system is known as dispersed phase.

DISPERSION MEDIUM :

The continuous phase of the colloidal system is known as dispersion medium.

TYPES OF COLLOIDAL SYSTEMS :

Dispersed phase	*Dispersion medium*	*Name*	*Examples*
Gas	Liquid	Foam	Shaving Cream, Soda Water froth
Gas	Solid	Solid foam	Pumice stone, corck, foam rubber
Liquid	Gas	Aerosol	Mist , cloud, fog
Liquid	Liquid	Emulsion	Hair cream, milk
Liquid	Solid	Gel	Cheese, butter
Solid	Gas	Smoke	Occluded gases, dust soot in air
Solid	Liquid	Sol	Colloidal gold
Solid	Solid	Solid sol	alloys

HYDROSOLS OR AQUASOLS :

For such sols the dispersion medium is water.

SOLVOSOLS :

Depending upon the nature of the dispersion medium sols may be named as **alcosols** (in alcohol), **benzosols** (in benzene). **Aerosols** (in air) and in general solvosols.

LYOPHILIC SOLS (Solvent loving) :

When dispersed phase has certain affinity for the dispersion medium it is known as lyophilic sol. eg sols of gum, starch etc.

LYOPHOBIC SOLS (Solvent Hating) :

When dispersed phase has no affinity for dispersion medium it is known as lyophobic sol. eg. sols of gold, iron and sulphur etc.

CHARACTERISTICS OF LYOPHILIC AND LYOPHOBIC SOLS :

Property	*Lyophilic Sol*	*Lyophobic Sol*
1. Preparation	Can be prepared easily	Prepared by special methods
2. Charge	May or may not carry any charge	Always carry positive or negative charge.
3. Solvation	Sol particles are heavily hydrated	Not solvated.
4. Precipitation	High concentration of the electrolytes required to cause . precipitation	Precipitated by low concentration of electrolytes.
5. Viscosity	Very high	Same as that of dispersion medium.
6. Surface tension	Low	Same as that of dispersion medium.
7. Reversibility	Reversible	Irreversible
8. Migration in electric field	May or may not migrate	Always migrate in electric field.
9. Tyndall effect	No	Yes
10. Stability	More stable	Less stable

CLASSIFICATION ON THE BASIS OF SIZE OF SOL PARTICLES :

(i) **Multimolecular colloids -** In this case the colloidal particles consists of aggregates of atoms or small molecules with diameters of less than 1nm eg gold sol, sulphur sol.

(ii) **Macromolecular colloids -** In this case dispersed particles are of colloidal size and are called macromolecules, usually polymers such as starch, cellulose, proteins or synthetic polymers etc.

(iii) **Associated colloids -** At low concentrations they behave as electrolytes and at higher concentrations as colloids. They are also known as **micelles**. Soaps and detergents are the examples. The micelles may contain about 100 molecules or more.

PREPARATION OF COLLOIDAL SOLUTIONS :

Lyophobic sols and lyophilic sols are prepared by different methods.

Preparation of lyophobic sols - The methods employed are :

(a) Condensation methods (b) Dispersion methods.

(a) Condensation methods :

In these methods small ions or molecules are induced to combine together to form aggregates of colloidal size and chemical or physical methods may be employed.

Chemical methods :

(i) ***Double decomposition -*** An arsenic sulphide (As_2S_3) sol is prepared by passing H_2S through cold solution of As_2O_3 till yellow colour deepens to its maximum

$$As_2O_3 + 3H_2S \rightarrow As_2S_3(Sol) + 3H_2O$$

(ii) ***Oxidation -*** A sol of sulphur is prepared by passing H_2S into solution of SO_2

$$2H_2S + SO_2 \rightarrow 2H_2O + S\downarrow$$

(iii) ***Reduction -*** Sols of gold, platinum and silver are prepared by reduction of their compounds in water using, formaldehyde or hydrazine or tannic acid

$$AgNO_3 + \text{Tannic acid} \rightarrow \text{Ag Sol}$$

$$AuCl_3 + \text{Tannic acid} \rightarrow \text{Au Sol}$$

(iv) ***Hydrolysis -*** Ferric hydroxide sol is prepared by pouring dilute solution of ferric chloride into boiling water

$$FeCl_3 + 3H_2O \longrightarrow \underset{\substack{\text{Red Sol} \\ \text{(Positive in nature)}}}{Fe(OH)_3} + 3HCl$$

Sols of chromium and aluminium can also be prepared by this method.

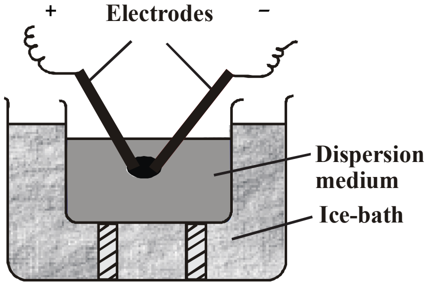
(v) ***Change of solvent -*** When ethanolic solution of **sulphur** is added to an excess of water, the sol of **sulphur** is obtained. This is physical method.

(b) **Dispersion methods :**

Here lumps of the substances broken down to colloidal size in presence of dispersion medium and suitable stabilizer.

(i) ***Mechanical dispersion -*** In this method colloid mill, ball mill or ultrasonic disintegrator are used.

(ii) ***Bredig's arc method (electrical disintegration).*** An arc is struck between two metal electrodes of silver, gold or platinum held at the surface of cold water containing traces of alkali when sol of metal is obtained.



Bredig's Arc method

(iii) ***By peptization -*** The dispersal of freshly precipitated substance into colloidal solution by the addition of some electrolyte having one ion common is known as peptization. The electrolyte used is called peptizing agent e.g.

(i) Ferric hydroxide $Fe(OH)_3$ is peptized by ferric chloride giving sol. of $[Fe(OH)_3]Fe^{3+}$

(ii) Silver chloride AgCl is peptized by HCl giving negative sol of $[AgCl]Cl^-$

(iii) Cadmium sulphide CdS is peptized by H_2S giving negative sol of $[CdS]S^{--}$

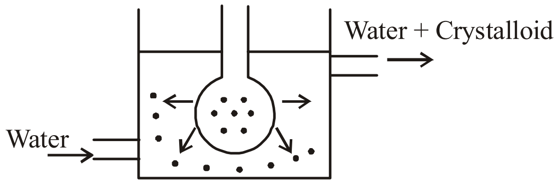
(iv) Cellulose nitrate is peptized by a mixture of ethanol and water. The product obtained is called "colloidon".

PURIFICATION OF COLLOIDAL SOLUTIONS :

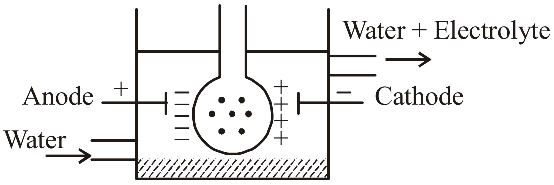
The removal of the particles of electrolytes from sols is known as purification of sols. It can be achieved by any of the following methods.

a) Dialysis b) Electrodialysis c) Ultra Filtration

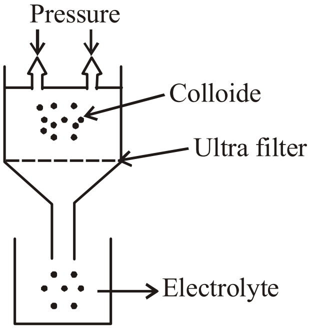
Dialysis : A mixture containing colloidal particles and particles of true solution is placed in a parchment bag. The bag is hanged in water vessel through which it is continously flowing. The particles of true solution come out of membrane leaving behind colloidal solution.



Electrodialysis : The process is the same as above. The vessel is fitted with electrodes which make the removal of electrolytes quick. On applying the EMF ions of electrolyte migrate out to the oppositely charged electrodes while the colloidal particles are held back.



Ultrafiltration : The pores of ordinary filter paper are made smaller in size by treating with solution of **gelatin** or **collodion** (4% solution of nitro cellulose in mixture of alcohol and ether) hardening by formaldehyde and drying. The colloidal particles left on the filter paper are then stirred with fresh dispersion medium to get pure colloidal solution.



PROPERTIES OF SOLS :

The following are the properties given by *sols*

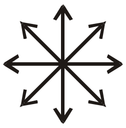
(a) Physical (b) Colligative (c) Optical

(d) Electrical and (e) Kinetic

(a) Physical properties

(b) Colligative properties - Except osmotic pressure other colligative properties are little affected.

(c) Optical properties - *tyndal effect* - The phenomenon of the scattering of light by sol particles in all possible directions is called *Tyndal effect*.



The colloidal particles absorb the incident light energy, become self-luminious, and scatter the light in all directions. Blue colour of sky and sea water, visibility of projector path etc are due to this effect.

(d) Electrical properties

(i) *Presence of charge* - All the particles of dispersed phase carry a positive or negative charge and dispersion medium carry the opposite charge. Sol as a whole is neutral. The origin of the charge may be due to

(a) ***Preferential adsorption of the common*** ion at the surface of sol particles eg.

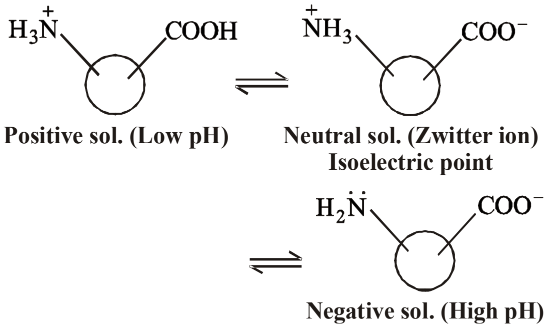
$$Fe(OH)_3 + Fe^{3+} \rightarrow [Fe(OH)_3]Fe^{3+} (+\text{ve sol})$$

$$As_2S_3 + S^{2-} \rightarrow [As_2S_3]S^{2-} (-\text{ve sol})$$

In ***Bredig's Arc*** method the negative charge on the metal sol is due to adsorption of hydroxyl ions furnished by alkali.

(b) ***Ionisation of surface* groups**

(i) ***Charge on protein sols*** - Protein sols may be negative, positive or neutral depending upon the pH value of the solution



Positive sol. (Low pH) **Neutral sol. (Zwitter ion) Isoelectric point**

Negative sol. (High pH)

At Low pH, concentration of H^+ is large, COOH group is not ionised and NH_2 group get protonated, hence positive sol.

At high pH, concentration of OH^- is large, COOH group is ionised and NH_2 group is not protonated, hence negative sol.

At intermediate pH, protein molecule exist as zwitter ion, hence no charge.

(ii) ***Charge on soaps and detergents*** - In soaps $-CO\bar{O}\overset{+}{Na}$ and in detergents $-OSO_3^-\overset{+}{Na}$ constitute the surface. Thus due to their ionisation soaps and detergents acquire negative charge.

(iii) ***Charge on basic and acidic dyes*** - An acidic dye ionises to give H^+ ions and acquire negative charge and a basic dye ionises to give OH^- ions and acquire positive charge.

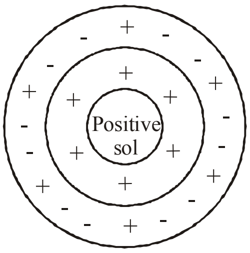
(c) Frictional electrification : It is due to rubbing of particles of dispersed phase with particles of dispersion medium.

Some examples of positively and negatively charged sols.

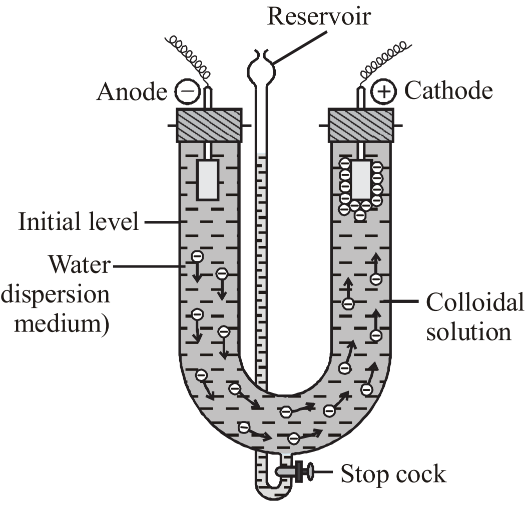
	Positively Charged sols	***Negatively charged sols***
1.	Hydroxide of Al, Cr and Fe $Al(OH)_3$, $Cr(OH)_3$ and $Fe(OH)_3$	Metallic Sols eg. Pt, Cu, Ag and Au etc.
2.	Basic dyes eg. methylene blue.	Sulphur, sulphides (CdS, As_2S_3), Silicic acid etc
3.	Proteins in acid solution eg. haemoglobin	Gelatin, Starch, acid dyes (eg. eosin) clay

(ii) ***Helmholtz electrical double layer -*** Each sol particle is surrounded by either positive or negatve ions in the form of fixed layer or compact layer. The second layer is diffuse or mobile layer consisting of ions of both the signs but net charge being equal and opposite to the fixed layer. This is known as Helmholtz electrical double layer.

Zeta potential - The potential difference developed between the two layers is known as *zeta potential or electric kinetic potential.*



(iii) ***Electrophoresis*** **-** The movement of sol particles under an applied electric potential is called electrophoresis or *cataphoresis*. The phenomenon helps in

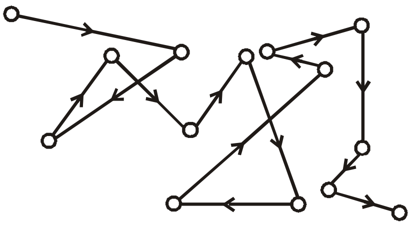


Electrophoresis

(a) removing suspended impurities
(b) removing smoke from chimney gases
(c) electroplating of rubber
(d) painting metals with colloidal pigments
(e) coagulation of sols
(f) determination of charge

(iv) ***Electro-osmosis*** **-** The movement of the dispersion medium under the influence of applied electric potential is known as *electro osmosis*. The phenomenon helps in
(a) Removing water from peat
(b) Dewatering of moist clay
(c) Drying dye pastes.

(v) ***Kinetic properties - Brownian movement -*** The zig - zag movement of colloidal particles in the dispersion medium is called *Brownian movement*.



Brownian movement

Factors affecting Brownian movement

(i) ***Size of particles*** - Small particles execute more rapid, brisk and vigrous motion than larger particles.

(ii) ***Temperature*** - It is increases with temperature.

Importance

(i) Stability of colloidal solution
(ii) Confirmation of kinetic theory
(iii) Determination of avogadro number

Brownian movement is due to the bombardment of the particles of the dispersion medium on the particles of dispersed phase.

COAGULATION, PRECIPITATION OR FLOCCULATION:

The settling down of the discharged sol particles is called coagulation or precipitation of the sol. It can be achieved by

(i) Electrophoresis
(ii) Addition of electrolytes
(iii) By boiling
(iv) Mixing two sols of opposite charge
(v) By persistant dialysis

HARDY SCHULZE RULE :

It states that the precipitating effect of an ion increases with the valency of the ion.

For precipitating a negative sol the precipitating power of cations follow the order

$Al^{3+} > Ba^{2+} > Na^{+}$

For precipitating a positive sol the precipitating power of anions follow the order

$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$

Blood is positively charged sol (pH=7.4) and is coagulated by alum, $Al_2(SO_4)_3$ or $FeCl_3$. These salts lower the pH and denaturate globular proteins.

FLOCCULATION VALUE :

The minimum concentration in millimoles per litre required to cause the precipitation of a sol in 2 hours. The smaller the flocculation value, the higher is the precipitating power of an ion.

PROTECTIVE ACTION OF LYOPHILIC SOLS :

The lyophobic sols are less stable than lyophilic sols. The lyophilic sols are thus used to protect the lyophobic sols. This property of lyophilic sols is known as protective action of lyophilic sols. A little gelatin stabilises As_2S_3 sol.

GOLD NUMBER :

The number of milligrams of a hydrophilic colloid that will just prevent the precipitation of 10 ml of a gold sol on the addition of 1 ml of 10% sodium chloride solution is known as gold number. The smaller the value of gold number of lyophilic sol, the greater is the protective action.

Gold number of some lyophilic sols.

1.	Gelatin	0.005 - 0.01
2.	Caseinate	0.01
3.	Haemoglobin	0.03
4.	Gum arabic	0.15
5.	Sodium Oleate	0.4
6.	Potato starch	25

STABILITY OF SOLS :

It is mainly due to two factors

(i) ***Presence of like charge*** on sol particles. It prevents them from aggregating and settling down under the influence of gravity.

(ii) ***Solvation of sol particles -*** In case of lyophilic sols a protective layer of solvent is formed around sol particles in addition to charge. Hence they are more stable than lyophobic sols.

EMULSIONS :

Emulsion is a liquid liquid system. They are of two types

(i) Oil dispersed in water (O/W type) eg milk and vanishing cream

(ii) Water dispersed in oil (W/O type) eg butter and cream.

The dispersed phase is always in the form of small droplets which increases the surface area and makes the emulsion unstable. Preparation of an emulsion is called **Emulsification**. Emulsions are generally unstable and are stabilized by the use of emulsifying agents (emulsifiers). For O/W emulsions the emulsifiers are **proteins**, **gums**, **natural** and **synthetic soaps**. For W/O emulsions the emulsifiers are **heavy metal salts** of fatty acids, and **long chain alcohols** etc. The emulsifier concentrates at the interface, reduces surface tension on the side of one liquid.

PROPERTIES OF EMULSIONS :

(i) They show Tyndal effect and Brownian movement.

(ii) They can be demulsified (broken) by heating, adding electrolytes, freezing and centrifuging

(iii) They can be diluted with dispersion medium.

GELS :

The liquid solid system is called gel. They are of two types

(a) **Elastic gels** - They can be temporarily deformed by applying force eg Gelatin, starch and soaps.

(b) **Non elastic gels** - They are rigid eg silica gel.

PROPERTIES OF GELS :

(a) ***Syneresis -*** Shrinkage of gels on standing by exudation of solvent is known as syneresis

(b) ***Thixotropy*** - Certain gels when shaken form a sol and on standing are converted into the form of gel They are known as thixotropic gels and sol - gel transofrmation is known as thixotropy.

(c) ***Swelling or imbibition of gels -*** The property of adsorbing definite amount of water and causing the volume of gel to increase is known as swelling or imbibition.

SOME USEFUL DEFINITIONS :

(i) ***Streaming potential -*** When liquid is forced through a porous material or a capillary tube, a potential difference is set up between the two sides. This is called streaming potential.

(ii) ***Sedimentation potential or dorn effect -*** When a particle is forced to move in a resting liquid a potential difference is set up which is known as sedimentation potential or dorn effect.

(iii) ***Isoelectric point -*** The concentration at which the colloidal particles have no charge is known as the isoelectric point. The isoelectric point of gelatin is at pH 4.7.

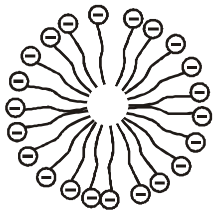
(iv) ***U - numbers -*** The number of mgs of a hydrophilic sol which is sufficient to produce the colour change from red to blue in 10 cc of gold sol.

(v) ***Congo - rubin number -*** The number of mgs of protective colloid which prevents the colour change in 100 ml of 0.01 % congo rubin dye to which 0.16 g equivalent of KCl is added

ASSOCIATED COLLOIDS :

The molecules of certain substances are smaller than colloidal particles but aggregate spontaneously in a given solvent to form particles of colloidal size. The aggregates are known as ***micelles*** and the substances as associated colloids. The soaps and detergents are the examples.

Insoluble tail Polar head
Soap molecule
e.g. $C_{17}H_{35}COONa$



A soap micelle

The tails being insoluble in water are directed towards the centre and soluble polar heads are on the surface in contact with water. The charge stabilises the micelle. The minimum concentration required for the micelle formation is called *critical micellisation concentration* (CMC).

CLEANSING ACTION OF SOAP :

It may be due the following two factors

(i) Solubilisation of grease into the micelle

(ii) Emulsification of grease

When soap is applied on to a fabric, the tails of the soap anions are pegged ino the grease stains and polar head form a charged layer around it. By mutual repulsion the grease droplets are suspended in water (formation of emulsion) and are washed away with water.

APPLICATIONS OF COLLOIDS :

(1) Industrial applications

(a) ***Purification of drinking water -*** By adding alum, the suspended impurities are coagulated and removed.

(b) ***Electrical precipitation of smoke -*** Smoke carry negative charge and is removed by the principle of electrophoresis in cottrell's precipitator.

(c) ***Sewage disposal*** - It is passed through big tanks fitted with electrodes. The colloidal particles lose their charge and settled down and removed.

(d) ***Electroplating of rubber*** - Latex is colloidal suspension of negatively charged rubber particles in water and can be deposited on metals by electrophoresis.

(e) ***Artificial rains*** - Clouds are aerosols (water dispersed in air). Aggregates of particles of water cause the rain fall which can be artificially achieved by throwing electrified sand or AgI on clouds and cause the artificial rain. AgI has similar crystal structure as that of ice.

(f) ***Leather tanning*** - Skin of animals is positively charged colloidal system. Extract of barks, wood leaves is negatively charged colloidal solution of tannin. When latter is applied on the surface of skin (leather) it becomes hard and does not putrefy.

(g) ***In warfare*** - Animal charcoal is used in gas masks to adsorb poisonous gases. Smoke screens are titanium oxide particles dispersed in air.

(2) In everyday life - Blood, milk, butter, cheese, clothes, shoes all are colloidal system.

(3) In medicines - Colloidal medicines are easily adsorbed and assimilated, hence are widely used. Colloidal antimony is effective medicine for ***kalazar***. Blood is coagulated by $FeCl_3$. Colloidal sols of Ag (argyrol and protargol) are used as eye lotions.

(4) In nature - Blue colour of sky, tails of comets are due to scattering of light.

Formation of deltas in rivers is due to coagulation of negatively charged sand particles by Na^+, Mg^{2+} etc present in sea water.

CATALYSIS

CATALYST :

A substance which when added in very small amount to a chemical reaction change the speed of that reaction without itself undergoing any chemical change is known as catalyst and the phenomenon is known as *catalysis.*

TYPES OF CATALYSIS :

The catalysis may be of two types

(i) Homogeneous Catalysis - When catalyst, reactants and the products all are present in one phase, the process is known as homogeneous catalysis eg.

(a) Oxidation of sulphur dioxide to sulphur trioxide with nitric oxide

$$\underset{gas}{2SO_2}+\underset{gas}{O_2}+\underset{gas}{[NO]} \rightarrow \underset{gas}{2SO_3}+\underset{gas}{[NO]}$$

(b) Combination of hydrogen and chlorine in presence of steam

$$\underset{gas}{H_2}+\underset{gas}{Cl_2}+\underset{gas}{[H_2O]} \rightarrow \underset{gas}{2HCl}+\underset{gas}{[H_2O]}$$

(c) Hydrolysis of an ester in presence of acid or alkali

$$\underset{liquid}{CH_3COOC_2H_5}+\underset{liquid}{H_2O}$$

$$\xrightarrow{H^+/OH^-} \underset{liquid}{CH_3COOH} + \underset{liquid}{C_2H_5OH}$$

(ii) Heterogeneous catalysis - When the catalyst is in a different phase than that of reactants and products the process is known as heterogeneous catalysis eg.

(a) Formation of ammonia by Haber's process

$$\underset{gas}{N_2}+\underset{gas}{3H_2}+\underset{solid}{[Fe]} \rightarrow \underset{gas}{2NH_3}+\underset{solid}{[Fe]}$$

(b) Formation of sulphur trioxide (contact process for sulphuric acid)

$$\underset{gas}{2SO_2}+\underset{gas}{O_2}+\underset{solid}{[Pt]} \rightarrow \underset{gas}{2SO_3}+\underset{solid}{[Pt]}$$

(c) In solution decomposition of hydrogen peroxide by MnO_2 or Pt

$$\underset{liquid}{2H_2O_2}+\underset{solid}{[Pt]} \rightarrow 2H_2O + O_2 + [Pt]$$

CLASSIFICATION OF CATALYSTS :

According to their mode of action they have been classified into four groups.

(i) Positive Catalysts - They always accelerate the speed of a chemical reaction eg.

(a) Decomposition of potassium chlorate in presence of manganese dioxide

$$2KClO_3 + [MnO_2] \rightarrow 2KCl + 3O_2 + [MnO_2]$$

(b) Manufacture of ammonia in presence of iron

$$N_2 + 3H_2 + [Fe] \longrightarrow 2NH_3 + [Fe]$$

(ii) Negative Catalysts :

They always retard the speed of chemical reaction eg

(a) Oxidation of chloroform in presence of ethanol

$$4CHCl_3 + 3O_2 + [C_2H_5OH] \rightarrow$$

$$4COCl_2 + 2Cl_2 + 2H_2O + [C_2H_5OH]$$

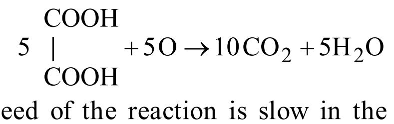
(b) Decomposition of hydrogen peroxide in presence of dilute acids or glycerol

$$2H_2O_2 + [H_3PO_4] \rightarrow 2H_2O + O_2 + [H_3PO_4]$$

(iii) Auto catalyst - In this case one of the products act as a catalyst eg.

Oxidation of oxalic acid by acidic permangnate

$$2KMnO_4 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 3H_2O + 5O$$



$$5\begin{array}{c}COOH\\ |\\ COOH\end{array} + 5O \rightarrow 10CO_2 + 5H_2O$$

The speed of the reaction is slow in the begining but increases rapidly due to the formation of Mn^{++} ions which act as auto catalyst.

(iv) Induced Catalyst - A substance which induces the similar reaction in another which is otherwise is not possible act an induced catalyst eg sodium sulphite solution oxidises in air to sodium sulphate but sodium arsenite is not oxidised by air. In presence of sodium sulphite it is also oxidised.

$$Na_2SO_3 + Na_3AsO_3 \xrightarrow[air]{[O]} Na_2SO_4 + Na_3AsO_4$$

Therefore sodium sulphite is induced catalyst.

(v) Catalyst promoters - The substances which increase the activity of catalyst are known as catalyst promoters eg Molybdenum (Mo) or aluminium oxide (Al_2O_3) increase the activity of iron catalyst in Haber's process for the manufacture of ammonia

$$2N_2 + 3H_2 \xrightarrow{Fe/Mo} 2NH_3$$

(vi) Catalyst poisoning - The substance which destroys the activity of a catalyst is called a poison and process is called catalytic poisoning eg.

$$2SO_2 + O_2 \xrightarrow[\text{poisoned by } As_2O_3]{pt} 2SO_3$$

$$2H_2 + O_2 \xrightarrow[\text{poisoned by CO}]{pt} 2H_2O$$

CHARACTERISTICS OF CATALYST :

The following are some important features for a catalyst or catalysis.

(i) Small quantity - Generally small amount of a catalyst is required but sometimes the large quantity of catalyst is effective eg anhydrous $AlCl_3$ in Friedel Craft's reaction is needed upto 30%.

(ii) Unchangeabiliy - Although there is no change in the chemical compostion and mass, there may be a change in physical state of catalyst eg granular MnO_2 changes to fine powder in decomposition of potassium chlorate

(iii) Specific action of catalyst - From the same reactants the different products are obtained with different catalysts eg.

(a) $$C_2H_5OH \xrightarrow[\Delta]{Al_2O_3} C_2H_4 + H_2O \text{ (Dehydration)}$$

$$C_2H_5OH \xrightarrow[Cu, 300°C]{hot} CH_3CHO + H_2 \text{ (Dehydrogenation)}$$

(b) $$4NH_3 + 3O_2 \xrightarrow[500°C]{Cu} 2N_2 + 6H_2O$$

$$4NH_3 + 5O_2 \xrightarrow[800°C]{Pt} 4NO + 6H_2O$$

(iv) Initiation of reaction - In general a catalyst does not start a chemical reaction, but there are reactions initiated by catalysts eg.

$$H_2 + O_2 \xrightarrow{\text{Room Temp.}} \text{No reaction}$$

$$2H_2 + O_2 \xrightarrow{\text{Pt Black}} 2H_2O$$

(v) Equilibrium - A catalyst does not affect the state of equilibrium, it simply helps to attain it quickly.

(vi) Optimum temperature - The rate of reaction is maximum at a particular temperature which is fixed for every reaction.

(vii) Physical state of catalyst - Finely divided catalyst gives better yield in a short period than lumps.

(viii) ***Activation energy*** **-** A positive catalyst lowers the activation energy of a chemical reaction.

THEORY OF CATALYSIS :

There are following main theories

(i) Intermediate theory
(ii) Adsorption theory
(iii) Modern theory

(i) Intermediate theory - A catalyst combines with one of the reactants and forms the unstable intermediate compound which in turn combines with another reactant and generates the catalyst eg. consider the oxidation of SO_2 by O_2 in presence of NO as catalyst

$$2SO_2 + O_2 + [NO] \rightarrow 2SO_3 + [NO]$$

Intermediate mechanism

$$O_2 + \underset{\text{Catalyst}}{2NO} \rightarrow \underset{\text{Intermediate}}{2NO_2}$$

$$\frac{[SO_2 + NO_2 \rightarrow SO_3 + NO] \times 2}{2SO_2 + O_2 + [2NO] \rightarrow 2SO_3 + 2[NO]}$$

Catalytic oxidation of hydrochloric acid by atmospheric oxygen in presence of cupric chloride (Deacon's process)

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

Mechanism - $(2CuCl_2 \rightarrow Cu_2Cl_2 + Cl_2) \times 2$

$$2Cu_2Cl_2 + O_2 \rightarrow \underset{\text{Intermediate}}{2Cu_2.OCl_2}$$

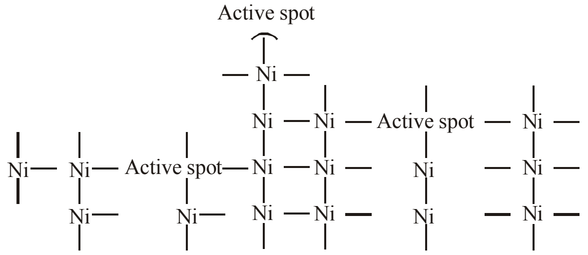
$$\frac{(Cu_2OCl_2 + 2HCl \rightarrow 2CuCl_2 + H_2O) \times 2}{4HCl + O_2 + [4CuCl_2] \rightarrow 2Cl_2 + 2H_2O + [4CuCl_2]}$$

Limitations of intermediate theory-

(a) Action of promoters and poisons.
(b) Participation of catalyst in chemical reaction.

(ii) Adsorption theory - By the adsorption of the reactants at the surface of a catalyst, their concentrations are increased. The rate being directly proportional to concentration, is increased.

(iii) Modern theory - It is the combination of intermediate theory and adsorption theory. At the surface of a catalyst there are residual or free valencies and reactant molecules are retained at the surface in distorted or strained positions. These molecules then react vigrously to give products and make space for other reactant molecules. The greater the surface area of the catalyst, the more is its activity. Further catalysts with rough surface, having greater number of corners, peaks, cracks have more active centres and more effective e.g. finely divided nickel or platinum



ACTION OF PROMOTERS :

It can be assumed that a loose compound is formed between the catalyst and the promoter which possesses an increased capacity of adsorption.

Action of catalytic poison - It may be due to the preferential adsorption of poison on the active spots of the catalyst thus reducing the number of free active spots for reacting molecules.

ACID BASE CATALYSIS :

A large number of reactions catalysed by acids or bases are known eg.

(a) Hydrolysis of an ester in presence of an acid

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

(b) Cyanides are hydrolysed by acids or alkalis

$$RCN + H_2O \xrightarrow[\text{or } OH^-]{H^+} RCONH_2 \xrightarrow{+H_2O} RCOOH + NH_3$$

Such reactions are called acid base catalysis and H^+ or OH^- ions act as catalyst.

MODERN CONCEPT OF ACID BASE CATALYSIS:

According to this concept

(i) A reaction which is catalysed by an acid is also catalysed by all substances having tendency to lose protons (H^+)

(ii) A reaction which is catalysed by a base is also catalysed by all substances having a tendency to gain protons.

ENZYMES OR BIOLOGICAL CATALYSTS :

Many complex chemical reactions like oxidation, reduction or hydrolysis take place in presence of enzymes which are highly complex, nitrogenous non living organic substances. They are highly specific in nature eg.

(a) Starch is catalysed by diastase maltose is formed and then maltose by maltase

$$2(C_6H_{10}O_5)_n + n\,H_2O \xrightarrow{\text{Diastase}} n\underset{\text{Maltose}}{C_{12}H_{22}O_{11}}$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}} 2\underset{\text{Glucose}}{C_6H_{12}O_6}$$

(b) Urea is converted into ammonium carbonate by Urease

$$H_2N.CO.NH_2 + 2H_2O \xrightarrow{\text{Urease}} (NH_4)_2CO_3$$

MECHANISM OF ENZYME ACTION :

Enzyme can increase the rate of biochemical reactions by 10^6 to 10^{12} times. They are highly selective and specific and act on certain molecules called substrates and leave the rest of the system unaffected (LOCK AND KEY THEORY). Michaelis and Menten proposed the following mechanism for enzyme catalysis

$$\underset{\text{Enzyme}}{E} + \underset{\text{Substrate}}{S} \rightleftharpoons \underset{\text{Activated Complex}}{ES} \longrightarrow \underset{\text{Product}}{P} + \underset{\text{Enzyme}}{E}$$

CHARACTERISITCS OF ENZYME CATALYSIS :

1. Enzymes are most efficient catalysts.
2. Enzymes are very selective and specific.
3. Enzymes require optimum condition of temperature and pH of the medium.
4. Enzymes are easily poisoned by addition of other substances particularly heavy metal ions (Hg^{2+} or Ag^+)
5. Activity of enzymes is increased by activators (certain metal ions Co^{2+}, Mn^{2+}, Na^+, Cu^{++} etc) or coenzymes.

ADSORPTION

ADSOPRTION :

Adsorption is the phenomenon of higher concentration of molecular species at the surface than in the bulk of a solid or liquid. Forces involved are van der waal's forces.

The unbalanced or residual forces acting along the surface of a solid or liquid attract the moleculs of other species when brought into their contact. These molecules remain at surface and do not go into bulk, hence making the concentration more at surface.

ADSORBATE :

The substance that concentrates at the surface is called adsorbate.

ADSORBENT :

Adsorbent is the solid or liquid at whose surface the concentration occurs.

ABSORPTION :

Absorption is the phenomenon of uniform distribution of a substance throughout the body of a solid or liquid. For *eg* water vapour is absorbed by a sponge or anhydrous $CaCl_2$ while it is adsorbed by silicagel. The pressure of gases (SO_2, Cl_2, NH_3) pressure decreases when treated with powdered charcoal in a closed vessel due to adsorption of gas on charcoal surface.

SORPTION :

Adsorption and absorption go hand in hand thus making it tough to distinguish between them. The general term sorption was introduced by McBain to include both processes.

CHARACTERISTICS OF ADSORPTION :

(i) It is a surface phenomenon.

(ii) It is a spontaneous process.

(iii) Adsorption is accompanied by evolution of heat as the residual forces acting along the surface of adsorbent decrease.

Heat evolved on adsorption of 1 mole of a gas is ***molar heat*** *of adsorption.*

(iv) Adsorption is accompanied by decrease in enthalpy. i.e. ΔH = -ve

(v) Adsorption is accompanied by decrease in entropy i.e. $T\Delta G$ is negative.

Also, $\Delta G = \Delta H - T\Delta S$. As ΔH is negative and so is ΔS, $\Rightarrow \Delta G$ is negative. But experimentally ΔH becomes less negative as the adsorption progresses and ultimately becomes zero as the equilibrium is reached.

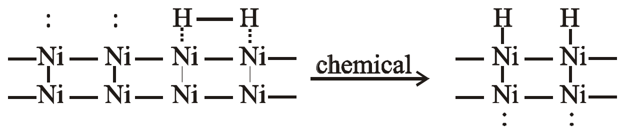
Adsorption of gases at the surface of metals like Ni, Pt, Pd etc is called ***Occlusion***.

PHYSICAL ADSORPTION :

It is also called van der Waal's adsorption which involves weak forces, physical in nature, with small heat of adsorption. For example adsorption of H_2 or O_2 on charcoal.

CHEMICAL ADSORPTION :

Forces of attraction between adsorbate and adsorbent being of the same strength as chemical bonds, given the name chemisorption. It may involve covalent or ionic bonds. e.g. H_2 is chemisorbed on Ni. Hydrogen is first adsorbed by van der waal's forces and then dissociates. Hence hydrogen atoms are chemisorbed on Ni.



Often adsorption involves combination of two types of adsorption

POINTS OF DISTINCTION BETWEEN PHYSICAL AND CHEMICAL ADSORPTION :

		Physical	*Chemical*
(i)	Forces	van der waals	Chemical bonds
(ii)	Temperature	at low temperature	at high temperature
(iii)	Layer	multimolecular	monomolecular
(iv)	Pressure	increases with high pressure	decrease with P. Infact change of pressure has no effect.
(v)	Liquification	related to liquification of gases	not related to liquification of gases
(vi)	Enthalpy	20 - 40 kj/mol	40 - 400 kj/mol
(vii)	Activation Energy	low	high
(viii)	Reversibility	reversible	irreversible
(ix)	Specificity	not specific	very specific

FACTORS AFFECTING ADSORPTION OF GASES BY SOLIDS :

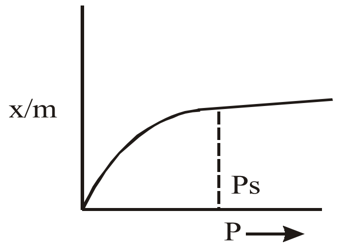
(i) Nature of gas - Easily liquifiable gases get adsorbed readily. Thus 1g of activated charcoal adsorbs 380 ml of SO_2 (critical temp. 157ºC). 16 ml. of methane (critical temp. = –83º), 4.5 ml of H_2 (critical temp. –20º C)

But chemisorption is more specific and occurs if there is a possibility of reaction between gas adsorbed and the solid.

(ii) Nature of adsorbent - Different solids adsorb same gas at given temperature and pressure to different extent. Adsorbing power depends upon chemical nature, surface area cleanliness of surface, distribution of capillaries or forces acting on surface. Finely divided metals (Ni, Pt) and porous substances (charcoal, silica gel) are best solid adsorbents as they provide large surface area.

(iii) Effect of pressure - Extent of adsorption increases with pressure as adsorption is a reversible process and is accompanied by decrease of pressure x/m is the extent of adsorption where m is the mass of adsorbent and x that of adsorbate at equilibrium.

The relation $\frac{x}{m} = k(P)_T$ solid, gas is called adsorption isotherm. Such isotherms are obtained when adsorbate forms a unimolecular layer on surface of adsorbent.

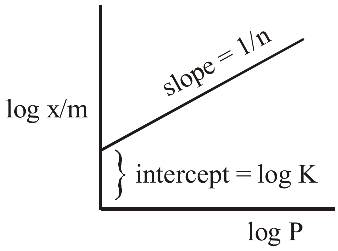


At low pressure, $x/m \propto p^1$ or $x/m = kp^1$ where k = constant

At high pressure, beyond saturation x/m is independent of p and $x/m \propto p^o$.

At intermediate pressures, $x/m \propto p^{1/n}$ where n > 1

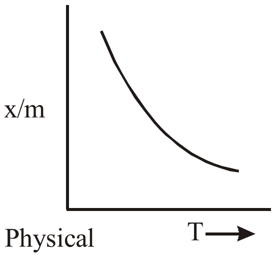
or $\log \frac{x}{m} = \log k + \frac{1}{n} \log p$ where k = constant.



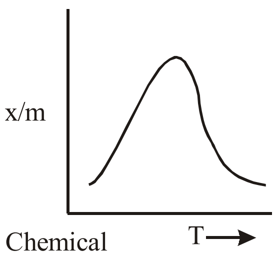
Above equation is called ***FREUNDLICH ISOTHERM***

(iv) Effect of temperature - According to Le chatelier's principle, physical adsorption occurs rapidly and lower temperature and decreases with increasing temperature. Chemisorption increases with temperature. Rise of temperature might cause physical adsorption to change to chemical adsorption e.g. N_2 is physically adsorbed on Fe at 190ºC but chemisorbed to form nitride at 500ºC.

The relation $\frac{x}{m} = k(T)_P$ liquid, solid is called adsorption isobar.



Physical



Chemical

(v) **Surface area -** Larger specific area (surface area per g of adsorbent) means greater adsorption.

(vi) **Heat of adsorption -** Energy released when 1g mole of a gas is adsorbed on solid surface is called heat of adsorption. Adsorption is an exothemic process similar to condensation. Heat of adsorption is small as attractive forces between gas molecules and solid surface are due to weak van der waal's forces.

ADSORPTION OF SOLUTES FROM SOLUTIONS:

Porous and finely divided solid substances can also adsorb dissolved substances from solution *eg* activated charcoal adsorbs dye stuffs. When solution of acetic acid is shaken with activated charcoal, part of acid is removed by adsorption and concentration of the soluion is decreased. Some precipitates act as adsorbents. For e.g. $Mg(OH)_2$ when precipitated in the presence of dyestuff magnesium forms a blue lake. Adsorption from solution follows same principles as that for adsorption of gases by solids. Thus

(i) Some adsorbents specifically adsorb some solute more effectively than others.

(ii) Increase in surface area causes increase in adsorption.

(iii) Adsorption increases with temperature.

(iv) It involves establishment of equilibrium between the amount adsorbed and the concentration of solute in solution.

Freundlich isotherm using concentration can be written as:

$$\frac{x}{m} = k \times c^{1/n}$$

where x = mass of solute adsorbed.

m = mass of adsorbent

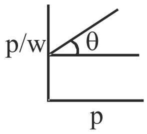
c = equilibrium concentration of solution.

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c \text{ is a straight line.}$$

LANGMUIR'S ADSORPTION ISOTHERM :

Langmuir exploited theoretical considerations based on kinetic theory of gases to derive an adsorption isotherm. If w is mass of gas adsorbed per unit mass of adsorbent and p is the pressure of the gas then

$$\frac{p}{w} = \frac{1}{A} + \left(\frac{B}{A}\right)p \qquad \text{where A and B are constant}$$



$$\text{slope} = \frac{B}{A}, \text{ intercept} = \frac{1}{A}$$

COMPETING ADSORPTION :

Different adsorbates compete among themselves to adsorb on the adsorbent. Strongly adsorbable substance can displace a weakly adsorbable substance. For e.g. Cl_2 and NH_3 can replace O_2 and N_2 already adsorbed on charcoal. Moisture is also strongly adsorbed by silica though it is present in small proportion in air and charcoal adsorbs polluting gases present in air in small amounts.

ACTIVATION OF ADSORBENT :

Activation or increasing the power of adsorption can be achieved in different ways.

(i) by increasing surface area

(ii) by making surface rough.

Small size of particles makes the interparticle space too small to allow penetration of gas molecules and thus may decrease the extent of adsorption.

APPLICATIONS :

(i) High vacuum can be generated if a partially evacuated vessel is connected to a container of activated charcoal cooled with liquid air. This is due to adsorption of gas molecules in vessel.

(ii) Gas masks contain activated charcoal or adsorbents to remove poisonous gases and thus purify the air.

(iii) Heterogenous catalysis (see chapter on catalysis)

(iv) Chromatographic analysis is based on principle of selective adsorption. Mixture of gases can also be separated by selective adsorption of gases by liquids (gas chromatography).

(v) Colouring matter can be removed from solutions by animal charcoal which adsorbs the colouring matter.

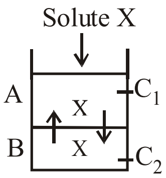
(vi) Froth floatation process which involves adsorption of mineral particles wetted with oil is used to free low grade sulphide ores (PbS, ZnS, Cu_2S) from silica.

not in AIEEE syllabus but given for additional information.

DISTRIBUTION LAW

NERNST DISTRIBUTION LAW OR PARTITION LAW:

When a solute is shaken with two immiscible liquids, having solubility in both, the solute distributes itself between the two liquids in such a way that the ratio of its concentrations in two liquids is constant at a given temperature, provided the molecular state of the solute remains the same in both the liquids.



$$\frac{\text{Concentiation of X in A}}{\text{Concentiation of X in B}} = \text{a constant} \qquad \text{or } \frac{C_1}{C_2} = K_D$$

(Where K_D = distribution coefficient or partition coefficient or distribution ratio)

Distribution of Succinic acid between ether and water illustrates the consistancy of the ratio of concentrations in each layer

C_1 in ether	C_2 in water	C_1/C_2
0.013	0.069	0.188
0.022	0.119	0.184

Since the solubility also represents concentration, the distribution law can also be written as

$$\frac{C_1}{C_2} = \frac{S_1}{S_2} = K_D$$

Where S_1 and S_2 are the solubilities of the solute in two solvents.

LIMITATIONS OF DISTRIBUTION LAW :

The law holds good when the following conditions are fulfilled.

(i) ***Molecular State :*** The molecular state of the solute must remain the same in both the solvents i.e. there should be no **association** or **dissociation** of solute molecules.

(ii) ***Constant temperature :*** The temperature is kept contant

(iii) ***Non-miscibility of solvents :*** The two solvents must be immiscible and the non miscibility must not change on addition of solute.

(iv) **Dilute solutions :** The law is applicable to dilute solutions only

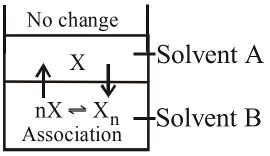
(v) ***Equilibrium concentrations :*** The C_1 and C_2 are the equilibrium concentrations

MODIFICATIONS :

The following modifications are applied under different conditions

(i) When solute associates : Apply the following formula

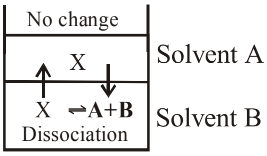
$$\frac{C_1}{n\sqrt{C_2}} = k(\text{constant})$$



Where n is the number of molecules undergoing association

(ii) When solute dissociates : Apply the following formula

$$\frac{C_1}{C_2(1-\alpha)} = k(\text{constant})$$



Where α is the degree of dissociation

(iii) When temperature varies : Variation of distribution coefficient with change of temperature is given by following relation

$$\frac{d\log K}{dT} = \frac{\Delta H}{RT^2}$$

HENRY'S LAW :

It states that at a constant temperature the solubility of a gas in a liquid is directly proportional to the pressure of the gas above it

$$\underline{C}\,\alpha\,P \quad \text{or} \quad C = K_H P$$

Where $\underline{C}$ is the solubility or concentration of the gas, K_H is a constant known as Henry's constant and p is the pressure of the gas.

- The law holds good for dilute solutions of gases which do not react with the solvent.
- When mixture of gases is there, the solubility of each gas is proportional to its partial pressure.

APPLICATIONS OF DISTRIBUTION LAW :

(i) Solvent extraction : The separation of organic substances from aqueous solutions by the use of organic solvent generally ether is based on partition law. The aqueous solution of organic substance is shaken with ether. The organic substance distributes itself in both the liquids which are separated by separating funnel. The solvent layer on evaporation leaves behind organic substance.

For more recovery of the substance, the number of operations should be more. The amount of organic substance left in aqueous solution is given by

$$x_n = A\left(\frac{KV}{KV+v}\right)^n$$

n = Number of operations
K = Distribution constant
V= Volume of aqueous solution
v = Volume of organic solvent
A = Amount of solute

(ii) Determination of degree of association

(iii) Determination of degree of dissociation

(iv) Determination of solubility

(v) Purification of organic substances by chromatography

(vi) Desilverisation of lead (Parke's proces)

(vii) Layer test for Bromide and Iodide

(viii) Study of complex formation

(ix) Distribution Indicators

(xi) Determination of molecular weight in different solvents

Miscellaneous Solved Examples

1. If the solubility of iodine in water is 0.8 g/l at 25° C, calculate the solubility of I_2 in CCl_4. The k_D of iodine in between CCl_4 and water is 85 in favour of CCl_4 at 25° C.

Sol. $k_D = \frac{[I_2]\text{in } CCl_4 \text{ layer}}{[I_2]\text{in water layer}}$ = Let the solubility of I_2 in CCl_4 be a g/litre

$$85 = \frac{a}{0.8}$$

$a = 68$ g litre^{-1}

2. Succinic acid has normal molecular weight in water. Succinic acid was allowed to distribute in water and benzene by shaking. The concentiation of acid in water and benzene are C_1 and C_2 having values.

	(i)	(ii)	(iii)
C_1 g/100 ml	0.150	0.195	0.289
C_2 g/100 ml	2.420	4.120	9.600

Find the molecular weight of acid in benzene

Sol. Calculating the value of k_D by applying the relation C_1/C_2 and $C_1/\sqrt{C_2}$

$$\text{In (i)} \frac{C_1}{C_2} = \frac{0.152}{2.420} = 0.062\,; \frac{C_1}{\sqrt{C_2}} = \frac{0.150}{\sqrt{2.420}} = 0.096$$

$$\text{In (ii)} \frac{C_1}{C_2} = \frac{0.195}{4.120} = 0.047\,; \frac{C_1}{\sqrt{C_2}} = \frac{0.195}{\sqrt{4.120}} = 0.096$$

$$\text{In (iii)} \frac{C_1}{C_2} = \frac{0.289}{9.600} = 0.030\,; \frac{C_1}{\sqrt{C_2}} = \frac{0.289}{\sqrt{9.600}} = 0.093$$

Since constant value of K_D is obtained by relation $C_1/\sqrt{C_2}$ hence succinic acid forms a dimer in benzene

Therefore its molecular weight in benzene = 2 × 118 = 236

3. The solubility of pure oxygen in water at 20° C and 1.00 atm pressure is 1.38×10^{-3} mole/litre. Calculate the concentration of O_2 (mole/litre) at 20° C and partial pressure of 0.21 atm.

Sol. Calculation of Henry's constant

$$k_H \text{ or } k \frac{\text{Conc. of } O_2}{\text{pressure of } O_2} = \frac{1.38 \times 10^{-3}}{1.00\,\text{atm}} \text{mole/litre}$$

$$= 1.38 \times 10^{-3} \frac{\text{mole/litre}}{\text{atm}}$$

Calculation of concentration of O_2

$$C = kP = 1.38 \times 10^{-3} \frac{\text{mole/litre}}{\text{atm}} \times 0.21\,\text{atm}$$

$= 2.9 \times 10^{-4}$ mole/litre

4. The distribution coefficient of an alkaloid between chloroform and water is 20 in favour of chloroform. Compare the weights of the alkaloid remaining in aqueous solution when 100 ml containing 1 gram has been shaken with (a) 100 ml chloroform and (b) two successive 50 ml portion.

Sol. $K = \frac{C_{\text{water}}}{C_{\text{chloroform}}} = \frac{1}{20}$

(a) When 100 ml is used in one lot, the amount unextracted is

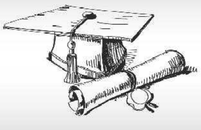
$$X_1 = 1 \times \left(\frac{KV}{KV + v}\right)$$

$$= 1 \times \left(\frac{1/20 \times 100}{1/20 \times 100 + 100}\right) = \frac{5}{105} = 0.0476\,\text{g}$$

(b) When 50 ml chloroform is used in each of two stages the amount unextracted is

$$X_2 = 1 \times \left(\frac{1/20 \times 100}{1/20 \times 100 + 50}\right)^2 = \left(\frac{5}{55}\right)^2 = 0.0083\,\text{g}$$

Exercise-1 | NCERT Based Questions



Very Short Answer Questions

1. Which of the following is adsorbed most preferably: O_2, NH_3, CO?

2. Can crystalloid be brought into colloidal state? Give one example.

3. Why are colloids good adsorbents?

4. Write the names of two gases which are adsorbed by transition metals such as nickel and cobalt.

5. Can a gas mixed with another gas form a colloidal solution? Give reasons.

6. Account for the following:
   (a) Ferric hydroxide sol is positively charged.
   (b) The extent of physical adsorption decreases with rise in temperature.
   (c) A delta is formed at the point where river enters the sea.

7. Detergents with straight chain hydrocarbons are preferred to branched chain hydrocarbons. Explain.

8. Smoke is passed through charged plates before allowing it to pass through chimneys in industries.

9. Comment on sign of ΔH, ΔS and ΔG for adsorption process.

10. What is demulsification? Name two demulsifiers.

11. Out of NH_3 and CO_2, which gas will be absorbed more readily on the surface of activated charcoal and why?

12. What is meant by chemisorption?

13. Explain the following terms :
   (i) Electrophoresis
   (ii) Dialysis
   (iii) Tyndall effect.

14. What is meant by coagulation of colloidal solution? Describe briefly and three methods by which coagulation of lyophobic sols can be carried out.

15. Explain the following terms giving a suitable example for each:
   (i) Aerosol
   (ii) Emulsion
   (iii) Micelle

16. Write the dispersed phase and dispersion medium of the following colloidal systems:
   (i) Smoke
   (ii) Milk

17. What are lyophilic and lyophobic colloids? Which of these sols can be easily coagulated on the addition of small amounts of electrolytes?

Multiple Choice Questions

18. Which one of the following statements is incorrect in the case of heterogeneous catalysis ?
   (a) The catalyst lowers the energy of activation
   (b) The catalyst actually forms a compound with the reactant
   (c) The surface of the catalyst plays a very important role
   (d) There is no change in the energy of activation.

19. Which one of the following in not a colloidal solution?
   (a) Smoke (b) Ink
   (c) Blood (d) Air

20. Which of the following statements is *not* true about the oil-in-water type emulsion?
   (a) On addition of small amount of water, no separate layer of water appears
   (b) On addition of oil, separate layer of oil is formed
   (c) Addition of an electrolyte causes the conductivity of the emulsion to increase
   (d) Addition of small amount of oil soluble dye renders the entire emulsion coloured.

21. Suspensions are
   (a) Visible to naked eye
   (b) Not visible by any means
   (c) Invisible under electron microscope
   (d) Invisible through microscope

22. Which of the following terms is not related with colloids ?
   (a) Brownian movement
   (b) Dialysis
   (c) Ultrafiltration
   (d) Wavelength

23. A colloid always :
   (a) Contains two phases
   (b) Is a true solution
   (c) Contains three phases
   (d) Contains only water soluble particles

24. When a colloidal solution is observed under an ultramicroscope, we can see
   (a) Light scattered by colloidal particles
   (b) Size of the particle
   (c) Shape of the particle
   (d) Relative size

25. One desires to prepare a positively charged sol of silver iodide. This can be achieved by
   (a) adding small amount of $AgNO_3$ solution to KI solution in slight excess
   (b) adding small amount of KI solution to $AgNO_3$ solution in slight excess
   (c) mixing equal volumes of equimolar solutions of $AgNO_3$ and KI
   (d) None of these

26. Cod Liver oil is
   (a) fat dispersed in water (b) water dispersed in fat
   (c) water dispersed in oil (d) fat dispersed in fat.

27. Colloid of which one of the following can be prepared by electrical dispersion method as well as reduction method ?
   (a) Sulphur (b) Ferric hydroxide
   (c) Arsenious sulphide (d) Gold

Exercise-2 | CONCEPTUAL MCQs

1. The size of colloidal particles is between
(a) 10^{-7} - 10^{-9} cm (b) 10^{-9} - 10^{-11} cm
(c) 10^{-5} - 10^{-7} cm (d) 10^{-2} - 10^{-3} cm

2. The size of colloidal particles is of the order
(a) $> 0.1\ \mu$ (b) $1 m\mu$ to 0.2μ
(c) $< 1\ m\mu$ (d) $> 10\ m\mu$

3. Butter is a colloid formed when
(a) fat is dispersed in water
(b) fat globules are dispersed in water
(c) water is dispersed in fat
(d) None of the these

4. Milk is a colloid in which
(a) A liquid is dispersed in liquid
(b) A solid is dispersed in liquid
(c) A gas is dispersed in liquid
(d) some sugar is dispersed in water

5. Cod Liver oil is
(a) Fat dispersed in water (b) Water dispersed in fat
(c) Water dispersed in oil (d) Fat dispersed in fat.

6. Cloud or fog is a colloidal system in which the dispersed phase and the dispersion medium are
(a) Gas, Liquid (b) Liquid, gas
(c) Liquid, liquid (d) Solid, Liquid

7. Which one among the following sols is hydrophobic ?
(a) Gum (b) Gelatin
(c) Starch (d) Sulphur

8. Which of the following constitutes irreversible colloidal system in water as dispersion medium?
(a) Clay (b) Platinum
(c) $Fe(OH)_3$ (d) All of these

9. Which of the following is a lyophillic colloid ?
(a) Milk (b) Gum
(c) Fog (d) Blood

10. Surface tension of lyophillic sols is
(a) lower than that of H_2O
(b) more than that of H_2O
(c) equal to that of H_2O
(d) can either lower or more than H_2O.

11. Peptization denotes
(a) Digestion of food
(b) Hydrolysis of proteins
(c) Breaking and dispersion into the colloidal state
(d) Precipitation of solid from colloidal dispersion

12. Colloidal gold is prepared by
(a) Mechanical dispersion (b) Peptisation
(c) Bredig's Arc method (d) Hydrolysis

13. When H_2S gas is passed through nitric acid, the product is
(a) Rhombic S (b) Prismatic S
(c) Amorphous S (d) Monoclinic S

14. Colloid of which one of the following can be prepared by electrical dispersion method as well as reduction method ?
(a) Sulphur (b) Ferric hydroxide
(c) Arsenious sulphide (d) Gold

15. The formation of colloid from suspension is
(a) Peptisation (b) Condensation
(c) Sedimentation (d) Fragmentation

16. Which one of the following substances is not used for preparing lyophillic sols ?
(a) Starch (b) Gum
(c) Gelatin (d) Metal sulphide

17. Blood may be purified by
(a) Dialysis (b) Electro osmosis
(c) Coagulation (d) Filtration

18. The cause of Brownian movement is
(a) Heat changes in liquid state
(b) Convectional currents
(c) The impact of molecules of the dispersion medium on the colloidal particles.
(d) Attractive forces between the colloidal particles and molecules of dispersion medium.

19. Brownian movement is found in
(a) Colloidal solution (b) Suspension
(c) Saturated solution (d) Unsaturated solution

20. Random motion of colloidal particles is known as
(a) Dialysis (b) Brownian movement
(c) Electroosmosis (d) Tyndall effect

21. Milk can be preserved by adding a few drops of
(a) Formic acid solution (b) Formaldehyde solution
(c) Acetic acid solution (d) Acetaldehyde solution.

22. In which of the following Tyndall effect is not observed ?
(a) Suspensions (b) Emulsions
(c) Sugar solution (d) Gold sol

23. Point out the false statement
(a) Brownian movement and Tyndall effect are shown by colloidal systems.
(b) Gold number is a measure of the protective power of a lyophillic colloid
(c) The colloidal solution of a liquid in liquid is called gel
(d) Hardy - Schulze rule is related with coagulation.

24. Tyndall effect is shown by
(a) Sol (b) Solution
(c) Plasma (d) Precipitate

25. Gold number is associated with
(a) Electrophoresis (b) Purple of caslus
(c) Protective colloids (d) Amount of pure gold

26. In Brownian movement or motion, the paths of the particles are
(a) Linear (b) Zig-zag
(c) Uncertain (d) Curved

27. The migration of colloidal solute particles in a colloidal solution, when an electric current is applied to the solution is known as
(a) Brownian movement (b) Electroosmosis
(c) Electrophoresis (d) Electrodialysis

28. When a strong beam of light is passed through a colloidal solution, the light will
(a) be reflected (b) be scattered
(c) be refracted (d) give a rainbow

29. The simplest way to check whether a system is colloidal is by
(a) Tyndall effect (b) Brownian movement
(c) Electrodialysis (d) Finding out particle size

30. A colloidal solution is subjected to an electrical field. The particles move towards anode. The coagulation of same sol is studied using NaCl, $BaCl_2$ and $AlCl_3$ solutions. Their coagulating power should be
(a) $NaCl > BaCl_2 > AlCl_3$ (b) $BaCl_2 > AlCl_3 > NaCl$
(c) $AlCl_3 > BaCl_3 > NaCl$ (d) $BaCl_2 > NaCl > AlCl_3$

31. In coagulating the colloidal solution of As_2S_3 which has the minimum coagulating value ?
(a) NaCl (b) KCl
(c) $BaCl_2$ (d) $AlCl_3$

32. Which of the following ions can cause coagulation of proteins ?
(a) Ag^+ (b) Na^+
(c) Mg^{2+} (d) Ca^{2+}

33. Which is used for ending charge on colloidal solution
(a) Electrons (b) Electrolytes
(c) Positively charged ions (d) Compounds

34. Which of the following is most effective in causing the coagulation of ferric hydroxide sol?
(a) KCl (b) KNO_3
(c) K_2SO_4 (d) $K_3[Fe(CN)_6]$

35. Arsenic sulphide is a negative sol. The reagent with least precipitating power is
(a) $AlCl_3$ (b) NaCl
(c) CaF_2 (d) Glucose

36. The stablity of lyophillic colloids is due to which of the following?
(a) Charge on their particles
(b) Large size of their particles
(c) Small size of their particles
(d) A layer of dispersion medium

37. The Rubin number which was proposed by Ostwald as an alternative to the Gold number in order to measure the protective efficiency of a lyophillic colloid may be defined as the
(a) Mass in milligrams of a colloid per 100 c.c. of solution which just prevents the colour change of standard sol of dye Congo - Rubin from red to violet when 0.16 g eq. KCl is added to it.
(b) Mass in grams of a colloid per 100 c.c. of solution which just prevents the colour change of standard sol of dye Congo - Rubin from red to violet when 0.1 M KCl is added to it
(c) Mass in grams of a colloid per 100 c.c. of solution which just prevents the colour change of standard sol of dye Congo - Rubin from red to violet when 0.2 M KCl is added to it.
(d) Mass in grams of a colloid per 100 c.c. of solution which just prevents the colour - change of standard sol of dye Congo - Rubin from red to violet when 1 M KCl is added to it

38. The function of gum arabic in the preparation of an Indian ink is
(a) Coagulation (b) Peptization
(c) Absorption (d) Protective action

39. At CMC the surfactant molecules
(a) Decompose
(b) Become completely soluble
(c) Associate
(d) Dissociate

40. Which one of the following is correctly matched?
(a) Emulsion - curd (b) Foam - mist
(c) Aerosol - smoke (d) Solid sol - cake

41. Alum helps in purifying water by
(a) forming Si complex with clay particles
(b) sulphate part which combines with the dirt and removes it
(c) aluminium which coagulates the mud particiles
(d) making mud water soluble

42. The process which is catalysed by one of the products is called
(a) Acid - base catalysis (b) Auto catalysis
(c) Negative catalysis (d) Positive catalysis

43. Which one of the following is an example of homogeneous catalysis ?
(a) Haber's process of synthesis of ammonia
(b) Catalytic conversion of SO_2 to SO_3 in contact process
(c) Catalytic hydrogenation of oils
(d) Acid hydrolysis of methyl acetate

44. In the case of auto catalysis
(a) reactant catalysis
(b) heat produced in the reaction catalysis
(c) product catalysis
(d) solvent catalysis

45. Which of the following statements about a catalyst is/are true ?
(a) A catalyst accelerates the reaction by bringing down the free energy of activation
(b) A catalyst also takes part in the reaction mechanism
(c) A catalyst makes the reaction more feasible by making the ΔG^o more negative
(d) A catalyst makes the equilibrium constant of the reaction more favourable for the forward reaction.

46. The role of a catalyst in a reversible reaction is to
(a) Increase the rate of forward reaction
(b) Decrease the rate of backward reaction
(c) alter the equilibrium constant of the reaction
(d) Allow the equilibrium to be achieved quickly

47. Which of the following kind of catalysis can be explained by the adsorption theory ?
(a) Homogeneous catalysis
(b) Acid - base catalysis
(c) Heterogeneous catalysis
(d) Enzyme catalysis

48. A biological catalyst is essentially
(a) An enzyme (b) A carbohydrate
(c) An amino acid (d) A nitrogenous base

49. In Zeigler - Natta polymerisation of ethylene, the active species is
(a) $AlCl_3$ (b) Et_3Al
(c) CH_2CH_2 (d) Ti^{3+}

50. Adsorbed acetic acid on activated charcoal is:
(a) Adsorber (b) Absorber
(c) Adsorbent (d) Adsorbate

51. Which of the following is less than zero during adsorption.
(a) ΔG (b) ΔS
(c) ΔH (d) All of these

52. The heats of adsorption in physisorption lie in the range (in kJ/mol)
(a) 40 - 400 (b) 40 - 100
(c) 10 - 40 (d) 1 - 10

53. In physical adsorption, gas molecules are bound on the solid surface by
(a) Chemical forces (b) Electrostatic forces
(c) Gravitational forces (d) van der waal's forces

54. How many layers are adsorbed in chemical adsorption ?
(a) One (b) Two
(c) Many (d) Zero

55. In physical adsorption, the forces associated are
(a) ionic (b) covalent
(c) van der Waal (d) H - bonding

56. Adsorption due to strong chemical forces is called
(a) Chemisorption (b) Physiosorption
(c) Reversible adsorption (d) Both (b) and (c)

57. Which one of the following is an incorrect statement for physisorption ?
(a) It is reversible process
(b) It requires less heat of absorption
(c) it requires activation energy
(d) It takes place at low temperature

58. Which is adsorbed in maximum amount by activated charcoal ?
(a) N_2 (b) CO_2
(c) Cl_2 (d) O_2

59. Which among the following statements is false?
(a) Increase of pressure increases the amount of adsorption
(b) Increase of temperature may decrease the amount of adsorption.
(c) The adsorption may be monolayered or multilayered
(d) Particle size of the adsorbent will not affect the amount of adsorption.

60. Rate of physisorption increases with
(a) decrease in temperature (b) increase in temperature
(c) decrease in pressure (d) decrease in surface area

61. Distribution law was given by
(a) Van't Hoff (b) Henry
(c) Nernst (d) Ostwald

62. When is the Distribution Law applicable?
(a) Temperature remains constant
(b) Dilute solutions are employed
(c) Two solvents are mutually insoluble
(d) All of these

63. The relation between pressure and solubility of a gas was given by
(a) Henry (b) Nernst
(c) Both (a) and (b) (d) Neither (a) nor (b)

64. The solubility of iodine in water is 0.35 g/ litre at 25°C. If distribution coefficient of iodine between CS_2 and water is 600, the solubility of iodine in CS_2 in g/ litre will be
(a) 210 (b) 510
(c) 195 (d) 250

65. Partition coefficient, $K = \frac{S_1}{S_2}$ is valid
(a) when dissociation takes place
(b) when association takes place
(c) when there is a complex formation
(d) in case of normal distribution

66. When a solute is shaken with two immiscible liquid, it associates in one of the liquids. The distribution constant is given by
(a) $\frac{C_1}{C_2}$ (b) $\frac{C_1}{C_2(1-\alpha)}$
(c) $\frac{S_1}{S_2}$ (d) $\frac{C_1}{\sqrt[n]{C_2}}$

67. The condition under which Nernst distribution law will not hold true is
(a) The molecular state of the solute is same in both solvents
(b) Temperature is constant
(c) The solute does not cause any change in the mutual solubility of the two solvents
(d) None of these

68. When benzoic acid is shaken with a mixture of 100 ml water and 50 ml ether, the ether layer was found to contain 0.127 g of acid and water layer 1.843 g of the acid. The partition coefficient between water and ether is
(a) 72.5 (b) 7.25
(c) 725 (d) 0.725

69. If in a pair of immiscible liquids, a common solute dissolves in both and equilibrium is reached, then the concentration of the solute in the upper layer is
(a) same as in lower
(b) in fixed ratio with that in the lower layer
(c) lower than in the lower layer
(d) higher than in the lower layer

70. The partition coefficient of a solute for ether and water is in the ratio 5:1. The amount of solute extracted from 100 cc of its aqueous solution with 100 cc of ether in one time will be
(a) 90% (b) 87.3%
(c) 91.8% (d) 83.3%

71. The partition coefficient of X between liquids A and B is 10. The partition coefficient of X between B and A is
(a) 100 (b) 1
(c) 0.1 (d) 10

72. You are given 100 ml of CCl_4 to extract iodine from 200 ml of its aqueous solution. For extracting the maximum amount of iodine, which one of the following process would you use
(a) Use 100 ml of CCl_4
(b) Use 50 ml of CCl_4 twice
(c) Use 10 ml of CCl_4 ten times
(d) Use 25 ml of CCl_4 4 times

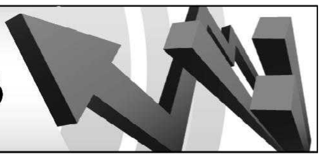
73. Distribution law cannot be applied to I_2 distributed between
(a) H_2O and C_2H_5OH (b) H_2O and CCl_4
(c) H_2O and CS_2 (d) H_2O and $C_2H_5OC_2H_5$

74. Which of the following applications is not shown by distribution law?
(a) Pallison's process
(b) Partition Chromatography
(c) Solvent extraction
(d) Parke's process

75. Which one of the following statements is false for distribution law?
(a) The two solvents must be mutually immiscible
(b) The concentration of the solute in both the solvents must be kept high
(c) The substrate must not react with any of the solvents
(d) The temperature should not change during experimentation

76. When solution of 5g of iodine in CS_2 was shaken with the same volume of water. The amount of iodine in water is
(Distribution coefficient $C_{CS_2}/C_{H_2O} = 420.0$)
(a) 1.19 (b) 0.0019
(c) 0.0119 (d) 0.119

Exercise-3 | PAST COMPETITION MCQs



1. The Langmuir adsorption isotherm is deduced by using the assumption **[CBSE-PMT 2007]**
(a) the adsorption sites are equivalent in their ability to adsorb the particles
(b) the heat of adsorption varies with coverage
(c) the adsorbed molecules interact with each other
(d) the adsorption takes place in multilayers.

2. If x is amount of adsorbate and m is amount of adsorbent, which of the following relations is not related to adsorption process ? **[CBSE-PMT 2011]**
(a) $x/m = f(p)$ at constant T.
(b) $x/m = f(\mathrm{T})$ at constant p.
(c) $p = f(\mathrm{T})$ at constant (x/m).
(d) $\frac{x}{m} = p \times T$

3. In Freundlich Adsorption isotherm, the value of $1/n$ is : **[CBSE-PMT 2012S]**
(a) between 0 and 1 in all cases
(b) between 2 and 4 in all cases
(c) 1 in case of physical adsorption
(d) 1 in case of chemisorption

4. Which one of the following, statements is incorrect about enzyme catalysis? **[CBSE-PMT 2012S]**
(a) Enzymes are mostly proteinous in nature.
(b) Enzyme action is specific.
(c) Enzymes are denaturated by ultraviolet rays and at high temperature.
(d) Enzymes are least reactive at optimum temperature.

5. The protecting power of lyophilic colloidal sol is expressed in terms of : **[CBSE-PMT 2012S]**
(a) coagulation value
(b) gold number
(c) critical miscelle concentration
(d) oxidation number

6. Which of the following is not the property of hydrophilic solutions ?
   (a) High concentration of dispersed phase can be easily obtained
   (b) Coagulation is reversible
   (c) Viscosity and surface tension are nearly the same as that of water.
   (d) The charge of the particle depends on the pH of the medium and it may be positive, negative or zero.

7. Which one of the following characteristics is **not** correct for physical adsorption ? **[AIEEE 2003]**
   (a) Adsorption increases with increase in temperature
   (b) Adsorption is spontaneous
   (c) Both enthalpy and entropy of adsorption are negative
   (d) Adsorption on solids is reversible

8. The disperse phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged, respectively. Which of the following statements is NOT correct ? **[AIEEE 2005]**
   (a) Coagulation in both sols can be brought about by electrophoresis
   (b) Mixing the sols has no effect
   (c) Sodium sulphate solution causes coagulation in both sols
   (d) Magnesium chloride solution coagulates, the gold sol more readily than the iron (III) hydroxide sol

9. In Langmuir's model of adsorption of a gas on a solid surface **[AIEEE 2006]**
   (a) the mass of gas striking a given area of surface is proportional to the pressure of the gas
   (b) the mass of gas striking a given area of surface is independent of the pressure of the gas
   (c) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered
   (d) the adsorption at a single site on the surface may involve multiple molecules at the same time

10. Gold numbers of protective colloids A, B, C and D are 0.50, 0.01, 0.10 and 0.005, respectively. The correct order of their protective powers is **[AIEEE 2008]**
    (a) D < A < C < B (b) C < B < D < A
    (c) A < C < B < D (d) B < D < A < C

11. Which of the following statements is incorrect regarding physisorptions? **[AIEEE 2009]**
    (a) More easily liquefiable gases are adsorbed readily.
    (b) Under high pressure it results into multimolecular layer on adsorbent surface.
    (c) Enthalpy of adsorption ($\Delta H_{adsorption}$) is low and positive.
    (d) It occurs because of van der Waal's forces.

12. According to Freundlich adsorption isotherm which of the following is correct? **[AIEEE 2012]**
    (a) $\frac{x}{m} \propto p^{\circ}$
    (b) $\frac{x}{m} \propto p^{1}$
    (c) $\frac{x}{m} \propto p^{1/n}$
    (d) All the above are correct for different ranges of pressure

13. The coagulating power of electrolytes having ions Na^+, Al^{3+} and Ba^{2+} for arsenic sulphide sol increases in the order : **[JEE M 2013]**
    (a) $Al^{3+} < Ba^{2+} < Na^+$ (b) $Na^+ < Ba^{2+} < Al^{3+}$
    (c) $Ba^{2+} < Na^+ < Al^{3+}$ (d) $Al^{3+} < Na^+ < Ba^{2+}$

14. Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient condition is : - **[IIT-JEE 2009S]**
    (a) $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$ (b) $CH_3(CH_2)_{11}OSO_3^- Na^+$
    (c) $CH_3(CH_2)_6COO^-Na^+$ (d) $CH_3(CH_2)_{11}N^+(CH_3)_3Br^-$

15. Among the electrolytes Na_2SO_4, $CaCl_2$, $Al_2(SO_4)_3$ and NH_4Cl, the most effective coagulating agent for Sb_2S_3 sol is **[IIT-JEE 2009S]**
    (a) Na_2SO_4 (b) $CaCl_2$
    (c) $Al_2(SO_4)_3$ (d) NH_4Cl

Exercise-4 | Applied MCQs

1. For the adsorption of a gas on a solid, the plot of log(x/m) versus log p is linear with slope equal to
   (a) k (b) log k
   (c) n (d) 1/n
   (where, p= pressure of gas, m = mass of the adsorbent, x = mass of the gas adsorbed)

2. Which of the following gas molecules have maximum value of enthalpy of physisorption?
   (a) C_2H_6 (b) Ne
   (c) H_2O (d) H_2

3. Adsorption is accompanied by the evolution of heat. So according to Le-Chatelier principle the amount of substance adsorbed should
   (a) increase with decrease in temperature
   (b) increase with increase in temperature
   (c) decrease with decrease in temperature
   (d) decrease with increase in temperature

4. At low pressure, the fraction of the surface covered follows
   (a) zero-order reaction (b) second-order reaction
   (c) first-order reaction (d) fractional order

5. At high pressure, the entire surface gets covered by a monomolecular layer of the gas follows

(a) three-halved order (b) second-order

(c) first-order (d) zero-order

6. Which of the following statements is incorrect ?

(a) Adsorption always leads to a decrease in enthaply and entropy of the system

(b) Adsorption arises due to unsaturation of valence forces of atoms or molecules on the surface

(c) Adsorption increases with rise in the temperature

(d) Adsorption decreases the surface energy

7. During adsorption

(a) $T\Delta S$ is positive (b) $\Delta H - T\Delta S$ is negative

(c) ΔH is positive (d) $T\Delta S$ and ΔG become zero

8. Which of the following statements is not correct?

(a) Decrease of temperature and increase of pressure, both tend to cause increase in the magnitude of adsorption of a gas on a solid.

(b) The easily liquefiable gases adsorb more on solid

(c) Greater the surface area per unit mass of the adsorbent, the greater is its capacity of adsorption

(d) None of these

9. The critical micelle concentration (CMC) is

(a) the concentration at which micellization starts

(b) the concentration at which the true solution is formed

(c) the concentration at which one molar electrolyte is present per 1000 g of the solution

(d) the concentration at which $\Delta H = 0$

10. The isoelectric-point of a colloidally dispersed material is the pH value at which

(a) the dispersed phase migrate in an electric field

(b) the dispersed phase does not migrate in an electric field

(c) the dispersed phase has pH equal to 7

(d) the dispersed phase has pH equal to zero

11. Peptization involves

(a) precipitation of colloidal particles

(b) disintegration of colloidal aggregates

(c) evaporation of dispersion medium

(d) impact of molecules of the dispersion medium on the colloidal particles

Hints & Solutions

EXERCISE 1

1. NH_3 is adsorbed most preferably.
2. Sodium chloride (NaCl) can be brought in to colloidal state in benzene.
3. They have enormous surface area per unit mass and are, thus, good adsorbents.
4. Hydrogen and oxygen.
5. No, this is because gases mix homogeneously in all proportions.
9. $\Delta H \Rightarrow -$ Ve
$\Delta S \Rightarrow -$ Ve
$\Delta G \Rightarrow -$ Ve

18. **(c)** **19.** **(d)** **20.** **(d)** **21.** **(a)** **22.** **(d)**
23. **(a)** **24.** **(a)** **25.** **(b)** **26.** **(c)** **27.** **(d)**

EXERCISE 2

1. **(c)** Size of colloidal particles is 10^{-5} - 10^{-7} cm.

2. **(b)** 1 micron $\mu = 10^{-4}$ cm and 1 millimicron $= 10^{-7}$ cm.

3. **(c)** Butter (liquid - solid) water dispersed in fat

4. **(a)** Milk is emulsion, liquid dispersed in liquid

5. **(c)** W/O emulsion water dispersed in oil

6. **(b)** Cloud and fog are colloidal system having dispersed phase liquid and dispersion medium gas

7. **(d)** Sulpher is hydrophobic sol.

8. **(d)** All are irreversible colloidal systems.

9. **(b)** Gum is lyophilic colloid.

10. **(a)** Surface tension of lyophilic sols is lower than water (dispersion medium).

11. **(c)** Peptization comes under dispersion methods of preparation of colloids

12. **(c)** Colloidal gold is prepared by Bredig's arc method.

13. **(c)** Sol of amorphous sulpher is formed.

14. **(d)** Gold by Bredig's method (Dispersion method) and by reduction method $AuCl_3 + \text{Tannic acid} \rightarrow \text{Gold sol}$

15. **(a)** Formation of colloid from suspension is known as peptization.

16. **(d)** Metal sulphide give lyophobic sol not lyophilic sol.

17. **(a)** Blood is purified by dialysis.

18. **(c)** It is due to impact of molecules of dispersion medium on the colloidal particles.

19. **(a)** Brownian movement is exhibited by colloidal system.

20. **(b)** Brownian movement is random motion.

21. **(b)** Formaldehyde is emulsifier.

22. **(c)** Sugar forms homogeneous solution hence no Tyndall effect is exhibited

23. **(c)** Liquid - liquid system is known as emulsion.

24. **(a)** Tyndall effect is shown by sols.

25. **(c)** Gold number is associated with protective colloids

26. **(b)** Brownian movement is zig zag motion of sol particles.

27. **(c)** It is electrophoresis (see definition of electrophoresis)

28. **(b)** It is Tyndall effect

29. **(a)** Tyndall effect is the simplest way to check colloidal system since path becomes visible due to scattering of light.

30. **(c)** The movement towards anode shows that sol is negative. For coagulation of negative sol. Cation with higher charge is more effective.

31. **(d)** As_2S_3 is negative sol. For coagulating negative sol. Al^{3+} is most effective. The higher the magnitude of the charge, the lower is coagulating value.

32. **(a)** Proteins are coagulated by Ag^+ ions.

33. **(b)** Charge carried by dispersed phase and dispersion medium is neutralised by electrolytes and coagulation takes place.

34. **(d)** $Fe(OH)_3$ is positive sol. $K_3[Fe(CN)_6]$ will provide $[Fe(CN)_6]^{3-}$ for coagulation.

35. **(d)** Glucose is non electrolyte hence least effective in precipitating As_2S_3 (negative sol)

36. **(d)** The stability of lyophilic colloids is due to layer of dispersion medium around sol particles.

37. **(a)** See definition in text

38. **(d)** Alum is good coagulating agent because of multivalent ions.

39. **(c)** CMC is critical micellization concentration, the surfactants at this concentration associate to form micelles. For soaps, the CMC value is 10^{-3} mole/litre

40. **(c)** Smoke is solid gas system, solid (D. P) and gas (D.M.)

Note : D.P. : Dispersed phase
D.M. : Dispersion medium

41. **(c)** Alum. coagulates mud particles and helps in purifying water.

42. **(b)** In auto catalysis one of the products act as catalyst

43. **(d)** In acid hydrolysis of methyl acetate all are present in one phase (liquid)

44. (c) **45. (a)** **46. (d)**

47. (c) Adsorption theory is applied to heterogeneous catalysis

48. (a) Enzymes are biological catalysts.

49. (d) Ti^{3+} Ziegler Natta catalyst is a mixture of $(C_2H_5)_3Al + TiCl_3$.

50. (d) The substance which is adsorbed is called adsorbate

51. (a) Adsorption is spontaneous process. Hence ΔG must be negative

52. (c) For physiosorption the ΔH value is 10 - 40 kJ/mol.

53. (d) In physisorption, gas molecule is held on the solid surface by weak van der Waal's forces.

54. (a) Chemical adsorption is monolayer

55. (c) In physical adsorption the forces between adsorbate and adsorbent are weak van der waal's forces.

56. (a) Chemisorption involves strong chemical forces.

57. (c) Physical adsorption does not require any activation energy.

58. (b) The gases having higher values for critical temperature are easily liquified and are adsorbed to the greater extent.

59. (d) Statement (d) is wrong (see text)

60. (a) Physical adsorption $\propto \dfrac{1}{\text{Temperature}}$.

61. (c) The distribution law was given by Nernst.

62. (d) All the conditons are correct.

63. (a) Henry gave the relation between pressure and solubility of a gas as, solubility α pressure.

64. (a) Let the solubility of iodine in CS_2 be a then

$$\frac{S_1}{S_2} = K_D, \frac{a}{0.35} = 600, \therefore a = 210$$

65. (d) $K_D = \dfrac{S_1}{S_2}$ is valid only when their is no association or dissociation of solute dissolved and no change of temperature. There is no complex formation.

66. (d) In case when solute associate, $k_D = \dfrac{C_1}{n\sqrt{C_2}}$

67. (d) All the statements are correct.

68. (b) $k_D = \dfrac{C_1}{C_2}, C_1 = \dfrac{1.843}{100}$

$$= \frac{1.843}{100} \text{ and } C_2 = \frac{0.127}{50},$$

$$\therefore k_D = \frac{1.843/100}{0.127/50} = 7.25$$

69. (b) At equilibrium stage $\dfrac{C_1}{C_2} = k_D$; where C_1 & C_2 are the concentrations of the solute in the upper and lower layer.

70. (d) Let the amount extracted be *a* then, $k_D = \dfrac{a}{100-a} = 5$,

$$\therefore a = 83.3\%$$

71. (c) Partition coefficient $k_D = \dfrac{C_{ether}}{C_{water}}$, k_D is in favour of ether. The value is reversed if we change it in favour of water.

72. (c) The greater the number of operations, the more is the recovery of the substances to be extracted.

73. (a) H_2O and C_2H_5OH are miscible liquids, the law is applicable to immiscible liquids.

74. (a) Pallison process is not based on distribution law.

75. (b) The concentration of the solute in both the solvents must be kept low and not high.

76. (c) Let the amount of iodine in water be *a* gm., $C_1 = 5$g in x ml of CS_2, $C_2 = 5 - a$ g in x ml of H_2O. Then

$$\frac{5-a}{a} = 420, \quad \therefore = 0.0118$$

EXERCISE 3

1. (a) Langmuir adsorption isotherm is based on the assumption that every adsorption site is equivalent and the ability of a particle to bind there is independent of whether nearby sites are occupied or not.

2. (d)

3. (a) According to Freundlich Adsorption isotherm

$$\frac{x}{m} = KP^{\frac{1}{n}}$$

at low pressure $\dfrac{1}{n} = 1$

$$\therefore \quad \frac{x}{m} \propto P^1$$

at high pressure $\dfrac{1}{n} = 0$

$$\frac{x}{m} \propto P^{\circ}$$

i.e., the value of *n* varies between 0 to 1

4. (d) Enzymes are most reactive at optimum temperature. The optimum temperature for enzyme activity lies between 40°C to 60°C.

5. (b) The lyophobic sols are less stable than lyophilic sols. The lyophilic sols are thus used to protect the lyophobic sols. This property of lyophilic sols is known as protective action of lyophilic sols which is represented by gold number.

6. (c) See properties of hydrophilic sols.

7. (a) As adsorption is an exothermic process.

$\therefore$ Rise in temperature will decrease adsorption.

8. **(b)** When oppositely charged sols are mixed their charges are neutralised. Both sols may be partially or completely precipitated.

9. **(a)** According to Langmuir's model of adsorption of a gas on a soild surface the mass of gas adsorbed(x)per gram of the adsorbent (m) is directly proportional to the pressure of the gas (p) at constant temperature i.e.

$$\frac{x}{m} \propto p$$

10. **(c)** For a protective colloid lesser the value of gold number more will be the protective power. Thus the correct order of protective power of A, B, C and D is

⇒	(A)	<	(C)	<	(B)	<	(D)
Gold number	0.50		0.10		0.01		0.005

Hence (c) is the correct answer

11. **(c)** Adsorption is an exothermic process, hence ΔH will always be negative.

12. **(d)** The Freundlich adsorption isotherm is mathematically represented as

$$\frac{x}{m} = kP^{1/n}$$

At high pressure $1/n = 0$. Hence, $x / m \propto P^{\circ}$

At low pressure $1/n = 1$ Hence, $x/m \propto P^1$

13. **(b)** According to Hardy Schulze rule, greater the charge on cation, greater is its coagulating power for negatively charged sol (As_2S_3), hence the correct order of coagulating power : $Na^+ < Ba^{2+} < Al^{3+}$

14. **(b)**

15. **(c)** As Sb_2S_3 is a negative sol, so $Al_2(SO_4)_3$ will be the most effective coagulant due to higher positive charge on Al (Al^{3+}) – **Hardy-Schulze rule**.

EXERCISE 4

1. **(d)** Freundlich equation is $\log\frac{x}{m} = \log K + \frac{1}{n}P$ where $\frac{1}{n} = \text{slope}$.

2. **(c)** The more the liquefiable nature of a gas, the more is the enthalpy of adsorption. Water is more liquefiable.

3. **(a)** The extent of adsorption increases with decrease in temperature.

4. **(c)** At low pressure the extent of adsorption is directly proportional to pressure which follows first order kinetics.

5. **(d)** At high pressure the extent of adsorption follows zero order kinetics.

6. **(c)** Adsorption increases with decrease in temperature.

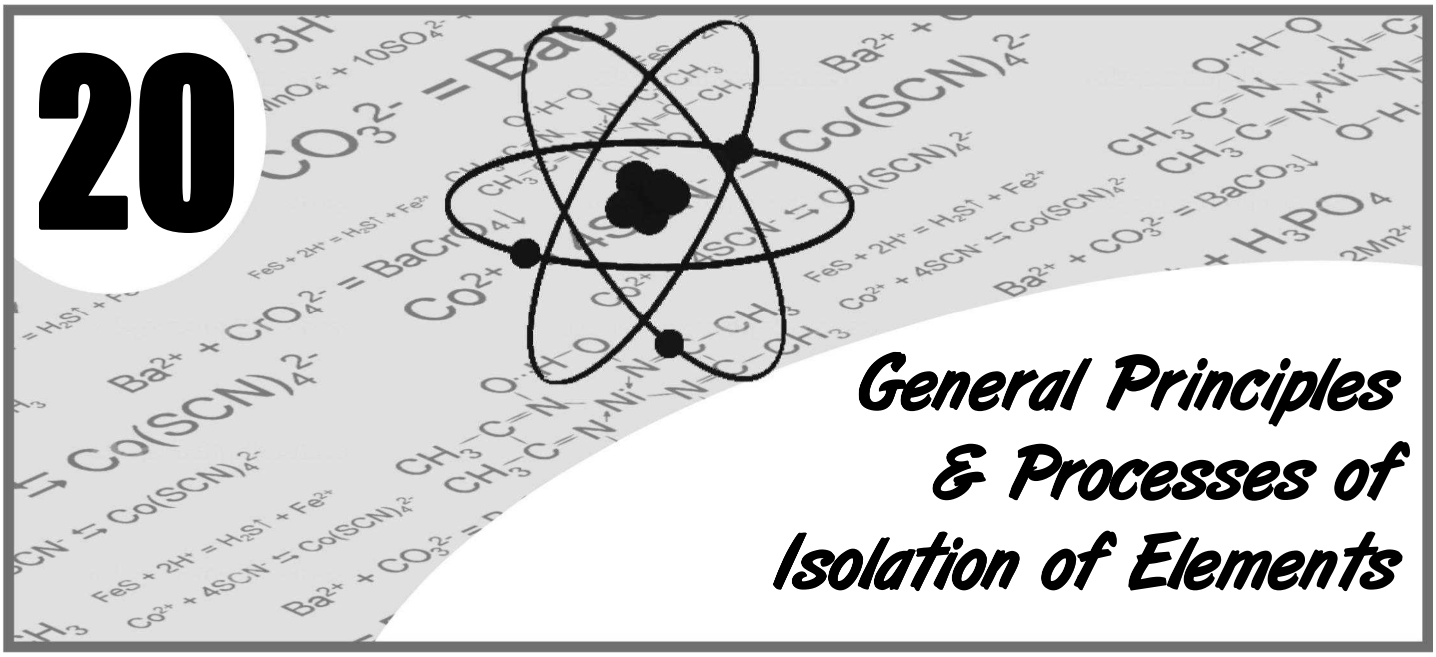
7. **(b)** $\Delta G = \Delta H - T\Delta S$. Adsorption is spontaneous process ΔG should be negative. Hence $\Delta H - T\Delta S$ should be negative.

8. **(d)** All statements are correct

9. **(a)** CMC is the concentration at which micellization starts i.e. surfactant molecules aggregate.

10. **(b)** At isoelectric point there is no migration of dispersed phase in an electric field.

11. **(b)** Peptisation is disintegration of colloidal aggregate.



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General Principles & Processes of Isolation of Elements

METALLURGY :

The science and technology of isolation of pure metals from their ores and preparing them for practical use. The process includes.

(i) ***Mining -*** getting the ore out of ground.

(ii) ***Concentration -*** preparing for further treatment.

(iii) ***Reduction -*** to obtain the metals in zero oxidation state.

(iv) ***Refining -*** to obtain the pure metal.

(v) ***Mixing with other metals -*** to form an alloy.

MINERALS :

Most metals are found in nature in the form of solid inorganic compounds called minerals. Names of minerals are based on the location of their discovery, the person who discovered them or some characteristics of the mineral.

ORE :

The mineral from which the metal can be extracted economically. Hence all minerals can not be classified as ores. The most important ores are oxide,sulphide and carbonate minerals.

GANGUE OR MATRIX :

The unwanted rocky,earthy or sandy materials almost always associated with the ores as impurities are called gangue or matrix.

FLUX AND SLAG :

Flux is a substance added to the ores before heating which combines chemically with earthy impurities (gangue) and form a fusible mass known as ***slag*** .

Flux can be Acidic e.g. SiO_2 (silica), $Na_2B_4O_7.10H_2O$ (borax); Basic e.g. CaO, MgO ; or Neutral - neutral compounds, and they decrease the melting point and make the order conducting in an electrolytic cell e.g. CaF_2, Na_3AlF_6, KF etc.

Slag consists mostly of molten silicates ,aluminates, phosphates, fluorides and another inorganic materials. The formation of slag is known as ***slagging*** .

CONCENTRATION OR DRESSING :

The process of the removal of gangue or matrix from the ore is known as concentration. It is achieved by

(i) Hand picking

(ii) Gravity separation (hydraulic -washing)

(iii) Magnetic separation

(iv) Electrostatic separation

(v) Froth flotation process -for sulphide ores.

(vi) Leaching

Froth flotation process - Finely divided ore is mixed with oil (pine oil, eucalyptus oil or camphor oil) and agitated with water containing a detergent (foaming agent). When air is bubbled through the mixture, the air bubbeles are stabilised by the detergent .These adsorb mineral particles wetted with oil and rise to the surface. The earthy matter wetted by water settles down at the bottom.

Collectors - Which increase the non wettability of ore particles e.g. pine oil, xanthates and fatty acids.

Froth stabiliser -Which stabilise the froth e.g. cresoles and aniline.

Depressants - Depressants prevent the formation of froth eg NaCN, when added to ore containing ZnS and PbS form a complex with ZnS as $Na_2[Zn(CN)_4]$ and prevent it from forming froth. PbS is then easily separated from ZnS.

Leaching- Leaching is the selective dissolution of the desired mineral leaving behind the impurities in a suitable dissolving agent eg bauxite when treated with strong solution of NaOH, Al_2O_3 dissolves leaving behind $Fe_2O_3.SiO_2$.

$$Al_2O_3 + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2O$$

$$Na_3AlO_3 + 3H_2O \rightarrow 3NaOH + Al(OH)_3$$

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

Leaching is also employed in Ag ore and native gold.

$$Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$$
$$4Au + 8KCN + 2H_2O + O_2 \rightarrow 4K[Au(CN)_2] + 4KOH$$

CALCINATION :

It is the heating of the ore in a suitable furnace in absence of air much below its melting point to cause decomposition and elimination of volatile products.

$$PbCO_3 \rightarrow PbO + CO_2$$

The process is generally applied to hydrated oxide or carbonate ores.

ROASTING :

It is the heating of the concentrated ore in a suitable furnace strongly in presence of air with or without certain substances below the melting point which causes chemical reaction to expel volatile impurities eg oxides of S, As and Sb.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$2MoS_2 + 7O_2 \rightarrow 2MoO_3 + 4SO_2$$

REDUCTION :

After calcination or roasting, the metal oxides are reduced and impurities are removed as slag. Reduction and slagging take place together.

(a) ***Removal of impurities as slag*** - For acidic impurities viz. SiO_2, P_2O_5 basic flux is added.

$$SiO_2 + CaO \rightarrow CaSiO_3$$

For basic impurities like MnO acidic flux is added.

$$MnO + SiO_2 \rightarrow MnSiO_3$$

(b) ***Reduction of oxides -***

(i) ***Decomposition of oxides by heating*** - For thermally unstable oxide.

$$HgS + O_2 \rightarrow Hg + SO_2$$

Hg is obtained from its sulphide ore cinnabar directly in the roasting step.

(ii) ***Chemical Reduction*** -

- ***Reduction by carbon*** - Sn from oxide ore cassiterite SnO_2 is obtained by heating with coke.

$$SnO_2 + C \rightarrow Sn + 2CO$$

Zn from sulphide ore Zinc blende (ZnS).

$$2ZnS + 3O_2 \xrightarrow{\text{Roasting}} 2ZnO + 2SO_2$$
$$ZnO + C \rightarrow Zn + CO$$

Iron is obtained from oxide ore haematite (Fe_2O_3).

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

- **Reduction by H_2 and CO-**

$$MoO_3 + 3H_2 \rightarrow Mo + 3H_2O$$
$$CuO + CO \rightarrow Cu + CO_2$$

- **Reduction by other metals** e.g. Al and Mg -

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$$
$$3Mn_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Mn$$
$$Rb_2O_3 + 3Mg \rightarrow 3MgO + 2Rb$$

(iii) Self reduction -Cu, Pb and Mg are obtained by self reduction in roasting.

$$Cu_2S + \frac{3}{2}O_2 \rightarrow Cu_2O + SO_2$$
$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$
$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
$$PbS + 2PbO \rightarrow 3Pb + SO_2$$

(iv) Electrolytic reduction -Oxides of very active metals like alkali or alkaline earth are not easily reduced by chemical reducing agents e.g. Na, Mg, Al etc. They are obtained by electrolytic reduction.

$$2NaCl \xrightarrow{\text{Fusion}} 2Na^+ + 2Cl^-$$

At anode : $2Cl^- - 2e^- \rightarrow Cl_2$

At Cathode : $2Na^+ + 2e^- \rightarrow 2Na$

(v) Amalgamation process - Ag and Au are obtained by leaching process using solution of KCN or NaCN to form argento cyanide or aurocyanide . Ag and Au is precipitated by adding Zn dust.

$$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag$$
$$2K[Au(CN)_2] + Zn \rightarrow \underset{\text{Soluble complex}}{K_2[Zn(CN)_4]} + 2Au$$

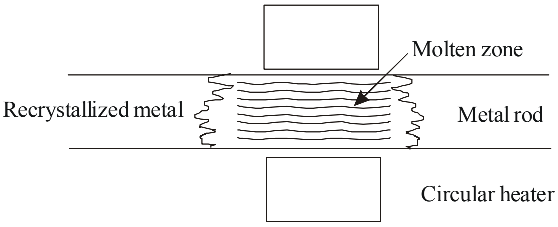
REFINING :

The methods employed for the refining of metals are

(i) ***Liquation*** -Impurities present must be less fusible than the metal to be purified . Impure metal is placed on the slopping hearth of reverberatory furnace at a temperature just above the melting point of the metal . The pure metal flows down leaving behind the impurities . Sn ,Pb, Bi are purified by this method.

(ii) ***Distillation -*** Zn and Hg are purified by distillation under reduced pressure provided the impurities are non volatile.

(iii) ***Fractional crystallisation -*** (Zone refining).



Impure metal rod is heated with the help of circular heater at one end. The metal melts and on cooling the pure metal gets solidified while impurities pass on into the molten zone. The process is repeated twice or thrice to get the pure metal.

(iv) ***Polling*** -The molten metal is stirred with green poles of wood, which liberates gas like methane. The latter reduces any oxide present in the metal eg CuO in the blister copper is reduced to copper.

(v) ***Electrolytic refining-*** The blocks of impure metal form the anode and pure metal form the cathode. Aqueous

solution of appropriate salt is then electrolised. On electrolysis at a suitable voltage the pure metal is deposited at cathode.

$$\text{At anode} \quad M - ne^- \rightarrow M^{n+}$$

$$\text{At cathode} \quad M^{n+} + ne^- \rightarrow M$$

Cu, Sn, Ag, Pb, Cr, Ni are refined by this process.

(vi) Vapour phase refining - Metal is removed as volatile compound which is then decomposed by heating to get pure metal. e.g.

(a) Mond's process - Ni is purified by this process.

$$Ni(s) + 4CO(g) \xrightarrow{300-350K} Ni(CO)_4(g)$$

$$Ni(CO)_4(g) \xrightarrow{450-470K} Ni(s) + 4CO(g)$$

(b) Van Arkel process-Zr, Hf, Si, Ti and Be are refined by this process.

$$Zr(s) + 2I_2(g) \rightarrow ZrI_4(g)$$

$$ZrI_4(g) \xrightarrow[\text{filament}]{\text{On hot}} Zr(s) + 2I_2(g)$$

(vii) Cupellation - This is the method of purifying silver containing lead as impurity. Impure silver is heated in a shallow (Cupel) which is made of bone ash under blast of air. Lead is easily oxidised and carried away by blast air .

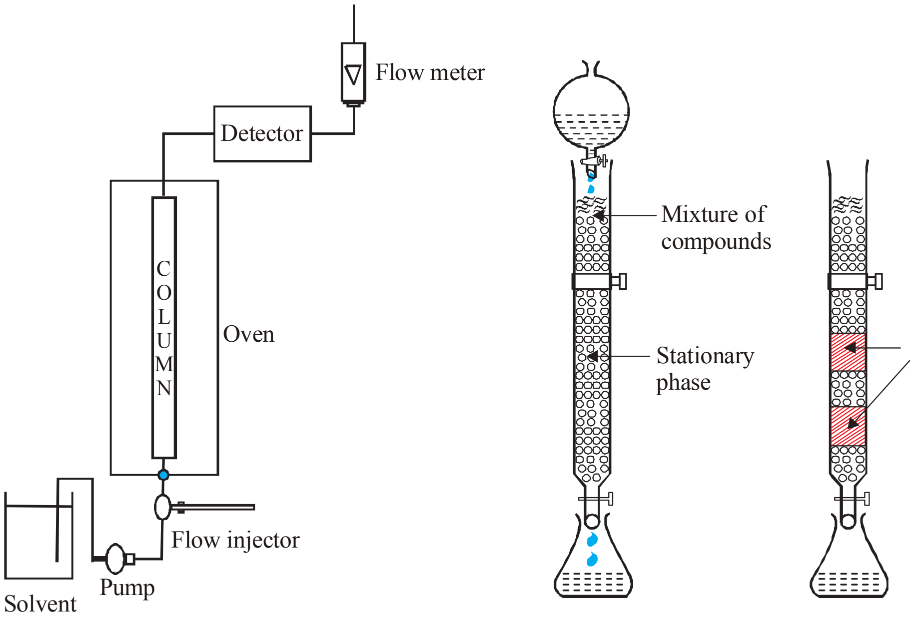
(viii) Desilverisation of lead -Lead obtained from galena (PbS) contains impurities of silver, removal of which is called desilverisation .The processes employed are

(a) Parke's process -Lead containing silver is melted in iron pots and 1% Zn is added then cooled. Zn -Ag alloy solidifies and being light floats over molten lead and removed .

$$(Pb \text{ and } Ag) + Zn \rightarrow (Zn - Ag) \text{ alloy} + Pb$$

(b) Pattison's process -Lead containing less than 2.5% of Ag melts at lower temperature than lead. Thus when an alloy of Pb-Ag containing more lead is melted then allowed to cool slowly, pure lead separates.

(ix) Chromatographic methods - It is based on the preferential adsorption of different compunds on an adsorbent. The mixture is put in the liquid or gaseous medium which is moved through the adsorbent. The different compounds are adsorbed at different levels on adsorbent in column chromatography and recoverd by using suitable solvent (eluent). The common adsorbent as Al_2O_3 or SiO_2 (silica). The least adsorbed component is recoverd first. The method is very useful for purification of elements available in minute quantities.



(a) Industrial method

(b) Laboratory method

Schematic diagrams showing column chromatography

There are several chromatographic techniques such as gas chromatography, paper chromatography, etc.

METAL SOURCE MAIN METHOD OF EXTRACTION

Metal	Occurrence (ore)	Common method of extraction
Li	Spodumene $LiAl(SiO_3)_2$	Electrolysis of fused LiCl with KCl .
K	Carnallite $KCl\,MgCl_2 . 6H_2O$; Kaenite $KCl\,MgSO_4 3H_2O$, **Sylvine** KCl ; Nitre KNO_3 ; Feldspar $K_2O\,Al_2O_3\,6SiO_2$; Mical $KH_2Al_3(SO_4)_3$;	Electrolysis of fused KCl with $CaCl_2$ added to it.

Ba	Witherite $BaCO_3$; *Barytes* $BaSO_4$;	Electrolysis of fused $BaCl_2$.
Ca	**Lime stone**, chalk, marble, calcite $CaCO_3$; Gypsum $CaSO_4H_2O$; Dolomite $CaCO_3.MgCO_3$; Fluorspar CaF_2; Phosphorite $Ca_3(PO_4)_2$;	Electrolysis of fused $CaCl_2$ and CaF_2 mixture.
Na	Rock salt, **Common Salt NaCl**; Chile Saltpetre $NaNO_3$; Borax or Sodium borate $Na_2B_4O_7$ $10H_2O$, Sodium Carbonate Na_2CO_3;	Electrolysis of fused NaCl with $CaCl_2$ added to it.
Mg	**Carnallite** $KCl.MgCl_2 6H_2O$ **Magnesite** $MgCO_3$; Dolomite $MgCO_3CaCO_3$; Kieserite $MgSO_4.H_2O$; Epsom salt $MgSO_4.7H_2O$:	Electrolysis of fused $MgCl_2$ with KCl added to it.
Be	:Beryl $3BeO.Al_2O_3.6SiO_2$; Chrysoberyl $BeO.Al_2O_3$;	Electrolysis of fused BeF_2 with NaF added to it.
Al	**Bauxite** $Al_2O_3.2H_2O$; Potash feldspar $K_2OAl_2O_3.6SiO_3$. Corundum Al_2O_3; Cryolite Na_3AlF_6; Kaolin $Al_2O_3 2SiO_2.2H_2O$	Electrolysis of molten Al_2PO_3 in molten Na_3AlF_6.
Mn	**Pyrolusite** MnO_2; Hausmannite Mn_3O_4; Braunite Mn_2O_3; Manganite $Mn_2O_3.H_2O$:	Reduction of oxide with Al or C: $3Mn_3O_4 + 8Al \rightarrow 9Mn + 4Al_2O_3$.
Ti	**Ilmenite** $TiO_2.FeO$; **Rutile** TiO_2:	Reduction of $TiCl_4$ with Mg or Na: $TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$.
Zn	**Zinc blende ZnS**;**Calamine** $ZnCO_3$, Zincite ZnO; Willemite Zn_2SiO_4:	Reduction of ZnO with C or electrolysis of $ZnSO_4$: $ZnO + C \rightarrow Zn + CO$.
Cr	**Chromite** $FeO.Cr_2O_3$;Chrome Ore Cr_2O_3:	Reduction of Cr_2O_3 with Al: $Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$
Fe	**Haematite** Fe_2O_3; **Magnetite** Fe_3O_4; Limonite $2Fe_2O_3.3H_2O$; **Iron Pyrites** FeS_2; Siderite Spathic Iron ore $FeCO_3$; Copper pyrites $CuFeS_2$:	Reduction of oxides with CO: $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$.
Co	Smaltite (CoNiFe) As_2; Cobaltite CoAsS;	Reduction of Co_3O_4 with Al: $3Co_3O_4 + 8Al \rightarrow 9Co + 4Al_2O_3$
Ni	**Millerite** NiS;	Reduction of NiO with CO: $NiO + CO \rightarrow Ni + CO_2$
Sn	**Cassiterite or Tin stone** SnO_2; Stannite $Cu_2S.FeS.SnS_2$:	Reduction of SnO_2 with C: $SnO_2 + 2C \rightarrow Sn + 2CO$.
Pb	**Galena** PbS; Cerussite $PbCO_3$, Anglesite $PbSO_4$:	Reduction of PbO with C: $PbO + C \rightarrow Pb + CO$.
Bi	Native; Bismuth glance Bi_2S_3; Bismuthite Bi_2O_3:	Reduction of Bi_2O_3 with arbon $Bi_2O_3 + 3C \rightarrow 2Bi + 3CO$.
Cu	Native; **Copper pyrites** or Chalcopyrites $CuFeS_2$ or Cu_2SFeS_3; **Cuprite** Cu_2O; Malachite $Cu(OH)_2.CuCO_3$; Copper glance Cu_2S; Azurite $2CuCO_3.Cu(OH)_2$:	Partial oxidation of sulphide ore: $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$.
Ag	**Native, Argentite, Silver glance** Ag_2S; Horn Silver (Chlorargyrite) AgCl; Ruby silver (pyrargyrite) Ag_3SbS_3;	Special method with NaCN: $Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$; $2Na[Ag(CN)_2] + Zn \rightarrow 2Ag + Na_2[Zn(CN)_4]$
Hg	**Cinnabar** HgS;	direct reduction of (by heat alone)HgS: $HgS + O_2 \rightarrow Hg + SO_2$

Pt	Native; Sperrylite $PtAs_2$:	Thermal decomposition of $(NH_4)_2Pt.Cl_6$ $(NH_4)_2PtCl_6 \rightarrow Pt + 2NH_4Cl + 2Cl_2$.
Au	Bismuth aurite BiAu; Sylvanite (Au Ag) Te_2	Cyanide process: $4Au + 8KCN + 2H_2O + O_2 \rightarrow 4K\left[Au(CN)_2\right] + 4KOH$; $2K\left[Au(CN)_2\right] + Zn \rightarrow K_2\left[Zn(CN)_4\right] + 2Au$.
U	Pitch blende or Uraninite U_3O_8 or $UO_2\,2UO_3$; Carnotite $K_2O.2UO_3.V_2O_5.3H_2O$. Antunite $(UO_2)PO_4.8H_2O$:	Reduction of U_3O_8 by C : $U_3O_8 + 8C \rightarrow 3U + 8CO$ 98-99% pure Uranium is obtained by reducing U_3O_8 by Mg, Ca or Al. $3U_3O_8 + 16Al \rightarrow 9U + 8Al_2O_3$
C	Free as diamond and graphite (also known as plumbago i.e.black lead)	
Si	Sand SiO_2 ; Clay; Talc $2MgSi_2O_5Mg(OH)_2$ or $Mg_3Si_4O_{11}.H_2O$; Quatrz SiO_2; Feldspar $KAlSi_3O_8$; Asbestos $(CaMg_3Si_4O_{12})$; beryl $Be_3Al_2Si_6O_{18}$; Mica $KAlSi_3O_{10}(OH)_2$	
N	Free in air ; Ammonia: Chile Saltpetre; nitre.	
P	Phosphorite $Ca_3(PO_4)_2$; Chlorapatite $3Ca_3(PO_4)_2.CaCl_2$; Fluorapatite $3Ca_3(PO_4)_2.CaF_2$.	
S	Native; Gypsum $CaSO_4.2H_2O$;Celestine $SrSO_4$; Galena PbS ; Zinc bledne ZnS ; Copper pyrites $Cu_2S.Fe_2S_3$ and Iron pyrites FeS_2	
F	Fluorspar CaF_2; Cryolite Na_3AlF_6, Fluorapatite $CaF_2.3Ca_3(PO_4)_2$.	
Cl	In sea water, rock salts as NaCl; Carnallite $MgCl_2.KCl.6H_2O$.	
Br	Carnallite $KCl.MgCl_2.6H_2O$ contains 0.01to 0.1% as $Mg\,Br_2$; sea water as $MgBr_2$.	
I	Sea weeds as NaI .In Caliche (Chili saltpetre $NaNO_3$) as $NaIO_3$ (Sodium iodate).	
Sb	Stibnite Sb_2S_3.	

SOME IMPORTANT TERMS USED IN METTALLURGY :

(i) ***Pyrometallurgy*** **-** In this process decomposition of the minerals and the extraction of the metal is brought about in dry state at high temperature by the action of heat. The steps employed are

(a) **Calcination** (b) **Roasting**

(c) **Smelting** (d) **Refining**

Smelting is melting process that causes the materials to separate into two or more layers.

Two important kinds of layers are slag and molten metal. Iron is obtained by pyrometallurgy.

(ii) ***Hydrometallurgy*** is the extraction of metals from ores using aqueous solution . It includes

(a) **Leaching**

(b) **Reduction**

Ag and Au are extracted by this process.

(iii) ***Electrometallurgy*** is the process of obtaining metals through electrolysis. The electropositive metals are obtained by this method e.g. Na, Mg etc.

(iv) ***Amalgamation process*** In this process the metal is extracted by using mercury. Most of the metals dissolve in Hg to form amalgams which when distilled in iron retorts leave behind free metal and Hg distills over

$$\text{Ore} + \text{Hg} \rightarrow \text{amalgam} \xrightarrow{\text{distilled}} \text{Hg} + \text{metal}$$

Ag, Au, Pt form amalgam.

(v) ***Thermit*** **-** It is mixture of Fe_2O_3 (3 parts) and Al powder (1part) when ignited with the help of barium peroxide, Fe_2O_3 is reduced to iron and an enormous amount of heat is produced due to exothermic nature of the reaction.

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe + 2500^{o}C$$

The molten is utilised for welding and the process is known as **thermit welding** known as **Goldschmidt Alumino thermic process**.

(vi) ***Refractory materials*** **-** The substance capable of withstanding at very high temperature without undergoing any deformation is called refractory material.

Acidic refractories -silica, quartz and sand stone

Basic refractories - lime ,dolomite and magnesite

Neutral refractories - chromite, bone ash and graphite.

(vii) ***Matte or regulus*** **-** Artificially obtained sulphides are known as matte or regulus e.g. Cu_2S in extraction of copper.

(viii) ***Sulphating roasting*** **-** It is partial oxidising roasting. Roasting of galena gives mixture of lead oxide and lead sulphate

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
$$PbS + 2O_2 \rightarrow 2PbSO_4$$

(ix) ***Chlorinating roasting*** **-** Silver ores mixed with common salt when heated in presence of air, the chloride is obtained.

$$Ag_2S + 2NaCl \rightarrow 2AgCl + Na_2S$$

(x) ***Bessemerisation*** **-**The oxidation of impurities by passing the hot blast of air through molten metal in bessemer converter is called bessemerisation . Pig iron and copper are purified by this method.

(xi) ***Sintering*** **-**The conversion of small pieces of a substances into larger one by partial fusion is known as sintering.

(xii) ***Pulverisation*** **-** The conversion of large pieces of a substance into small fine pieces or powder is known as pulverisation.

(xiii) ***Anodizing*** **-**The process of forming an oxide coating on metal surface by making it an anode by electrolytic method in called anodizing.

(xiv) Mode of extraction of some metals-

(a) Metals obtained by electrolytic reduction are - Li, Na, K, Mg, Ca , Al, Sr, Ba

(b) Metals obtained by reduction of oxides by carbon are - Zn from ZnO, Sn from SnO_2.

(c) Metals obtained by reduction of oxides by thermite process, (Alumino thermic process) are Cr from Cr_2O_3, Mn from Mn_3O_4.

(d) Metals obtained by air reduction method are - Hg from HgS, Pb from PbS.

(e) Metals obtained by precipitation method are - Ag ,Au

(f) Metals obtained by reduction with Co, Fe

(g) Metals obtained by reduction with water gas are - Ni

(xv) ***Alloys*** **-**Alloys contain more than one element and have the characteristics of metals.

- Pure metals and alloys have different physical properties.
- Solution alloys are **homogeneous** mixtures and they are of two types
  - (a) **Subtitutional alloys** (Solute atoms take the positions of solvent atom)
  - (b) **Interstitial alloys** (Solute atoms occupy interstitial sites)
- **Heterogeneous alloys -** Components are not dispersed uniformally e.g. pearlite steel .

RELATIVE ABUNDANCE :

Abundance of elements in the earth's crust (by weight)

$$O > Si > Al > Fe > Ca > Na > K > Mg > H > Ti > Cl > F$$

Abundance of elements in the earth's crust (in terms of number of atoms per 100 atoms)

$$O > Si > Al > H > Na > Ca > Fe > Mg > K > Ti > C > Mn > S > F > Cl > Cr$$

THERMODYNAMIC PRINCIPLES OF METALLURY :

Theory of metallurgical transformations can be interpreted by Gibb's free energy change at any specified temp.

$$\Delta G = \Delta H - T\Delta S \text{ or } \Delta G^{o} = -RT\ \ell nK$$

where, ΔH = enthalpy change and

ΔS = entropy change

K = equilibrium constt. at temp. T

The reducing agent is oxidised and metal oxide is reduced. The role of reducing agent is to provide ΔG^{o} negative.

During reduction the metal oxide decomposes.

$$M_xO(s) \longrightarrow xM \text{ (Solid or liquid)} + \frac{1}{2} O_2(g)$$

The reducing agent (C or CO) is oxidised

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$$

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

If net ΔG of two possible reactions (Reduction/Oxidation) is negative, the overall reaction will occur.

H.J.T. Elligham diagram (plots of ΔG Vs T) provides a sound basis for considering the choice of reducing agent in the reduction of oxides.

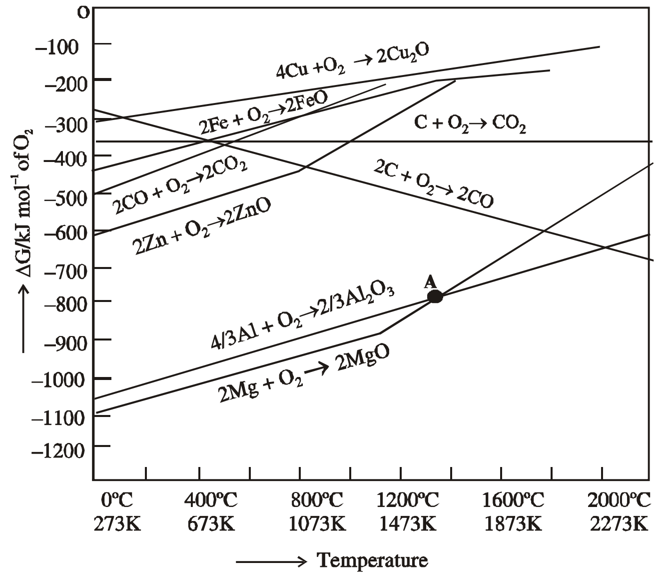


Fig. Gibbs energy (ΔG°) vs T plots (schematic) for formation of some oxides (Ellingham diagram)

When alumina is reduced by magnesium, the two equations are

(i) $4\ \mathrm{Al} + 3\mathrm{O}_2 \longrightarrow 2\mathrm{Al}_2\mathrm{O}_3$ (ii) $2\,\mathrm{Mg} + \mathrm{O}_2 \longrightarrow 2\mathrm{MgO}$

ΔG becomes ZERO at the point of intersection of the Al_2O_3 and MgO curves (marked "A"). Above this point the magnesium can reduce alumina.

Note: Although thermodynamically feasible the magnesium metal, is not used for the reduction of aluminas. The temperature required would be so high and the process would be technologically difficult and uneconomic.

EXTRACTION OF IRON FROM ITS OXIDES:

The two simple reactions are

(i) $\mathrm{FeO(s)} \longrightarrow \mathrm{Fe}(s/\ell) + \frac{1}{2}\mathrm{O}_2(g);\ \Delta G(\mathrm{FeO,Fe})$

(ii) $\mathrm{C(s)} + \frac{1}{2}\mathrm{O}_2(g) \rightarrow \mathrm{CO}(g);\ \Delta G(\mathrm{C,CO})$

Adding the two reactions, we get

$\mathrm{FeO(s)} + \mathrm{C(s)} \rightarrow \mathrm{Fe}(s/\ell) + \mathrm{CO}(g)$

$\Delta G(\mathrm{FeO, Fe}) + \Delta G\,(\mathrm{C, CO}) = \Delta G$

The resultant ΔG is –ve above 1073K (approx).

If the metal is obtained in liquid state the reduction becomes easier. (entropy increases and ΔG decreases).

LIMITATIONS OF ELLINGHAM DIAGRAM :

1. It fails to predict the kinetics of reduction processes i.e. how fast it could be
2. When the reactant/product are solid ΔG° cannot be interpreted by the equation $\Delta G° = -\,RT \log K$

Exercise-1 | NCERT BASED QUESTIONS

Very Short/Short Answer Questions

1. Write the names of two oxides which cannot be reduced with carbon but can be reduced with aluminium powder to get the corresponding metals.
2. Why are metal carbonates and sulphides first converted into corresponding oxides for finally obtaining the corresponding metals?
3. Copper and silver lie below in the electrochemical series and yet they are found in the combined state as sulphides in nature. Comment.
4. Indicate the temperature at which carbon can be used as a reducing agent for FeO.
5. What is the metal extracted from malachite and azurite? Give one important use of the metal.
6. Name two metals each of which can be obtained
   (a) by thermite process
   (b) by electrolytic reduction
   (c) refined by liquation, and
   (d) refined by electrolysis.
7. Name the type of reduction processes by which the following metals are obtained from their oxides:
   (a) Metal *x* which is low in the reactivity series.
   (b) Metal *y* which is in the middle of the reactivity series.
   (c) Metal *z* which is high up in the reactivity series.
8. What method for concentration of ore is preferred in each of the following cases and why:
   (a) The ore has higher density particles interspersed with a large bulk of low density impurities.
   (b) The ore consists of copper sulphide intermixed with clay particles.
9. At a site, low grade copper ores are available and zinc and iron scraps are also available. Which of the two scraps will be more suitable for reducing the leached copper ore and why?
10. Although thermodynamically feasible, in practice, magnesium metal is not used in for the reduction of alumina in the metallurgy of aluminium. Why?
11. Differentiate between a mineral and an ore.
12. Describe the principle controlling each of the following processes:
    (i) Zone refining of metals
    (ii) Electrolytic refining of metals
13. Which methods are usually employed for purifying the following metals?
    (i) Nickel
    (ii) Germanium
14. Explain the role of each of the following:
    (i) NaCN in the extraction of silver.
    (ii) SiO_2 in the extraction of copper.
15. (a) Which solution is used for the leaching of silver metal in the presence of air in the metallurgy of silver?
    (b) Out of C and CO, which is a better reducing agent at the lower temperature range in the blast furnace to extract iron from the oxide ore?
16. (a) Which of the following ores can be concentrated by froth floatation method and why?
    Fe_2O_3, ZnS, Al_2O_3
    (b) What is the role of silica in the metallurgy of Copper?

Multiple Choice Questions

17. The metal always found in the free states is
    (a) Au (b) Ag
    (c) Cu (d) Na
18. Bronze is a mixture of
    (a) Pb + Sn (b) Cu + Sn
    (c) Cu + Zn (d) Pb + Zn
19. Which reagent is used in Bayer's process?
    (a) Na_2CO_3 (b) Carbon
    (c) NaOH (d) Silica
20. Matrix is defined as –
    (a) the unwanted foreign material present in the ore
    (b) the flux added to remove the unwanted impurities from ore
    (c) the slag formed as a result of the reaction of flux with gangue
    (d) the material used in the reduction of metal oxide to metal
21. The process to heat the ore in the presence of excess supply of air below its melting point is called –
    (a) roasting (b) calcination
    (c) smelting (d) liquation
22. Thomas slag is
    (a) $Ca_3(PO_4)_2$
    (b) $CaSiO_3$
    (c) Mixture of (a) and (b)
    (d) $FeSiO_3$
23. Blister copper is
    (a) Impure Cu (b) Cu alloy
    (c) Pure Cu (d) Cu having 1% impurity

24. Which of the following fluxes is used to remove acidic impurities in metallurgical process?
(a) Silica
(b) Lime stone
(c) Sodium chloride
(d) Sodium carbonate

25. Match list I with list II and select the correct answer using the codes given below the lists:

	List I	***List II***
I.	Cyanide process	A. Ultrapure Ge
II.	Floatation process	B. Pine oil
III.	Electrolytic reduction	C. Extraction of Al
IV.	Zone refining	D. Extraction of Au

Codes:
(a) I-C, II-A, III-D, IV-B
(b) I-D,II-B,III-C,IV-A
(c) I-C,II-B,III-D, IV-A
(d) I-D,II-A,III-C,IV-B

26. In forth flotation process many chemicals (frother , collector, activator, and depressant) are used . Which is called a frother:
(a) $CuSO_4$ (b) NaCN+ alkali
(c) Pine oil (d) Potassium xanthate.

Exercise-2 | CONCEPTUAL MCQs

1. An example of an oxide ore is
(a) bauxite (b) malachite
(c) zinc blende (d) feldspar

2. The natural materials from which an element can be extracted economically are called
(a) ores (b) minerals
(c) gangue (d) None of these

3. The impurities associated with mineral used in metallurgy are called collectively?
(a) Slag (b) Flux
(c) Gangue (d) Ore

4. The most abundant metal on the surface of the earth is
(a) Fe (b) Al
(c) Ca (d) Na

5. The most abundant element in the earth's crust (by weight) is
(a) Si (b) Al
(c) O (d) Fe

6. During smelting an additional substance is added which combines with impurities to form a fusible product. It is known as
(a) slag (b) mud
(c) gangue (d) flux

7. When a metal is to be extracted from its ore and the gangue associated with the ore is silica, then
(a) an acidic flux is needed
(b) a basic flux is needed
(c) both acidic and basic fluxes are needed
(d) Neither of them is needed

8. A basic lining is given to a furnace by using
(a) calcined dolomite (b) lime stone
(c) haematite (d) silica

9. Which of the following fluxes is used to remove acidic impurities in metallurgical process?
(a) Silica (b) Lime stone
(c) Sodium chloride (d) Sodium carbonate

10. Cryolite is
(a) Na_3AlF_6 and used in the electrolysis of alumina for decreasing electrical conductivity
(b) Na_3AlF_6 and used in the electrolysis of alumina for lowering the melting point of alumina
(c) Na_3AlF_6 and used in the electrolytic purification of alumina
(d) Na_3AlF_6 and used in the electrolysis of alumina

11. Flux is used to
(a) remove all impurities from ores
(b) reduce metal oxide
(c) remove silica
(d) remove silica and undesirable metal oxide

12. Cassiterite is concentrated by
(a) levigation
(b) electromagnetic separation
(c) floatation
(d) liquefaction

13. Froth floatation process is used for the metallurgy of
(a) chloride ores (b) amalgams
(c) oxide ores (d) sulphide ores

14. Electromagnetic separation is used in the concentration of
(a) copper pyrites (b) bauxite
(c) cassiterite (d) cinnabar

15. For which ore of the metal, froth floatation method is used for concentration?
(a) Horn silver (b) Bauxite
(c) Cinnabar (d) Heamatite

16. Which of the following metal is leached by cyanide process
(a) Ag (b) Na
(c) Al (d) Cu

17. Which one of the following ores is not concentrated by froth floatation process?
(a) Copper pyrites (b) Pyrargyrite
(c) Pyrolusite (d) Zinc blende

18. Calcination is used in metallurgy for removal of?
(a) Water and sulphide (b) Water and CO_2
(c) CO_2 and H_2S (d) H_2O and H_2S

19. Which of the following reactions is an example for calcination process ?
(a) $2Ag + 2HCl + (O) \rightarrow 2AgCl + H_2O$
(b) $2Zn + O_2 \rightarrow 2ZnO$
(c) $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$
(d) $MgCO_3 \rightarrow MgO + CO_2$

20. Heating of ore in the absence of air below its melting point is called
(a) leaching (b) roasting
(c) smelting (d) calcination

21. Heating pyrites to remove sulphur is called
(a) smelting (b) calcination
(c) liquation (d) roasting

22. The process of converting hydrated alumina into anhydrous alumina is called
(a) roasting (b) smelting
(c) dressing (d) calcination

23. Mac Arthur process is used for
(a) Ag (b) Fe
(c) Cl (d) O_2

24. In Goldschmidt aluminothermic process, reducting agent is used
(a) coke (b) Al powder
(c) Na (d) Ca

25. Aluminothermic process is used for metallurgy of
(a) Pb (b) Ag
(c) Al (d) None of these

26. Which metal can't be obtained from electrolysis?
(a) Ca (b) Mg
(c) Cr (d) Al

27. Which of the following metals is obtained by electrolytic reduction process?
(a) Fe (b) Cu
(c) Ag (d) Al

28. The common method of extraction of metals from oxide ores is
(a) reduction with carbon
(b) reduction with hydrogen
(c) reduction with aluminium
(d) electrolytic method

29. Use of electrolysis is
(a) Electroplating (b) Electrorefining
(c) Both (a) and (b) (d) Neither (a) nor (b)

30. In electrorefining of copper some gold is deposited as
(a) anode mud (b) cathode mud
(c) electrolyte (d) None of these

31. Purification of silicon element used in semiconductors is done by
(a) zone refining (b) heating
(c) froth floatation (d) heating in vacuum

32. Silver containing lead as an impurity is removed by
(a) poling (b) cupellation
(c) lavigation (d) distillation

33. Nickel is purified by thermal decomposition of its
(a) hydride (b) chloride
(c) azide (d) carbonyl

34. The chief source of iodine, in which it is present as sodium iodate, is
(a) Carnallite (b) Sea weeds
(c) Caliche
(d) Iodine never exists as sodium iodate.

35. Malachite is an ore of
(a) iron (b) copper
(c) mercury (d) zinc

36. The important oxide ore of iron is
(a) siderite (b) haematite
(c) pyrites (d) bauxite

37. In the commercial electrochemical process for aluminium extraction the electrolyte used is
(a) $Al(OH)_3$ in NaOH solution
(b) An aqueous solution of $Al_2(SO_4)_3$
(c) A molten mixture of Al_2O_3 and Na_3AlF_6
(d) A molten mixture of Al_2O_3 and $Al(OH)_3$

38. Cassiterite is an ore of
(a) Mn (b) Ni
(c) Sb (d) Sn

39. Which of the following element is extracted commercially by the electrolysis of an aqueous solution of its compound?
(a) Chlorine (b) Bromine
(c) Sodium (d) Aluminium

40. Galena is an ore of
(a) Pb (b) Hg
(c) Zn (d) Zn

41. Which one of the following element does not exits in the native form?
(a) Au (b) Pt
(c) Fe (d) S

42. The most electropositive metals are isolated from their ores by
(a) high temperature reduction with carbon
(b) self reduction
(c) thermal decomposition
(d) electrolysis of fused ionic salts

43. The metal always found in the free states is
(a) Au (b) Ag
(c) Cu (d) Na

44. Pyrolusite is a/an
(a) oxide ore (b) sulphide ore
(c) carbide ore (d) Not an ore

45. Which of the following metals is extracted by the electrometallurgical method ?
(a) Cu (b) Fe
(c) Na (d) Ag

46. Among the following statements the incorrect one is
(a) Calamine and siderite are carbonates
(b) Argentite and cuprite are oxides
(c) Zinc blende and iron pyrites are sulphides
(d) Malachite and azurite are ores of copper.

47. When an aqueous solution of sodium chloride is electrolysed using platinum electrodes, the ion discharged at the electrodes are
(a) sodium and hydrogen (b) sodium and chloride
(c) hydrogen and chloride (d) hydroxyl and chloride

48. In the extraction of iron , slag is produced.Slag is
(a) CO (b) $FeSiO_3$
(c) $MgSiO_3$ (d) $CaSiO_3$

49. Match list I with list II and select the correct answer using the codes given below the lists:

List I	*List II*
I. Cyanide process	A. Ultrapure Ge
II. Floatation process	B. Pine oil
III. Electrolytic reduction	C. Extraction of Al
IV. Zone refining	D. Extraction of Au

Codes:
(a) I-C, II-A, III-D, IV-B (b) I-D,II-B,III-C,IV-A
(c) I-C,II-B,III-D, IV-A (d) I-D,II-A,III-C,IV-B

50. Which of the following condition favours the reduction of a metal oxide to metal?
(a) $\Delta H = +ve$, $T\Delta S = +$ ve at low temperature
(b) $\Delta H = +ve$, $T\Delta S = -$ ve at any temperature
(c) $\Delta H = -ve$, $T\Delta S = -$ ve at high temperature
(d) $\Delta H = -ve$, $T\Delta S = +$ ve at any temperature

51. Ellingham diagram normally consists of plots of
(a) ΔS^o vs T (b) $\Delta_f G^o$ vs ΔS^o
(c) ΔG^o vs T (d) ΔH^o vs ΔT

52. A coupled reaction is takes place as follow–
$A + B \longrightarrow C + D,$ $\Delta G^o = +x$ kj
$D + E \longrightarrow F$ $\Delta G^o = -y$ kj
for the spontaneity of reaction $A + B + E \longrightarrow C + F$, which of the following is correct?
(a) $2x = y$ (b) $x < y$
(c) $x > y$ (d) $x = (y) \times T\Delta S$

Exercise-3 | PAST COMPETITION MCQs

1. Which of the following statements, about the advantage of roasting of sulphide ore before reduction is not true? **[CBSE-PMT 2007]**
(a) The ΔG_f^o of the sulphide is greater than those for CS_2 and H_2S.
(b) The ΔG_f^o is negative for roasting of sulphide ore to oxide.
(c) Roasting of the sulphide to the oxide is thermodynamically feasible.
(d) Carbon and hydrogen are suitable reducing agents for reduction of metal sulphides.

2. Sulphide ores of metals are usually concentrated by froth flotation process. Which one of the following sulphide ores offer an exception and is concentrated by chemical leaching? **[CBSE-PMT 2007]**
(a) Galena (b) Copper pyrite
(c) Sphalerite (d) Argentite

3. Which of the following elements is present as the impurity to the maximum extent in the pig iron ? **[CBSE-PMT 2011]**
(a) Manganese (b) Carbon
(c) Silicon (d) Phosphorus

4. Which of the following pairs of metals is purified by van Arkel method ? **[CBSE-PMT 2011]**
(a) Ga and In (b) Zr and Ti
(c) Ag and Au (d) Ni and Fe

5. The following reactions take place in the blast furnace in the preparation of impure iron. Identify the reaction pertaining to the formation of the slag. **[CBSE-PMT 2011 M]**
(a) $Fe_2O_3(s) + 3\,CO(g) \rightarrow 2\,Fe\,(l) + 3\,CO_2\,(g)$
(b) $CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$
(c) $CaO\,(s) + SiO_2(s) \rightarrow CaSiO_3(s)$
(d) $2C(s) + O_2\,(g) \rightarrow 2\,CO(g)$

6. Aluminium is extracted from alumina (Al_2O_3) by electrolysis of a molten mixture of : **[CBSE-PMT 2012 S]**
(a) $Al_2O_3 + HF + NaAlF_4$ (b) $Al_2O_3 + CaF_2 + NaAlF_4$
(c) $Al_2O_3 + Na_3AlF_6 + CaF_2$ (d) $Al_2O_3 + KF + Na_3AlF_6$

7. Which one of the following is a mineral of iron ? **[CBSE-PMT 2012 S]**
   (a) Malachite (b) Cassiterite
   (c) Pyrolusite (d) Magnetite

8. In the extraction of copper from its sulphide ore, the metal is finally obtained by the reduction of cuprous oxide with : **[CBSE-PMT 2012 S]**
   (a) Copper (I) sulphide (Cu_2S)
   (b) Sulphur dioxide (SO_2)
   (c) Iron sulphide (FeS)
   (d) Carbon monoxide (CO)

9. Which one of the following ores is best concentrated by froth-flotation method ? **[AIEEE 2004]**
   (a) Galena (b) Cassiterite
   (c) Magnetite (d) Malachite

10. Heating mixture of Cu_2O and Cu_2S will give **[AIEEE 2005]**
    (a) Cu_2SO_3 (b) $CuO + CuS$
    (c) $Cu + SO_3$ (d) $Cu + SO_2$

11. Which of the following factors is of ***no significance*** for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly? **[AIEEE 2008]**
    (a) Metal sulphides are thermodynamically more stable than CS_2
    (b) CO_2 is thermodynamically more stable than CS_2
    (c) Metal sulphides are less stable than the corresponding oxides
    (d) CO_2 is more volatile than CS_2

12. Pb and Sn are extracted from their chief ore by **[IIT-JEE 2004S]**
    (a) carbon reduction and self reduction.
    (b) self reduction and carbon reduction.
    (c) electrolysis and self reduction.
    (d) self reduction and electrolysis.

13. Extraction of zinc from zinc blende is achieved by **[IIT-JEE 2007]**
    (a) electrolytic reduction
    (b) roasting followed by reduction with carbon
    (c) roasting followed by reduction with another metal
    (d) roasting followed by self-reduction

14. In the cyanide extraction process of silver from argentite ore, the oxidising and reducing agents used are **[IIT-JEE 2012]**
    (a) O_2 and CO respectively
    (b) O_2 and Zn dust respectively
    (c) HNO_3 and Zn dust respectively
    (d) HNO_3 and CO respectively

15. Sulfide ores are common for the metals ***(JEE Advanced 2013)***
    (a) Ag, Cu and Pb (c) Ag, Mg and Pb
    (b) Ag, Cu and Sn (d) Al, Cu and Pb

Exercise-4 | Applied MCQs

1. Which process represents the change,
   $Ti + 2I_2 \rightarrow TiI_4 \rightarrow Ti + 2I_2$
   (a) Cupellation (b) Van Arkel
   (c) Polling (d) Zone Refining

2. In froth flotation process many chemicals (frother , collector, activator, and depressant) are used . Which of the folloiwng is a frother:
   (a) $CuSO_4$ (b) NaCN+ alkali
   (c) Pine oil (d) Potassium xanthate.

3. Froth flotation process is based on
   (a) wetting properties of ore particle
   (b) specific gravity of ore particles
   (c) magnetic properties of ore particles
   (d) electrical properties of ore particles .

4. In the electrolysis of alumina, cryolite is added to:
   (a) lower the melting point of alumina and to increase the electrical conductivity
   (b) minimise the anode effect
   (c) remove impurities from alumina
   (d) None of these

5. In the metallurgy of Zn the Zn dust obtained from roasting and reduction of zinc sulphide contains some ZnO. It is removed by
   (a) absorbance of ultraviolet light- and reemission of white light
   (b) shock cooling by contact with a shower of molten lead.
   (c) X-ray method
   (d) smelting.

6. Among the following groups of oxides, the group containing oxides that cannot be reduced by carbon to give the respective metals is
   (a) Cu_2O, SnO_2 (b) Fe_2O_3, ZnO
   (c) CaO, K_2O (d) PbO, Fe_3O_4

7. The electrolytic reduction technique is used in the extraction of
   (a) highly electronegative elements
   (b) highly electropositive elements
   (c) metalloids
   (d) transition metals.

8. In electro-refining of metal the impure metal is made the anode and a strip of pure metal, the cathode, during the electrolysis of an aqueous solution of a complex metal salt. This method cannot be used for refining of
   (a) silver (b) copper
   (c) aluminium (d) sodium

9. In the froth flotation process of concentration of ores, the ore particles float because they:

(a) are light

(b) are insoluble

(c) have the surface which is not wetted easily

(d) have a constant electrical charge

10. Thomas slag is

(a) calcium silicate

(b) calcium phosphate

(c) tricalcium phosphate and calcium silicate

(d) calcium ammonium phosphate

11. Extraction of Ag from commercial lead is possible by

(a) Parke's process (b) Clarke's process

(c) Pattinson's process (d) Electrolytic process

12. Iron is obtained on large scale from Fe_2O_3 by

(a) Reduction with CO (b) Reduction with Al

(c) Calcination (d) Passing H_2

13. After partial roasting the sulphide of copper is reduced by

(a) cyanide process (b) electrolysis

(c) reduction with carbon (d) self reduction

14. Before introducing FeO in blast furnace , it is converted to Fe_2O_3 by roasting so that

(a) it may not be removed as slag with silica

(b) it may not evaporate in the furnace

(c) presence of it may increase the m.pt. of charge

(d) None of these.

15. The phenomenon of removing layers of basic oxides from metals before electroplating is called

(a) galvanising (b) anodising

(c) pickling (d) poling.

16. Aluminothermic process is used for the extraction of metals , whose oxides are

(a) fusible

(b) not easily reduced by carbon

(c) not easily reduced by hydrogen

(d) strongly basic.

17. When the sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are

	cathode	**anode**
(a)	pure zinc	pure copper
(b)	impure sample	pure copper
(c)	impure zinc	impure sample
(d)	pure copper	impure sample.

18. Δ G° Vs T plot in the Ellingham's diagram slopes downward for the reaction

(a) $Mg + \frac{1}{2}O_2 \rightarrow MgO$ (b) $2Ag + \frac{1}{2}O_2 \rightarrow Ag_2O$

(c) $C + \frac{1}{2}O_2 \rightarrow CO$ (d) $CO + \frac{1}{2}O_2 \rightarrow CO_2$

19. Which of the following reactions taking place in the bast furnace during extraction of iron is endothermic?

(a) $CaCO_3 \rightarrow CaO + CO_2$

(b) $2C + O_2 \rightarrow 2CO$

(c) $C + O_2 \rightarrow CO_2$

(d) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

20. Consider the following reactions at 1000°C

A. $Zn(s) + \frac{1}{2}O_2(g) \rightarrow ZnO(s);\ \Delta G° = -360\,kJ\,mol^{-1}$

B. $C(gr) + \frac{1}{2}O_2(g) \rightarrow CO(g);\ \Delta G° = -460\,kJ\,mol^{-1}$

Choose the correct statement at 1000°C

(a) zinc can be oxidised by carbon monoxide.

(b) zinc oxide can be reduced by graphite

(c) carbon monoxide can be reduced by zinc.

(d) both statements (a) and (b) are true

21. The substance **not** likely to contain $CaCO_3$ is

(a) calcined gypsum (b) sea shells

(c) dolomite (d) a marble statue

22. The value of $\Delta_f G°$ for formation of Cr_2O_3 is – 540 $kJmol^{-1}$ and that of Al_2O_3 is – 827 kJ mol^{-1} What is the value of $\Delta_r G°$ for the reaction?

$$\frac{4}{3}Al(s) + \frac{2}{3}Cr_2O_3(s) \rightarrow \frac{2}{3}Al_2O_3(s) + \frac{4}{3}Cr(s).$$

(a) – 574 kJ mol^{-1} (b) –287kJ mol^{-1}

(c) + 574 kJ mol^{-1} (d) +287kJ mol^{-1}

23. Which of the following statement is not correct about Ellingham diagram?

(a) Δ G increases with an increase in temperature

(b) It consists of plots of $\Delta_f G°$ Vs T for formation of oxides

(c) A coupling reaction can be well expressed by this diagram

(d) It express the kinetics of the reduction process

Hints & Solutions

EXERCISE 1

1. Manganese oxide (MnO_2) and chromium oxide (Cr_2O_3).
2. Reduction of oxides is easier
3. This is due to high polarising power of Cu and Ag ions
4. Carbon can be used as a reducing agent above 1123 K.
5. Copper is extracted from malachite and azurite.
6. (a) Chromium and manganese
   (b) Sodium and mangnesium
   (c) Tin and lead
   (d) Copper and silver
7. (a) x is obtained by heating metal oxide alone.
   (b) y is obtained by the reducing its oxide with carbon.
   (c) z is obtained by electrolytic reduction.

10. Because magnesium is a more costlier metal than aluminium

17. (a) **18. (b)** **19. (c)** **20. (a)** **21. (a)**

22. (c) **23. (d)** **24. (b)** **25. (b)** **26. (c)**

EXERCISE 2

1. (a) Bauxite ore of aluminium is $Al_2O_3.2H_2O$.

2. (a) Ores (see text).

3. (c) Impurities associated with minerals are called gangue or matrix.

4. (b) Al, see text.

5. (c) O, see text.

6. (d) Flux is added which combines with impurities to form slag.

7. (b) Since silica is acidic impurity the flux must be basic.

$$CaO + SiO_2 \rightarrow CaSiO_3$$

8. (a) Dolomite on calcination gives CaO.MgO which provides basic lining in furnace.

9. (b) To remove acidic impurities basic flux is added which is $CaCO_3$.

10. (b) Na_3AlF_6 is cryolite and used in the electrolysis of alumina to lower the melting point and increase electrical conductivity.

11. (d) Flux removes acidic or basic impurities e.g. silica and other metal oxides etc.

12. (b) Cassiterite contains the magnetic impurities of $FeSO_4$ and concentrated by electromagnetic separation.

13. (d) Froth floatation process is used for the concentration of sulphide ores.

14. (c)

15. (c) Cinnabar is sulphide ore (HgS). Hence purified by froth floatation process.

16. (a) Ag is leached by cyanide process (see text).

17. (c) Pyrolusite is MnO_2. Hence not concentrated by froth floatation process.

18. (b) Calcination is used for removal of volatile impurities and decompose carbonates.

19. (d) Decomposition of carbonates and hydrated oxides.

20. (d) It is definition of calcination (see text).

21. (d) Pyrites are sulphur ores and are converted into oxide by roasting.

22. (d) $Al_2O_3.2H_2O \rightarrow Al_2O_3 + 2H_2O$ is calcination.

23. (a) Mac Arthur process is used for Ag and Au (see text).

24. (b) In Goldschmidt aluminothermic process reducing agent is Al powder.

25. (d)

26. (c) Chromium is obtained by reduction with Al.

27. (d) Al is obtained by electrolytic reduction of Al_2O_3 in presence of cryolite (see text).

28. (a) The common method for the extraction of metal from oxide ore is by reduction with carbon.

29. (c) Electrolysis is used for electroplating and electrorefining both.

30. (a) Gold is deposited as anode mud (see refining of copper).

31. (a) Silicon is purified by zone refining . Metals of high purity are always purified by zone refining.

32. (b) Silver containing lead is purified by cupellation (see text).

33. (d) Ni is purified by Mond's process by decomposition of $Ni(CO)_4$.

34. (c) Caliche is crude chilesaltpetre ($NaNO_3$) and contains $NaIO_3$, source of iodine.

35. (b) Malachite is an ore of copper $Cu(OH)_2.CuCO_3$.

36. (b) Important ore of iron is Haematite Fe_2O_3.

37. (c)

38. (d) Cassiterite is an ore of Sn also known as tin stone SnO_2.

39. (a) Cl_2 is obtained by electrolysis of (aqueous) NaCl.

40. (a) Galena is an ore of lead. It is PbS.

41. (c) Fe does not exist native.

42. (d) Most electropositive metals are obtained by electrolysis of their fused ionic salts.

43. (a) Gold being least reactive found native.

44. (a) MnO_2 is pyrolusite (oxide ore).

45. (c) Na is obtained by elctrolytic reduction being electropositive in nature.

46. (b) Cuprite is Cu_2O and Argentite is Ag_2S.

47. (c) $NaCl \rightleftharpoons Na^+ + Cl^-$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$\begin{array}{ccc} \frac{1}{2}H_2 \leftarrow H \;\big\downarrow e^- & ; & Cl^- \rightarrow Cl \rightarrow \frac{1}{2}Cl_2 + e^- \\ \text{(At cathode)} & & \text{(At anode)} \end{array}$$

Reduction potential of H is more than Na.

48. (d) Slag formed in the extraction of iron is $CaSiO_3$.

49. (b) Cyanide process is for gold (I-D); floatation process - pine oil (II-B); Electrolytic reduction - Al (III-C); Zone refining -Ge (IV-A).

50. (d)

51. (c) Ellingham diagram normally consists of plots of $\Delta_f G^\circ$ Vs T for the formation of oxides of elements.

52. (d) For a spontaneous reaction , ΔG^o must be negative and it can be possible only in this case when $x < y$

EXERCISE 3

1. (d) The sulphide ore is roasted to oxide before reduction because the ΔG_f^o of most of the sulphides are greater than those of CS_2 and H_2S, therefore neither C nor H can reduce metal sulphide to metal. Further, the standard free energies of formation of oxide are much less than those of SO_2. Hence oxidation of metal sulphides to metal oxide is thermodynamically favourable.

2. (d) Leaching is the selective dissolution of the desired mineral leaving behind the impurities in a suitable dissolving agent e.g.,

Argentitie or Silver glance, Ag_2S is an ore of silver. Silver is extracted from argentite by the mac-Arthur and Forest process (leaching process).

$$Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$$

$$4Au + 8KCN + 2H_2O + O_2 \rightarrow 4K[Au(CN)_2] + 4KOH$$

3. (b) Pig iron or cast iron contains 3 – 5% carbon and varying amounts of Mn, Si, P and S which makes the iron hard and brittle.

4. (b) Zr and Ti are purified by van Arkel method.

$$Zr(s) + 2I_2(g) \xrightarrow{870K} ZrI_4(g)$$

$$ZrI_4(g) \xrightarrow[\text{Tugsten filament}]{2075K} Zr(s) + 2I_2(g)$$

$$Ti(s) + 2I_2(s) \xrightarrow{523K} TiI_4(g)$$

$$\big\downarrow 1700K$$

$$Ti(s) + 2I_2(g)$$

Pure titanium

5. (c) In blast furnace at about 1270 K, calcium carbonate is almost completely decomposed to give CaO which acts as a flux and combines with SiO_2 present as impurity (gangue) in the ore to form calcium silicate (fusible slag)

$$CaO(s)\text{ (basic flux)} + SiO_2(s)\text{ (acidic flux)} \longrightarrow CaSiO_3(s)\text{ (slag)}$$

6. (c) Fused alumina (Al_2O_3) is a bad conductor of electricity. Therefore, cryolite (Na_3AlF_6) and fluorspar (CaF_2) are added to purified alumina which not only make alumina a good conductor of electricity but also reduce the melting point of the mixture to around 1140 K.

7. (d) Fe_3O_4 – Magnetite

$CuCO_3 \cdot Cu(OH)_2$ – Malachite

Pyrolusite – MnO_2 and Cassiterite – SnO_2.

8. (a) Cuprous oxide formed during roasting of cuprous sulphide is mixed with few amount of cuprous sulphide and heated in a reverberatory furnace to get metallic copper.

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

9. (a) Galena is PbS and purified by froth floatation method

10. (d) During bessemerisation, cuprous sulphide is oxidised which combines with remaining cuprous sulphide to form free copper metal

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

11. (c) The reduction of metal sulphides by carbon reduction process is not spontaneous because ΔG for such a process is positive. The reduction of metal oxide by carbon reduction process is spontaneous as ΔG for such a process is negative. From this we find that on thermodynamic considerations CO_2 is more stable than CS_2 and the metal sulphides are more stable than corresponding oxides.

In view of above the factor listed in choice (c) is incorrect and so is of no significance.

12. (b) PbO & $PbSO_4$ get reduced by PbS itself which is already present in mixture so because the reduction took place by itself, hence is known as self reduction.

$$2PbO + PbS \xrightarrow{\Delta} 3Pb + SO_2\uparrow$$

$$PbSO_4 + PbS \xrightarrow{\Delta} 2Pb + 2SO_2\uparrow$$

13. (b) Extraction of Zn from ZnS (Zinc blende) is achieved by roasting followed by reduction with carbon.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

$$ZnO + C \longrightarrow Zn + CO$$

14. **(b)** The reactions involved in cyanide extraction process are :

$$\underset{\text{(argentite)}}{Ag_2S} + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$$

$$4Na_2S + \underset{\substack{\text{Oxiding}\\\text{agent}}}{5O_2} + 2H_2O \rightarrow 2Na_2SO_4 + 4NaOH + 2S$$

$$2Na[Ag(CN)_2] + \underset{\substack{\text{(reducing}\\\text{agent)}}}{Zn} \rightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

15 **(a)** Silver, copper and lead are commonly found in earth's crust as Ag_2S (silver glance), $CuFeS_2$ (copper pyrites) and PbS (galena)

EXERCISE 4

1. **(b)** The given reaction is the method named as Van Arkel for the purification of titanium
2. **(c)** Froth reduces the surface tension of water and the solution forms froth.
3. **(a)** Froth flotation process is based on wetting properties of ore particles.
4. **(a)** Cryolite lowers the m.p of alumina and increases the electrical conductivity
5. **(d)** See metallurgy of Zn
6. **(c)** Ca and K are strong reducing agents, hence their oxides cannot be reduced with carbon
7. **(b)** Highly electropositive elements are obtained by electrolytic reduction.
8. **(d)** Na reacts vigorously with water (exothermic process)
9. **(c)** The surface of particles not wetted hence they float at the surface
10. **(c)** Tricalcium phosphate and calcium silicate is Thomas slag
11. **(a)** See Parke's process
12. **(a)** $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ (in blast furnace)
13. **(d)** $2CuO + CuS \rightarrow 3Cu + SO_2$ (Self - reduction)
14. **(a)** FeO is capable forming slag with SiO_2

    $SiO_2 + FeO \rightarrow FeSiO_3$
15. **(c)** Pickling is removel of basic oxide layers on metals before electroplating.
16. **(b)** When reduction by carbon is not satisfactory in case of metals having high m.pt., aluminothermic process is used .
17. **(d)** Pure metal always deposits at cathode.
18. **(c)** 19. **(a)** 20. **(b)**
21. **(a)** Gypsum is $CaSO_4.2H_2O$
22. **(b)** The two equation are:

$$\frac{4}{3}Al(s) + O_2(g) \rightarrow \frac{2}{3}Al_2O_3(s),\ \Delta_fG° = -827kJ\ mol^{-1} \quad \ldots(1)$$

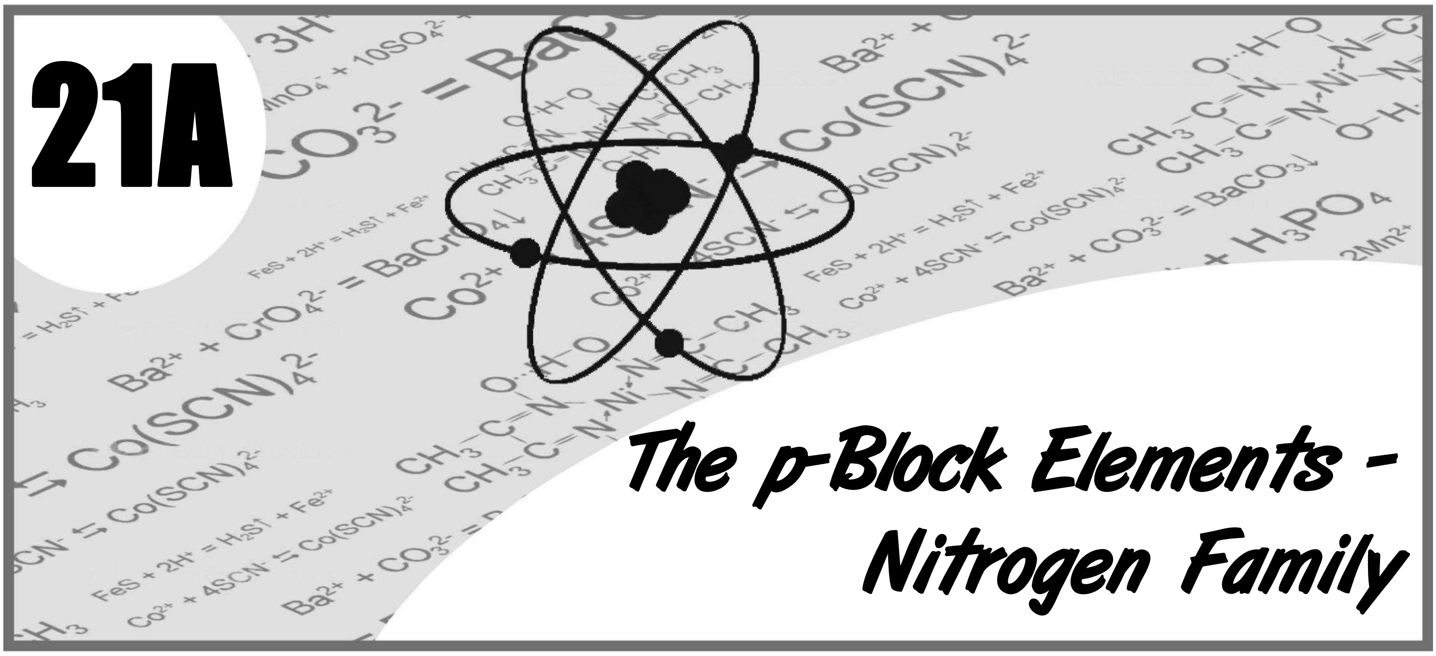
$$\frac{4}{3}Cr(s) + O_2(g) \rightarrow \frac{2}{3}Cr_2O_3(s),\ \Delta_fG° = -540kJ\ mol^{-1} \quad \ldots(2)$$

Subtracting equation (ii) from equation (i) we have,

$$\frac{4}{3}Al(s) + \frac{2}{3}Cr_2O_3(s),$$

$$\rightarrow \frac{2}{3}Al_2O_3(s) + \frac{4}{3}Cr(s),\quad \Delta_rG° = -287kJ\ mol^{-1}$$

23. **(d)** Ellingham diagrams are based on thermodynamic concepts. It does not tell anything about the kinetics of the reduction process.



21A

The p-Block Elements - Nitrogen Family

GENERAL CHARACTERISTICS :

The group 15 of the periodic table consists of nitrogen, phosphorous, arsenic, antimony and bismuth. These elements are known as ***pnicogens*** and their compounds as ***pnicomides***.

1. **Electronic configuration :**

Element	*At. No.*	*Electronic configuration*	*Valence shell electronic configuration*
Nitrogen	7	[He] $2s^2\ 2p^3$	$2s^2\ 2p^3$
Phosphorous	15	[Ne] $3s^2,\ 3p^3$	$3s^2\ 3p^3$
Arsenic	33	[Ar] $3d^{10},\ 4s^2\ 4p^3$	$4s^2\ 4p^3$
Antimony	51	[Kr] $4d^{10},\ 5s^2\ 5p^3$	$5s^2\ 5p^3$
Bismuth	83	[Xe] $4f^{14},\ 5d^{10}\ 6s^2\ 6p^3$	$6s^2\ 6p^3$

2. **Metallic character :** N, P(non metals), As, Sb(metalloids), Bi(metal)
3. **Physical state :** Nitrogen is first element after hydrogen to be a diatomic gas in normal form. All other elements in the group are normally solids.
4. **Atomicity :** N_2 is diatomic while others are tetra-atomic M_4
5. **Melting and boiling points :** The melting point increases from nitrogen to arsenic. The boiling points increase regularly on moving down the group.
6. **Density :** Density increases down the group.
7. **Atomic radii :** Atomic radii increases with increase in atomic number.
8. **Covalent radii :** Covalent radii increases in a regular fashion down the group.
9. **Allotropy :** All the elements (except bismuth) show allotropy.

   Nitrogen - α-nitrogen, β-nitrogen

   Phosphorous - white, Red, scarlet, violet, α-black, β-black

   Arsenic - Grey, Yellow, Black

   Antimony - Metallic, Yellow, Explosive
10. **Oxidation state :**

N	P	As	Sb	Bi
–3 to +5	–3, +3, +4, +5	+3, +5	+3, +5	+3, +5

Nitrogen has a wide range of oxidation states

Oxidation state	*Example*
+5	N_2O_5, HNO_3, NO_3^-
+4	NO_2, N_2O_4
+3	HNO_2, NO_2^-, NF_3
+2	NO
0	N_2
–1	NH_2OH, NH_2F
–2	N_2H_4
–3	NH_3, NH_4^+, NH_2^-

11. **Negative oxidation states :** –3 oxidation state is exhibited by other elements also. Ca_3P_2, Na_3As, Zn_3Sb_2
12. **Inert pair effect :** Inert pair effect increases down the group and due to this effect the stability of +3 oxidation state increases and stability of +5 oxidation state decreases on moving down the group.
13. **Ionisation energy :** Ionisation energy of nitrogen is very high due to small atomic radius. The ionisation energy decreases down the group.

14. **Electronegativity :** The electronegativity decreases from nitrogen to bismuth.
15. **Catenation :** They exhibit the property of catenation but due to weak M–M bond to less extent than 14 group elements.

Bond	C–C	N–N	P–P	As–As
kJ/mol	353.3	163.7	201.6	147.4

16. **Reactivity :** Elemental nitrogen is higly unreactive largely because of its strong triple bond. (almost as inert as noble gases).

    While phosphorus is extremely reactive and kept in water. It is inflamable and can be ignited at 45°C. It shows green *luminiscence* or glow in dark on account of its slow oxidation. This glow phenomenon is known as *phosphorescence*.
17. **Multiple bond formation :** Only nitrogen has a tendency to form pπ—pπ multiple bonds. Others forms dπ–pπ multiple bonds easily.

COMPOUNDS OF GROUP 15 ELEMENTS :

a) ***Hydrides :*** All the elements of this group form hydrides of the type MH_3 which are covalent and pyramidal in shape. Some properties follow the order which are

NH_3 >	PH_3 >	AsH_3 >	SbH_3 >	BiH_3
Ammonia	Phosphine	Arsine	Stabene	Bismuthene

1. Ease of formation
2. Stability
3. Basic character
4. Solubility
5. Bond angle (NH_3 107.5° ; PH_3 92°, AsH_3 91, SbH_3 90°)
6. Strength of M – H bond
7. Dipole moment
8. Decomposition temperature

Some properties follow the order

$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

1. Reducing character
2. Covalent character
3. Poisonous character
4. Rate of combustion

Boiling points : $BiH_3 > SbH_3 > NH_3 > AsH_3 > PH_3$

Preparation of hydrides : Some hydrides can be prepared as follows :

1. ***Ammonia :***

(a) Any ammonium salt + metal oxide or hydroxide $\xrightarrow{\Delta} NH_3$

eg. $NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + H_2O + NH_3$

$2NH_4NO_2 + K_2O \rightarrow 2NH_3 + 2KNO_2 + H_2O$

or $(NH_4)_3PO_4$, NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_2SO_3$, $(NH_4)_2S$ or $(NH_4)_2\,(C_2O_4)$

(b) Any nitride $+ H_2O \rightarrow NH_3 \uparrow$

$BN + 3H_2O \rightarrow H_3BO_3 + NH_3$

$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$

2. ***Phosphine :***

a) **Any metal phosphide** $+ H_2O \rightarrow PH_3$

$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

b) $P_4 + 3KOH + 3H_2O \rightarrow PH_3 + 3KH_2PO_2$

c) $PH_4I + NaOH \rightarrow NaI + H_2O + PH_3$

3. ***Other hydrides :***

(a) $Zn_3M_2(s) + 6HCl \rightarrow 2MH_3(g) + 3ZnCl_2(aq)$

$M = As, Sb, Bi$

(b) ***Halides*** *:* All the elements of this group form trihalides of the type $\mathbf{MX_3}$ and except nitrogen all form pentahalides of the type $\mathbf{MX_5}$

MX_3 M = N, P, As, Sb, Bi and X = F, Cl, Br or I

MX_5

when X = F, M can be P, As, Sb and Bi

when X = Cl, M can be P, As and Sb

when X = Br, M can be P

NF_3 is a colourless, odourless gas and the most stable of this series. It has low reactivity.

NCl_3 is a yellow oily liquid that reacts with water to form ammonia and hypochlorous acid.

NI_3 is shock sensitive and decomposes explosively when touched.

Hydrolysis *:*

$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$

$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

$2AsCl_3 + 3H_2O \rightarrow As_2O_3 + 6HCl$

$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$

$BiCl_3 + H_2O \rightarrow BiOCl + 2HCl$

* Ease of hydrolysis $BiCl_3 > SbCl_3 > AsCl_3 > PCl_3 > NCl_3$

* Trihalides except BiF_3 are covalent in nature

* Trihalides have pyramidal structure.

(c) ***Pentahalides*** *:* As nitrogen does not contain-vacant d-orbitals in the second shell and cannot expand its outer shell hence it does not form pentahalides.

* The hybridisation in pentahalides is sp^3d (trigonal bipyramidal)

* Thermally less stable than trihalides

* Act as Lewis acids $PCl_5 + Cl^- \rightarrow [PCl_6^-]$

* On complete hydrolysis they produce acids

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$$

(d) ***Oxides :*** All the elements of this group form oxides of the type M_2O_3 and M_2O_5. either by direct combination with O_2 or indirectly.

Oxides of N $\underset{\text{strongly acidic}}{N_2O_5, N_2O_4, N_2O_3,}$ $\underbrace{NO,\quad N_2O}_{\text{neutral}}$

Oxides of P $\underset{\text{strongly acidic}}{P_2O_5(P_4O_{10})}$ $P_2O_3(P_4O_6)$

Oxides of As	As_2O_5	$\underset{\text{Amphoteric}}{As_2O_3}$
Oxides of Sb	Sb_2O_5	$\underset{\text{Amphoteric}}{Sb_2O_3}$
Oxides of Bi	Bi_2O_5	$\underset{\text{Basic}}{Bi_2O_3}$

N_2O (dinitrogen oxide or nitrous oxide) known as **laughing gas**

Preparation :

(i) Priestley's method :

$$2NO + H_2O + Fe \rightarrow N_2O + Fe(OH)_2$$

(ii) Bertholet's (common method) :

$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$

(iii) $2NaNO_3 + (NH_4)_2SO_4 \rightarrow N_2O + 2H_2O + Na_2SO_4$

Properties :

Colourless, fairly unreactive, pleasing odour, sweet taste, supports combustion. It is neutral.

$$2N_2O(g) \xrightarrow{\Delta} 2N_2(g) + O_2(g)$$

Structure : Linear $\underset{\cdot\cdot}{\overset{\overset{-}{\cdot\cdot}}{N}} = \overset{+}{N} = \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \longleftrightarrow \overset{\cdot\cdot}{N} \equiv \overset{+}{N} - \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-}$

Uses : Mixed with oxygen it is used as anaesthetic

NO (nitrogen oxide or nitric oxide) :

Preparation :

Common method

$$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$$

(i) $N_2(g) + O_2(g) \xrightarrow{\Delta} 2NO(g)$ (commercial)

(ii) $3Cu(s) + 8HNO_3(dil) \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$ (Lab method)

(iii) $4NH_3 + 5O_2 \xrightarrow[750°C,6atm]{\Delta,\,Pt} 4NO + 6H_2O$ (Ostwald's process)

Properties : Colourless, paramagnetic, slightly toxic gas, blue in liquid state. It is combustible and supports combustion. It is neutral.

$$FeSO_4 + NO \rightarrow \underset{\text{dark brown}}{FeSO_4.NO} \xrightarrow{\Delta} FeSO_4 + \underset{\text{pure gas}}{NO}$$

$$[Fe(H_2O)_6]SO_4 + NO \rightarrow \underset{\substack{\text{Hydrated nitrosyl}\\ \text{complex}}}{[Fe(H_2O)_5NO]SO_4} \xrightarrow{\Delta}$$

$$\cdot FeSO_4 + NO + 5H_2O$$

$2NO + O_2 \rightarrow 2NO_2(\text{brown})$

It is reducing as well as oxidsing in nature.

Uses :

i) For manufacturing of nitric acid

ii) For detection of Oxygen

iii) For manufacturing of sulphuric acid as catalyst (Lead chamber process)

Structure :

$$:\overset{\bullet}{N} = \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \longleftrightarrow \underset{\cdot\cdot}{\overset{\overset{-}{\cdot\cdot}}{N}} = \overset{\overset{+}{\cdot}}{O}:$$

NO_2 (nitrogen dioxide)

Preparation :

i) $2NO + O_2 \rightarrow 2NO_2$

ii) $2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$ (Common method)

iii) $Cu + 4HNO_3(conc.) \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$

Properties : Highly toxic, paramagnetic, reddish brown gas with choking odour, acidic

Reactions :

i) $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$ (Hence it is mixed anhydride of HNO_2 and HNO_3)

ii) $\underset{\text{brown}}{2NO_2} \rightleftharpoons \underset{\text{colourless, solid/liquid, acidic}}{N_2O_4}$

iii) $NO_2 \xrightarrow{h\nu} NO + O$

iv) It is combustible and supports the combustion of burning P, Mg or charcoal. Burning S or candle is extinguished.

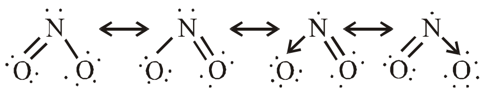
v) It is oxidising and reducing in nature

Uses :

i) For Manufacturing of HNO_3

ii) As Catalyst in lead chamber process for Sulphuric acid

Structure :



N_2O_3 (dinitrogen trioxide) Nitrogen sesquioxide

Common method : $2NO + N_2O_4 \xrightarrow{253K} 2N_2O_3$

Preparation : $NO + NO_2 \rightarrow N_2O_3$

Properties : It is blue solid, acidic

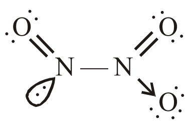
$$N_2O_3 + H_2O \rightarrow 2HNO_2$$

Hence it is anhydride of HNO_2

Absorbed by sulphuric acid

$$N_2O_3 + 2H_2SO_4 \rightarrow \underset{\substack{\text{Nitroso}\\ \text{sulphuric acid}}}{2NO[HSO_4]_2} + H_2O$$

Uses and Structure : Shape and structure is not definitely known



N_2O_5 (dinitrogen pentaoxide)

Preparation :

i) $2HNO_3 + P_2O_5 \rightarrow N_2O_5 + 2HPO_3$ (common method)

ii) $4AgNO_3 + 2Cl_2 \xrightarrow{90°C} 4AgCl + 2N_2O_5 + O_2$

iii) $N_2O_4 + O_3 \rightarrow N_2O_5 + O_2$

Properties : Colourless crystalline solid and sublimes

$N_2O_5 + H_2O \rightarrow 2HNO_3$

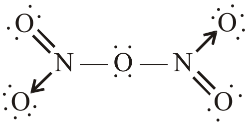
It is anhydride of nitric acid

$N_2O_5 + 2NaOH \rightarrow 2NaNO_3 + H_2O$

$N_2O_5 + H_2O_2 \rightarrow \underset{\text{Pernitric acid}}{HNO_4} + HNO_3$

Uses : It is powerful oxidising agent

Structure :



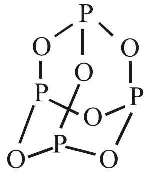
It's ionic structure (by X-ray) is $NO_2^+NO_3^-$. It is also called **nitronium nitrate**.

P_2O_3 or P_4O_6 (phosphorous trioxide)

Preparation : $\underset{\text{white}}{P_4} + \underset{\text{limited}}{3O_2} \xrightarrow{\Delta} P_4O_6$

Properties : white solid like wax, garlic odour, highly poisonous.

Structure :



P_2O_5 or P_4O_{10} (phosphorus pentaoxide) flower of phosphorous

Preparation : i) $\underset{\text{white}}{P_4} + \underset{\text{excess}}{5O_2} \rightarrow P_4O_{10}$

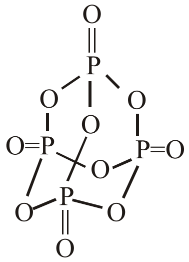
Properties : White crystalline solid smells like garlic, sublimes

$P_4O_{10} + 2H_2O(\text{cold}) \rightarrow \underset{\text{meta phosphoric acid}}{4HPO_3}$

$P_4O_{10} + 6H_2O(\text{hot}) \rightarrow \underset{\text{ortho phosphoric acid}}{4H_3PO_4}$

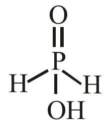
Uses : Powerful dehydrating agent

Structure :

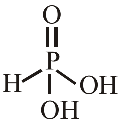


(d) ***Oxyacids of N and P :*** Both form a number of oxy acids which are as follows :

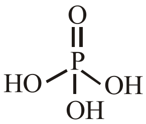
			Oxidation number	Basicity
1.	Hyponitrous acid	$H_2N_2O_2$	+1	
2.	Nitroxylic acid	$H_4N_2O_4$	+2	
3.	Nitrous acid	HNO_2	+3	
4.	Nitric acid	HNO_3	+5	
5.	Peroxy nitric acid	HNO_4	+5	
6.	Hydronitrous acid	H_2NO_2	+2	
7.	Hypophosphorous acid	H_3PO_2	+1	1
8.	Phosphorous acid	H_3PO_3	+3	2
9.	Orthophosphoric acid	H_3PO_4	+5	3
10.	Pyrophosphoric acid	$H_4P_2O_7$	+5	4
11.	Meta phosphoric acid	HPO_3	+5	1
12.	Hypophosphoric acid	$H_4P_2O_6$	+4	4



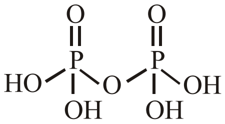
Hypophosphorous acid



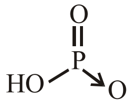
Phosphorous acid



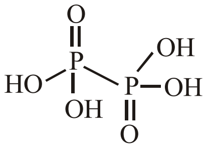
Phosphoric acid



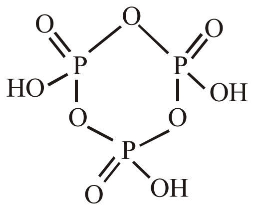
Pyrophosphoric acid



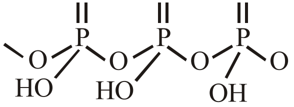
Metaphosphoric acid



Hypophosphoric acid



$(HPO_3)_3$
Cyclo meta phosphoric acid



Polymetaphosphoric acid $(HPO_3)_n$

NITROGEN :

Discovered by Daniel Rutherford. Abundance in air is 78.15% by volume. It occurs in combined state as saltpetre (KNO_3) and Chile Saltpetre ($NaNO_3$). It is also known as Azote (without life)

Preparation :

i) $NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$

ii) $2NH_3 + 3CuO \rightarrow N_2 + 3H_2O + 3Cu$

iii) $8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$

iv) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$. It is violent reaction with flashes of light (volcano experiment)

v) $H_2NCONH_2 + 2HNO_2 \rightarrow 2N_2 + CO_2 + 3H_2O$

Preparation of very pure N_2 : By heating Sodium azide

$2NaN_3 \rightarrow 2Na + 3N_2$

Manufacturing : By Linde's or Claude's process

Atmospheric air is compressed and then released into a bigger area when liquid air is obtained (Joule Thomson effect) which is mainly mixture of N_2 and O_2. They are separated by fractional distillation.

Properties : It is colourless, odourless, tasteless, slightly lighter than air, slightly soluble in water, non poisonous gas.

It is incombustible and non supporter of combustion. It combines with metals and non metals to form number of compounds.

Uses : To decrease concentration of oxygen in air and make combustion less rapid. To create inert atmosphere and in the preparation of NH_3, HNO_3, $CaCN_2$, etc.

AMMONIA (NH_3) :

Preparation : Lab method :

$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$

Manufacturing :

(a) ***Haber's process*** *:*

$$N_2 + 3H_2 \xrightarrow[450°C,\ 245\ Atm.]{Fe/Mo} 2NH_3$$

Other catalysts employed are

(i) finely divided Os or U

(ii) Finely divided Ni deposited over pumice stone

(iii) $Fe(OH)_3$ with traces of SiO_2 and K_2O

(b) ***Cyanamide process*** *:*

$$CaC_2 + N_2 \rightarrow \underset{\text{Nitrolim}}{(CaCN_2 + C)}$$

Mixture of Calcium Cyanamide and graphite under the name of nitrolim is used as fertilizer.

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$$

(c) ***Serpeks process*** *:* As by product during hydrolysis of AlN

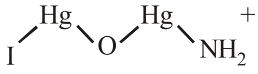
$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$

Properties *:* Colourless gas, characteristic pungent odour, brings tears into eyes, collected by downward displacement of air. Extremely soluble in water due to H-bonding. It is a strong lewis base.

* Ammonia is dried over any metal oxide but CaO is cheaper.

* When passed through alkaline solution of Nesslers reagent a brown coloured complex known as Millon's base is formed.

$2K_2HgI_4 + 3KOH + NH_3 \longrightarrow$


$+ 7KI + 2H_2O$

Millon's base

NITRIC ACID (HNO_3) (ALSO KNOWN AS AQUA FORTIS) :

Preparation :

Lab method *:*

$$2NaNO_3 + H_2SO_4(conc.) \rightarrow Na_2SO_4 + 2HNO_3$$

Manufacturing :

(a) ***Birkland - Eyde process*** *:* Air is passed through an electric arc (3000ºC) when N_2 combines with O_2 to form NO. It is cooled and allowed to combine with O_2 to form NO_2. The latter is passed in water in presence of excess of air to give HNO_3.

$N_2 + O_2 \rightarrow 2NO$

$2NO + O_2 \rightarrow 2NO_2$

$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$

(b) ***Ostwald's Process*** *:* From ammonia

$4NH_3 + 5O_2 \xrightarrow[800°C]{Pt\ gauge} 4NO + 6H_2O$

$2NO + O_2 \rightarrow 2NO_2$

$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$

Properties : Syrupy, colourless, pungent liquid usually available as 68% and 15.7 M. Aqueous solution is often yellow due to small concentrations of NO_2

FUMING NITRIC ACID (HNO_3 + NO_2)

Chemical properties *:* As an acid - It is a strong acid and in aqueous solution the ionisation is virtually complete.

$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$

Thus it reacts with basic oxides, hydroxides, carbonates etc.

$CaO + 2H_3O^+ \rightarrow Ca^{2+} + 3H_2O$

As oxidising agent

$$NO_3^- + 2H_3O^+ + e^- \xrightarrow{conc.} NO_2 + 3H_2O$$

$NO_3 + 4H_3O^+ + 3e^- \xrightarrow{dil.} NO + 6H_2O$

or $2HNO_3 \rightarrow H_2O + 2NO_2 + O$ (concentrated HNO_3)

$2HNO_3 \rightarrow H_2O + 2NO + 3O$ (dil. HNO_3)

Oxidation of non metals, - ic acids are formed eg.

$S + H_2O + 3O \rightarrow H_2SO_4$ (Sulphuric acid)

$C + H_2O + 2O \rightarrow H_2CO_3$ (Carbonic acid)

$2P + 3H_2O + 5O \rightarrow 2H_3PO_4$ (Phosphoric acid)

$I_2 + H_2O + 5O \rightarrow 2HIO_3$ (Iodic acid)

$3As + 3H_2O + 5O \rightarrow 2H_3AsO_4$ (Arsenic acid)

$Sn + H_2O + 2O \rightarrow H_2SnO_3$ (meta stannic acid)

$Se + H_2O + 2O \rightarrow H_2SiO_3$ (selenious acid)

$Te + H_2O + 2O \rightarrow H_2TeO_3$ (Tellurous acid)

Oxidation of compounds :

$2HNO_3 \rightarrow H_2O + 2NO_2 + O$, $SO_2 + H_2O + O \rightarrow H_2SO_4$

$H_2S + O \rightarrow H_2O + S$, $2HBr + O \rightarrow H_2O + Br_2$

$FeS + 4O \rightarrow FeSO_4$

$C_{12}H_{22}O_{11} + 18O \rightarrow 6(COOH)_2 + 5H_2O$

The action of Nitric acid on metals : Armstrong's theory - The metal first displaces nascent hydrogen from acid which further reacts with acid to give secondary reactions.

$Metal + HNO_3 \rightarrow Metal\ nitrate + H$ (Primary reaction)

$$\left.\begin{array}{l} 2HNO_3 + 2H \rightarrow 2NO_2 + 2H_2O \\ 2HNO_3 + 6H \rightarrow 2NO + 4H_2O \\ 2HNO_3 + 8H \rightarrow N_2O + 5H_2O \\ 2HNO_3 + 10H \rightarrow N_2 + 6H_2O \\ 2HNO_3 + 16H \rightarrow 2NH_3 + 6H_2O \end{array}\right\} \text{secondary reactions}$$

Factors affecting the secondary reactions

i) Nature of the metal ii) Concentration of the acid

iii) Temperature iv) Presence of impurities

Action of nitric acid on zinc under different conditions

(i) Cold and very dil. acid evolves ammonia which reacts with HNO_3 forming ammonium nitrate

$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3$

(ii) Cold and dil HNO_3

$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$

(iii) Cold and moderately conc.

$3Zn + 8HNO_3 \rightarrow 3Zn(NO_3)_2 + 4H_2O + 2NO$

(iv) Cold and concentrated

$Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$

Action of nitric acid on Copper under different conditions

(i) Cold and dil.

$4Cu + 10HNO_3 \rightarrow 4Cu(NO_3)_2 + 5H_2O + N_2O$

(ii) Cold and moderately concentrated

$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$

(iii) Cold and concentrated

$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$

(iv) Hot and conc.

$5Cu + 12HNO_3 \rightarrow 5Cu(NO_3)_2 + 6H_2O + N_2$

Metals like Mg and Mn give hydrogen with dil. HNO_3

$Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2$

$Mn + 2HNO_3 \rightarrow Mn(NO_3)_2 + H_2$

Passivity : Metals like, Fe, Cr, Ni, Al or Co become inactive or passive due to stable oxide layers.

Noble Metals like Pt, Pd, Os, Ir and Au do not react with nitric acid. They react with **aqua regia** (1 vol. Conc. HNO_3 + 3 vol. Conc. HCl). eg.:

$HNO_3 + 3HCl \rightarrow NOCl + 2H_2O + \underset{\text{nascent chlorine}}{2Cl}$

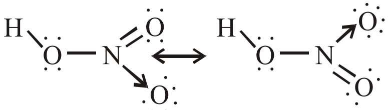
$Au + 3Cl \rightarrow AuCl_3$

$AuCl_3 + HCl \rightarrow \underset{\text{Chloro auric acid}}{HAuCl_4}$

Similarly platinum forms - $Pt + 4Cl \rightarrow PtCl_4$

$PtCl_4 + 2HCl \rightarrow \underset{\text{Chloroplatanic acid}}{H_2PtCl_6}$

Structure of nitric acid :



Uses : In the manufacture of fertilizers ii) For purification of silver and gold iii) In the manufacture of explosives iv) oxidising reagent v) As nitrating reagent

NITROUS ACID (HNO_2) :

Preparation :

(i) $Ba(NO_2)_2 + H_2SO_4(\text{dil.}) \rightarrow BaSO_4 \downarrow + 2HNO_2$

(ii) $2NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_2$

(iii) $N_2O_3 + H_2O \rightarrow 2HNO_2$

(iv) $NH_3 + 3H_2O_2 \rightarrow HNO_2 + 4H_2O$

Properties : It has slight bluish colour in solution may be due to anhydride N_2O_3. It is very unstable.

(i) ***Decomposition*** *:*

$3HNO_2 \rightarrow 2NO + HNO_3 + H_2O$ (auto oxidation)

(ii) ***Action of heat*** *:*

$2HNO_2 \rightarrow H_2O + N_2O_3 \rightarrow NO_2 + NO$

(iii) ***Oxidising nature*** *:* $2HNO_2 \rightarrow 2NO + H_2O + O$

$H^+ + HNO_2 + e^- \rightarrow H_2O + NO$ (electron acceptor)

(iv) ***Reducing nature*** *:* $HNO_2 + O \rightarrow HNO_3$

$H_2O + HNO_2 \rightarrow HNO_3 + 2H^+ + 2e^-$ (electron donor)

(v) ***Reaction with ammonia :***

$NH_3 + HNO_2 \rightarrow NH_4NO_2 \rightarrow N_2 + 2H_2O$

(vi) ***Formation of diazonium compounds :***

$C_6H_5NH_2HCl + HNO_2 \rightarrow C_6H_5N = NCl + 2H_2O$

Uses : In the manufacture of azo dyes.

Structure : It is a tautomeric mixture of the following forms

PHOSPHOROUS :

Discovered by **Brand**

Occurence : It occurs in combination only as phosphates

(i) **Phosphorite** $Ca_3(PO_4)_2$

(ii) **Chlorapatite** $CaCl_2.3Ca_3(PO_4)_2$

(iii) **Fluorapatite** $CaF_2.3Ca_3(PO_4)_2$.

In phosphoproteins of brain, bones, teeth, milk, egg, nervous tissues of animal and plants.

Manufacturing : By reduction of calcium phosphate with carbon in presence of SiO_2 in an electric furnance

$$2Ca_3(PO_4)_2 + 6SiO_2 \rightarrow 6CaSiO_3 + P_4O_{10}$$

$$P_4O_{10} + 10C \rightarrow P_4 + 10CO$$

Purification : By melting under acidified solution of $K_2Cr_2O_7$. The impurities are oxidised and redistilled.

Properties : Freshly prepared phosphorous is colourless. On standing acquires pale lemon colour due to formation of red phosphorus on the surface. It is therefore called yellow phosphorous. Due to its poisonous nature the jaw bones decay and disease is known as **"Phossy jaw"**

Allotropic forms of phosphorous and their preparation :

i) ***Red phosphorous*** : It is prepard by carefully heating yellow phosphorous in an inert atmosphere for about 8 days.

ii) ***Violet phosphorous*** : By crystallisation of white phosphorous from molten lead

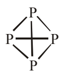
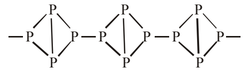
iii) ***Scarlet*** :

1. By exposing the solution of red P in PBr_3 to light or by boiling.
2. By heating PBr_3 with Hg at 513 K

$$4PBr_3 + 6Hg \rightarrow 6HgBr_2 + P_4$$

iv) ***Black*** : By heating white P to 473K under 1000kg/sq. cm.. It is the most stable form, good conductor of electricity.

Some points of distinction between white and red phosphorous

Property	*White*	*Red*
1. Structure		
2. Colour	Light yellow	Violet
3. Odour	Garlic	Odourless
4. Conductivity	Bad Conductor	Semi Conductor
5. Physiological action	Poisonous	Non poisonous
6. Density	1.81	2.1
7. Melting point	44ºC	500ºC
8. Ignition temperature	35ºC	240ºC
9. Hardness	Soft	Brittle
10. Solubility in CS_2, CCl_4 & benzene	Soluble	Insoluble
11. Action of KOH	PH_3	No action
12. Action of $CuSO_4$	Cu_3P_2	No action
13. Action of Cl_2	PCl_3 or PCl_5	On heating PCl_3 or PCl_5
14. In dark	Shines	does not

Chemical properties :

(i) ***With non metals*** :

$$4P + 3O_2 \rightarrow 2P_2O_3, \quad 4P + 5O_2 \rightarrow 2P_2O_5$$

$$2P + 3Cl_2 \rightarrow 2PCl_3, \quad 2P + 5Cl_2 \rightarrow PCl_5$$

(ii) ***With metals*** :

$$3Na + P \rightarrow Na_3P \qquad 3Ca + 2P \rightarrow Ca_3P_2$$

(iii) ***With compounds*** :

$$4P + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$$

$$P + 5HNO_3 \rightarrow H_3PO_4 + H_2O + 5NO_2$$

$$2P + 5H_2SO_4 \rightarrow 2H_3PO_4 + 2H_2O + 5SO_2$$

Uses :

In matches, explosives, as rat poison and in fertilizers and alloys.

Match box :

Side contains : Red P or P_2S_3 + Sand + Glue

On tip : Red P + Oxidising agent like $KClO_3$ or KNO_3 or Pb_3O_4 + glass powder or chalk for friction + glue

PHOSPHINE (PH_3) :

Preparation :

(i) **Any phosphide** $+H_2O \rightarrow PH_3$

$$Ca_3P_2 + H_2O \rightarrow 2PH_3 + Ca(OH)_2$$

$$Na_3P + 3H_2O \rightarrow PH_3 + 3NaOH$$

$$2AlP + 3H_2SO_4 \rightarrow 2PH_3 + Al_2(SO_4)_3$$

(ii) ***Decomposition* of H_3PO_3** :

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

(iii) ***Lab. method*** :

$$4P + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$$

(iv) ***Pure* PH_3** : $PH_4I + NaOH \rightarrow PH_3 + NaI + H_2O$

Properties : Colourless, highly poisonous, with rotten fish odour gas, slightly soluble in water

Chemical properties :

(i) ***Basic nature*** : $PH_3 + HI \rightarrow PH_4I$

(ii) ***Decomposition*** : $4PH_3 \xrightarrow{311K} P_4 + 6H_2$

(iii) ***Combustibility*** : $4PH_3 + 8O_2 \rightarrow P_4O_{10} + 6H_2O$

Pure PH_3 is not spontaneously inflammable. Ordinary PH_3 is spontaneously inflammable due to the presence of P_2H_4

(iv) ***With metallic salts*** :

$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$$

(v) ***With chlorine*** : $PH_3 + 3Cl_2 \rightarrow PCl_3 + 3HCl$

Uses :

(i) ***Holme's signals*** : A mixture of CaC_2 and Ca_3P_2 when treated with water, phosphine is liberated which catches fire and lights up acetylene. Burning gases serve the purpose of a signal. They are used in ships.

(ii) ***Smoke screen*** : Ca_3P_2 is used smoke screen. PH_3 obtained from it catches fire to give the needed smoke.

(iii) ***Cellphos*** : It is trade name of AlP, aluminium phosphide and used as fumigant. In presence of moisture it gives PH_3 which kills insects and pests

(iv) **Rat poison** : Zinc phosphide Zn_3P_2 is a rat poison, which gives PH_3

ORTHOPHOSPHORIC ACID (H_3PO_4) :

Preparation :

(i) $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

(ii) $\text{Red P} + 5HNO_3 \xrightarrow{\Delta} H_3PO_4 + H_2O + 5NO_2$

(iii) $Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4$

(iv) $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

Properties : Colourless syrupy liquid

(i) **Action of heat** :

$$2H_3PO_4 \xrightarrow{250°C} \underset{\text{Pyrophosph oric acid}}{H_4P_2O_7} + H_2O \xrightarrow{316°C}$$

$$\underset{\text{meta phosphoric acid}}{2HPO_3} + H_2O$$

(ii) **It is tribasic and ionises in three steps**

$$H_3PO_4 \rightarrow H^+ + H_2PO_4^- \text{ (Readily)}$$

$$H_2PO_4^- \rightarrow H^+ + HPO_4^{--} \text{ (Weakly)}$$

$$HPO_4^{--} \rightarrow H^+ + PO_4^{---} \text{ (very weak ionisation)}$$

(iii) $H_3PO_4 + 12\underset{\text{Ammonium molybdate}}{(NH_4)_2MoO_4} + 21HNO_3 \rightarrow$

$$\underset{\text{Ammonium phosphomolybdate}}{(NH_4)_3PO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

Uses :

(i) For preparation of HBr, HI in laboratory

(ii) For preparing metaphosphoric acid

(iii) stabiliser for H_2O_2

ORTHOPHOSPHOROUS ACID (H_3PO_3) :

Preparation :

(i) $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$

(ii) $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

Properties : It crystallises as deliquescent white solid

(i) ***Acidic nature*** *:*

$$H_3PO_3 \rightleftharpoons H^+ + (H_2PO_3^-) \rightleftharpoons H^+ + (HPO_3)^{2-}$$

(ii) ***Decomposition*** *:* $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

This reaction is disproportionation

(iii) ***Reducing nature*** *:*

$$SO_2 + 2H_3PO_3 \rightarrow 2H_3PO_4 + S\downarrow$$

$$3PCl_5 + H_3PO_3 \rightarrow PCl_3 + 3POCl_3 + 3HCl$$

$$H_3PO_3 + I_2 + H_2O \rightarrow H_3PO_4 + 2HI$$

(colour of I_2 discharged)

$$2KMnO_4 + 3H_2SO_4 + 5H_3PO_3 \rightarrow$$

$$K_2SO_4 + 3H_2O + H_3PO_4 + 2MnSO_4$$

$$CuSO_4 + H_3PO_3 + H_2O \rightarrow Cu + H_2SO_4 + H_3PO_4$$

$$Hg_2Cl_2 + H_3PO_3 + H_2O \rightarrow 2Hg + 2HCl + H_3PO_4$$

Uses : As reducing agent

FERTILIZERS :

Fertilizers are the chemical substances which are added to soil in order to make up the deficiency of nutrients required by plants. Nutrients are classified as

(i) Primary nutrients : which are consumed in large quantities eg. Nitrogen, Phosphorous and Potassium

(ii) Secondary nutrients : Calcium and Magnesium

(iii) Micro nutrients : which are required in minute quantities eg. Copper, Zinc, Manganese, Boron, Molybdenum, chlorine and Iron

TYPES OF FERTILIZERS :

(i) Nitrogenous fertilizers : These provide nitrogen to the plants. They are

(a) ***Urea*** *:*

$$2NH_3 + CO_2 \xrightarrow{200\text{ Atm.}} H_2NCOONH_4$$

$$2H_2NCOONH_4 \rightarrow H_2N.CONH_2 + H_2O$$

It contains about 47% N_2

(b) ***Ammonium sulphate (Sindri fertilizer)*** *:*

$$NH_3 + H_2O \rightarrow NH_4OH$$

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$

$$(NH_4)_2CO_3 + CaSO_4 \rightarrow (NH_4)_2SO_4 + CaCO_3\downarrow$$

(c) ***Basic Calcium nitrate*** *: (nitrate of lime or Norwegian saltpetre)*

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2$$

$$Ca(NO_3)_2 + CaO \rightarrow Ca(NO_3)_2.CaO$$

(d) ***Calcium cyanamide*** *:*

$$CaC_2 + N_2 \xrightarrow{850-1000°C} \underset{\text{Nitrolim}}{[CaCN_2 + C]}$$

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$$

or $CaCN_2 + 2H_2O + CO_2 \rightarrow CaCO_3 + H_2N.CONH_2$

$$H_2N.CO.NH_2 + H_2O \rightarrow CO_2 + 2NH_3$$

(ii) Phosphatic fertilizers : These provide phosphorous to plants

(a) ***Super phosphate of lime*** *:*

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow \underbrace{Ca(H_2PO_4)_2 + 2CaSO_4}$$

available phosphorous 16 - 18% P_2O_5

(b) ***Phosphatic slag or Thomas slag*** *:*

$$4P + 5O_2 \rightarrow P_4O_{10}$$

$$6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$$

It is by product of steel industry, available phosphorous 14-18% P_2O_5

(c) ***Triple super phosphate*** *:*

$$Ca_3(PO_4)_2 + 4H_3PO_4 + 3Ca(H_2PO_4)_2$$

(d) ***Nitrophos*** *:*

$$Ca_3(PO_4)_2 + 4HNO_3 \rightarrow \underbrace{Ca(H_2PO_4)_2 + 2Ca(NO_3)_2}$$

(iii) Potash fertilizers : These provide potassium to plants. Eg. : KCl, KNO_3, K_2SO_4

(iv) Mixed fertilizers : a) Ammoniated superphosphate : It is prepared by spraying ammoniation solution (NH_4NO_3 = 65.0%, NH_3 = 21.7% and H_2O = 13.27%) on superphosphate.

Exercise-1 | NCERT BASED QUESTIONS

Very Short/Short Answer Questions

1. On being slowly passed through water, PH_3 forms bubbles but NH_3 dissolves. Why is it so?

2. What is the difference between the nature of pi-bonds present in H_3PO_3 and HNO_3?

3. NO_2 is coloured but its dimer is colourless. Why?

4. N atom possesses 5 valence electrons but does not form NCl_5. Why?

5. NF_3 is an exothermic compound but NCl_3 is an endothermic compound. Explain.

6. What is laughing gas? How is it prepared?

7. PCl_5 is ionic in nature in the solid state. Why?

8. In trimethylamine, nitrogen has a pyramidal geometry whereas in trisilylamine $N(SiH_3)_3$ it has a planar geometry?

9. Molecular nitrogen N_2 is not particularly reactive. Explain.

10. NH_3 is more basic than PH_3. Explain.

11. Present a comparative account of proton affinities of NH_3 and PH_3.

12. Which of the following is/are not known and why: PCl_3, $AsCl_3$, $SbCl_3$, NCl_5, $BiCl_5$

13. Both PCl_4^+ and $SiCl_4$ have tetrahedral structures. Explain.

Long Answer Questions

14. In what ways nitrogen differs in its chemical behaviour from that of its heavier congeners?

15. Discuss the pattern of variation in the oxidation states of P to Bi

Multiple Choice Questions

16. Which one of the following statements is true for HNO_2 ?
(a) It can not act as reducing agent
(b) It can not act as oxidising agent
(c) It can not act both as oxidant reductant
(d) It is stable only in aqueous solution.

17. Of the following which is paramagnetic and has three electron bond in its structure
(a) N_2O (b) NO
(c) N_2O_3 (d) N_2O_5

18. With respect to protonic acids, which of the following statements is correct ?
(a) PH_3 is more basic than NH_3
(b) PH_3 is less basic than NH_3
(c) PH_3 is equally basic as NH_3
(d) PH_3 is amphoteric while NH_3 is basic.

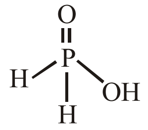
19. If you touch concentrated HNO_3 with your finger and immediately wash it with water, then the skin at the place where it came into contact with HNO_3 becomes yellow. This is because of :
(a) the formation of Xanthoprotein
(b) the absorption of HNO_3 by skin
(c) the blood absorbing HNO_3
(d) the absorption of yellow/brown NO_2 gas

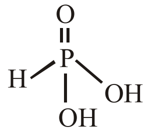
20. PCl_5 is possible but NCl_5 does not exist :
(a) in N, d-sub-shell is absent
(b) ionization energy of N is very high
(c) it does not like Cl
(d) none of these

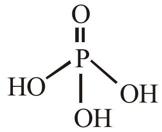
21. The boiling points of the following hydrides follow the order of
(a) $SbH_3 > NH_3 > AsH_3 > PH_3$
(b) $NH_3 > AsH_3 > PH_3 > SbH_3$
(c) $SbH_3 > AsH_3 > PH_3 > NH_3$
(d) $NH_3 > PH_3 > AsH_3 > SbH_3$

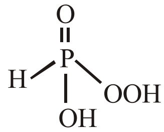
22. Which of the following statements is not correct for nitrogen ?
(a) Its electronegativity is very high
(b) d-orbitals are available for bonding
(c) It is a typical non-metal
(d) Its molecular size is small

23. The structural formula of hypophosphorous acid is

(a) 

(b) 

(c) 

(d) 

24. Producer gas is a mixture of :
(a) CO and N_2 (b) CO_2 and H_2
(c) N_2 and O_2 (d) CH_4 and N_2

25. Which of the following oxides of nitrogen is a coloured gas?
(a) N_2O (b) NO
(c) N_2O_5 (d) NO_2

26. Which is the most thermodynamically stable allotropic form of phosphorus?
(a) Red (b) White
(c) Black (d) Yellow

27. The number of P – O – P bonds in cyclic metaphosphoric acid is
(a) zero (b) two (c) three (d) four

Exercise-2 | CONCEPTUAL MCQs

1. Which one of the following elements is most metallic ?
(a) P (b) As
(c) Sb (d) Bi

2. In NH_3 and PH_3 the common is
(a) odour (b) combustibility
(c) basic nature (d) None of these

3. Which element from group 15 gives most basic compound with hydrogen
(a) Nitrogen (b) Bismuth
(c) Arsenic (d) Phosphorus

4. Ionic radii (in Å) of As^{3+}, Sb^{3+} and Bi^{3+} follow the order
(a) $As^{3+} > Sb^{3+} > Bi^{3+}$ (b) $Sb^{3+} > Bi^{3+} > As^{3+}$
(c) $Bi^{3+} > As^{3+} > Sb^{3+}$ (d) $Bi^{3+} > Sb^{3+} > As^{3+}$

5. The three important oxidation states of phosphorus are
(a) –3, +3 and +5 (b) –3, +3 and –5
(c) –3, +3 and +2 (d) –3, +3 and +4

6. The basic character of hydrides of the group 15 elements decreases in the order
(a) $SbH_3 > PH_3 > AsH_3 > NH_3$
(b) $NH_3 > SbH_3 > PH_3 > AsH_3$
(c) $NH_3 > PH_3 > AsH_3 > SbH_3$
(d) $SbH_3 > AsH_3 > PH_3 > NH_3$

7. The stability of the hydrides follows the order
(a) $NH_3 > PH_3 > AsH_3 > SbH_3$
(b) $NH_3 < PH_3 < AsH_3 < SbH_3$
(c) $PH_3 > NH_3 > AsH_3 > SbH_3$
(d) $AsH_3 > NH_3 > PH_3 > SbH_3$

8. In nitrogen family, the H-M-H bond angle in the hydrides gradually becomes closer to 90º on going from N to Sb. This shows that gradually
(a) the basic strength of the hydrides increases
(b) almost pure *p*-orbitals are used for M-H bonding
(c) the bond energies of M-H bonds increases
(d) the bond pairs of electrons become nearer to the central atom

9. The boiling points of the following hydrides follow the order
(a) $SbH_3 > NH_3 > AsH_3 > PH_3$
(b) $NH_3 > PH_3 > AsH_3 > SbH_3$
(c) $NH_3 > AsH_3 > PH_3 > SbH_3$
(d) $SbH_3 > AsH_3 > NH_3 > PH_3$

10. Which of the following has highest dipole moment?
(a) NH_3 (b) PH_3
(c) AsH_3 (d) SbH_3

11. The correct sequence of decrease in the bond angle of the following hydrides is
(a) $NH_3 > PH_3 > AsH_3 > SbH_3$
(b) $NH_3 > AsH_3 > PH_3 > SbH_3$
(c) $SbH_3 > AsH_3 > PH_3 > NH_3$
(d) $PH_3 > NH_3 > AsH_3 > SbH_3$

12. Among the trihalides of nitrogen which one is most basic ?
(a) NF_3 (b) NCl_3
(c) NI_3 (d) NBr_3

13. The one which does not form pentachloride is
(a) nitrogen (b) phosphorus
(c) arsenic (d) antimony

14. Which of the following compounds does not exist?
(a) $AsCl_5$ (b) $SbCl_3$
(c) $BiCl_5$ (d) $SbCl_5$

15. What is hybridization of P in PCl_5 ?
(a) sp^3 (b) sp^3d^2
(c) sp^3d (d) sp^2

16. Nitrous oxide is
(a) soluble in cold water (b) soluble in hot water
(c) acidic in nature (d) None of these

17. Which of the following oxides of nitrogen reacts with $FeSO_4$ to form a dark brown compound
(a) N_2O (b) NO
(c) NO_2 (d) N_2O_3

18. Which of the following oxides is the most acidic?
(a) N_2O_5 (b) P_2O_5
(c) As_2O_5 (d) Sb_2O_5

19. In the reaction

$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + X$, the product X is
(a) N_2O_5 (b) N_2O_3
(c) NO_2 (d) H_2O

20. Which oxide of nitrogen is obtained on heating ammonium nitrate at 250ºC ?
(a) Nitric oxide (b) Nitrous oxide
(c) Nitrogen dioxide (d) Dinitrogen tetraoxide

21. Which of the following can be used as an anaesthesia ?
(a) N_2O (b) NO
(c) NCl_3 (d) NO_2

22. The brown ring test for NO_2^- and NO_3^- is due to the formation of complex ion with a formula
(a) $[Fe(H_2O)_6]^{2+}$ (b) $[Fe(NO)(CN)_5]^{2+}$
(c) $[Fe(H_2O)_5NO]^{2+}$ (d) $[Fe(H_2O)(NO)_5]^{2+}$

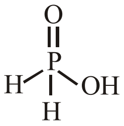
23. A deep brown gas is formed by mixing two colourless gases which are
(a) NO_2 and O_2 (b) N_2O and NO
(c) NO and O_2 (d) NH_3 and HCl

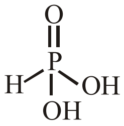
24. Which one of the following oxides of nitrogen is blue solid ?
(a) NO (b) N_2O_3
(c) N_2O (d) N_2O_5

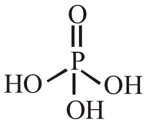
25. Of the following compounds, the most acidic is
(a) As_2O_{30} (b) P_2O_5
(c) Sb_2O_3 (d) Bi_2O_3

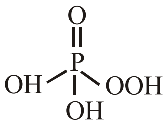
26. Which of the following is a cyclic phosphate ?
(a) $H_3P_3O_{10}$ (b) $H_6P_4O_{13}$
(c) $H_5P_5O_{15}$ (d) $H_7P_5O_{16}$

27. The structural formula of hypophosphorous acid is

(a) 
$\mathrm{H-\overset{\overset{O}{\|}}{\underset{H}{P}}-OH}$

(b) 
$\mathrm{H-\overset{\overset{O}{\|}}{\underset{OH}{P}}-OH}$

(c) 
$\mathrm{HO-\overset{\overset{O}{\|}}{\underset{OH}{P}}-OH}$

(d) 
$\mathrm{OH-\overset{\overset{O}{\|}}{\underset{OH}{P}}-OOH}$

28. P—O—P bond is present in
(a) $H_4P_2O_6$
(b) $H_4P_2O_5$
(c) Both (a) and (b)
(d) Neither (a) nor (b)

29. Orthophosphoric acid is
(a) monobasic
(b) dibasic
(c) tribasic
(d) tetrabasic

30. The oxyacid of phosphorous in which phosphorous has the lowest oxidation state is
(a) hypophosphorous acid
(b) orthophosphoric acid
(c) pyrophosphoric acid
(d) metaphosphoric acid

31. The number of P—O—P bonds in cyclic metaphosphoric acid is
(a) zero
(b) two
(c) three
(d) four

32. The triple bond between N atoms of nitrogen molecule ($N \equiv N$) consists of
(a) three σ-bonds
(b) two σ-bonds and one π-bond
(c) one σ-bond and two π-bonds
(d) three π-bonds

33. The molecule having bond order 3 is
(a) H_2
(b) N_2
(c) O_2
(d) He_2^+

34. An element (X) forms compounds of the formula XCl_3, X_2O_5 and Ca_3X_2 but does not form XCl_5. Which of the following is the element X ?
(a) B
(b) Al
(c) N
(d) P

35. Which of the following is obtained when N_2 reacts with calcium carbide ?
(a) Calcium cyanate
(b) Calcium acetate
(c) Calcium cyanamide
(d) Calcium carbonate

36. On heating ammonium dichromate, the gas evolved is
(a) oxygen
(b) ammonia
(c) nitrous oxide
(d) nitrogen

37. What causes nitrogen to be chemically inert ?
(a) Multiple bond formation in the molecule
(b) Absence of bond polarity
(c) Short internuclear distance
(d) High bond energy

38. In which the NH_3 is not used ?
(a) Cold storage
(b) Anaesthetic
(c) Manufacture of rayon and plastic
(d) None of these

39. Ammonia can be dried by
(a) conc. H_2SO_4
(b) P_4O_{10}
(c) CaO
(d) anhydrous $CaCl_2$

40. The shape of ammonia molecule is
(a) tetrahedral
(b) pyramidal
(c) planar triangle
(d) octahedral

41. P_4O_{10} is not used to dry NH_3 gas because
(a) P_4O_{10} reacts with moisture in NH_3
(b) P_4O_{10} is not a drying agent
(c) P_4O_{10} is acidic and NH_3 is basic
(d) P_4O_{10} is basic and NH_3 is acidic

42. When ammonia is heated with cupric oxide, a molecule of ammonia will
(a) gain 3 electrons
(b) lose 3 electrons
(c) gain 2 electrons
(d) lose 2 electrons

43. Brown colour in HNO_3 can be removed by
(a) adding Mg powder
(b) boiling the acid
(c) passing NH_3 through acid
(d) passing air through warm acid

44. HNO_2 acts as an/a
(a) acid
(b) oxidising agent
(c) reducing agent
(d) All the above

45. Which of the following phosphorus is most reactive ?
(a) Red phosphorus
(b) White phosphorus
(c) Scarlet phosphorus
(d) Violet phosphorus

46. White phosphorus is
(a) a monoatomic gas
(b) P_4, a tetrahedral solid
(c) P_8, a crown
(d) a linear diatomic molecule

47. One mole of calcium phosphide on reaction with excess of water gives
(a) one mole of phosphine
(b) two moles of phosphoric acid
(c) two moles of phosphine
(d) one mole of phosphorus oxide

48. PH_3, the hydride of phosphorus is
(a) metallic
(b) ionic
(c) non-metallic
(d) covalent

49. The acid which forms two series of salts is
(a) H_3PO_4
(b) H_3PO_3
(c) H_3BO_3
(d) $H_3PO_2^-$

50. The equivalent weight of phosphoric acid (H_3PO_4) in the reaction

$NaOH + H_3PO_4 \rightarrow NaH_2PO_4 + H_2O$ is
(a) 25
(b) 49
(c) 59
(d) 98

51. In the following reaction

$$PCl_5 \xrightarrow{H_2O} HCl + A$$

the product 'A' is
(a) $H_2P_2O_4$
(b) $H_2P_2O_7$
(c) H_3PO_4
(d) H_3PO_3

52. Which of the following undergoes sublimation
(a) $ZnCl_2$
(b) $CuCl_2$
(c) AgCl
(d) NH_4Cl

53. BCl_3 is a planar molecule whereas NCl_3 is pyramidal because
(a) BCl_3 has no lone pair of electrons but NCl_3 has a lone pair of electrons
(b) B—Cl bond is more polar than N—Cl bond
(c) nitrogen atom is smaller than boron atom
(d) N—Cl bond is more covalent than B—Cl bond

54. The electronic configuration of an elements is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^3$. Its properties would be similar to which of the following elements ?
(a) Boron (b) Oxygen
(c) Nitrogen (d) Chlorine

55. Which of the following has least covalent P—H bond ?
(a) PH_3 (b) $P_2H_6^{2+}$
(c) $P_2H_5^+$ (d) PH_4^+

56. Among the followng species, identify the isostructural pairs

NF_3, NO_3^-, BF_3, H_3O^+, HN_3

(a) $[NF_3, NO_3^-]$ and $[BF_3, H_3O^+]$
(b) $[NF_3, HN_3\}$ and $[NO_3^-, BF_3]$
(c) $[NF_3, H_3O^+]$ and $[NO_3^-, BF_3]$
(d) $[NF_3, H_3O^+]$ and $[HN_3, BF_3]$

57. In PO_4^{3-} ion, the formal charge on each oxygen atom and P—O bond order respectively are
(a) –0.75, 1.25 (b) –3, 1.25
(c) –0.75, 1.0 (d) –0.75, 0.6

58. In nitroprusside ion, the iron and NO exist as Fe^{++} and NO^+ rather than Fe^{+++} and NO. These forms can be differentiated by
(a) estimating the concentration of iron
(b) measuring the concentration of CN^-
(c) measuring the solid state magnetic moment
(d) thermally decomposing the compound

59. Nitrogen atom has an atomic number of 7 and oxygen has an atomic number 8. The total number of electrons in a nitrate ion will be
(a) 8 (b) 16
(c) 32 (d) 64

60. If HNO_3 changes into N_2O, the oxidation number is changed by
(a) 2 (b) 6
(c) 0 (d) +4

61. The hybridized state of N in R_2NH is
(a) sp^3 (b) sp^2
(c) sp (d) dsp^2

62. The hybridization of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ are
(a) sp, sp^3 and sp^2 respectively
(b) sp, sp^2 and sp^3 respectively
(c) sp^2, sp and sp^3 respectively
(d) sp^2, sp^3 and sp respectively

63. The nitride ion in lithium nitride is composed of
(a) 7 Protons + 10 electrons (b) 10 Protons + 10 electrons
(c) 7 Protons + 7 electrons (d) 10 Protons + 7 electrons

64. Which of the following leaves no residue on heating ?
(a) $Pb(NO_3)_2$ (b) NH_4NO_3
(c) $Cu(NO_3)_2$ (d) $NaNO_3$

65. Which of the following molecules is linear ?
(a) SO_2 (b) NO_2^+
(c) NO_2^- (d) SCl_2

66. A metal X on heating in nitrogen gas gives Y. Y on treatment with H_2O gives a colourless gas which when passed through $CuSO_4$ solution gives a blue colour. Y is
(a) $Mg(NO_3)_2$ (b) Mg_3N_2
(c) NH_3 (d) MgO

67. Which one of the following molecules will have bonds of unequal lengths ?
(a) NF_3 (b) BF_3
(c) PF_5 (d) SF_6

68. In which of the following the bond angle is maximum ?
(a) NH_3 (b) NH_4^+
(c) PCl_3 (d) SCl_2

69. One of the oxidants used with liquid propellants is
(a) ammonium perchlorate (b) nitrocellulose
(c) sulphuric acid (d) nItrogen tetroxide (N_2O_4)

70. The aqueous solution/liquid that absorbs nitric oxide to a considerable extent is
(a) lead nitrate (b) nitric acid
(c) ferrous sulphate (d) sodium hydroxide

71. Which one of the following arrangements of molecules is correct on the basis of their dipole moments ?
(a) $BF_3 > NF_3 > NH_3$ (b) $NF_3 > BF_3 > NH_3$
(c) $NH_3 > BF_3 > NF_3$ (d) $NH_3 > NF_3 > BF_3$

72. Sodium hexametaphosphate is known as
(a) calgon (b) permutit
(c) natalite (d) nitrolim

73. The oxidation number of As in $H_2AsO_4^-$ is
(a) +6 (b) +5
(c) –7 (d) +9

74. Which of the following compounds is explosive in nature ?
(a) Phosphorus trichloride (b) Nitrogen trichloride
(c) Hyponitrous acid (d) Nitrosyl chloride

75. Among the 15th group elements, as we move from nitrogen to bismuth, the pentavalency becomes less pronounced and trivalency becomes more pronounced due to
(a) Non metallic character (b) Inert pair effect
(c) High electronegativity (d) Large ionization energy

76. In NO_3^- ion, the number of bond pair and lone pair of electrons on nitrogen atom are
(a) 2,2 (b) 3, 1
(c) 1, 3 (d) 4, 0

77. Pentavalence in phosphorus is more stable when compared to that of nitrogen even though they belong to same group. This is due to
(a) dissimilar electronic configuration
(b) due to presence of vacant d-orbitals
(c) reactivity of phosphorus
(d) inert nature of nitrogen

Exercise-3 | Past Competition MCQs

1. Which of the following is a nitric acid anhydride?
(a) NO (b) NO_2 **[CBSE PMT 1988]**
(c) N_2O_5 (d) N_2O_3.

2. Which of the following metal evolves hydrogen on reacting with cold dilute HNO_3 ? **[CBSE PMT 1989]**
(a) Mg (b) Al
(c) Fe (d) Cu.

3. Each of the following is true about white and red phosphorus except that they **[CBSE PMT 1989]**
(a) Are both soluble in CS_2
(b) Can be oxidised by heating in air
(c) Consist of the same kind of atoms
(d) Can be converted into one another

4. When orthophosphoric acid is heated to 600°C, the product formed is **[CBSE PMT 1989]**
(a) PH_3 (b) P_2O_5
(c) H_3PO_3 (d) HPO_3

5. Which of the following statements is not correct for nitrogen? **[CBSE PMT 1990]**
(a) Its electronegativity is very high
(b) d-orbitals are available for bonding
(c) It is a typical non-metal
(d) Its molecular size is small

6. P_2O_5 is heated with water to give **[CBSE PMT 1991]**
(a) Hypophosphorous acid
(b) Phosphorous acid
(c) Hypophosphoric acid
(d) Orthophosphoric acid

7. PCl_3 reacts with water to form **[CBSE PMT 1991]**
(a) PH_3 (b) H_3PO_3, HCl
(c) $POCl_3$ (d) H_3PO_4

8. $PH_4I + NaOH$ forms **[CBSE PMT 1991]**
(a) PH_3 (b) NH_3
(c) P_4O_6 (d) P_4O_{10}

9. Pure nitrogen is prepared in the laboratory by heating a mixture of **[CBSE PMT 1991]**
(a) $NH_4OH + NaCl$ (b) $NH_4NO_3 + NaCl$
(c) $NH_4Cl + NaOH$ (d) $NH_4Cl + NaNO_2$.

10. Sugarcane on reaction with nitric acid gives
(a) CO_2 and SO_2 **[CBSE PMT 1992]**
(b) $(COOH)_2$
(c) 2 HCOOH (two moles)
(d) No reaction.

11. H_3PO_2 is the molecular formula of an acid of phosphorus. Its name and basicity respectively are **[CBSE PMT 1992]**
(a) Phosphorus acid and two
(b) Hypophosphorous acid and two
(c) Hypophosphorous acid and one
(d) Hypophosphoric acid and two

12. Which of the following fertilizers has the highest nitrogen percentage ? **[CBSE PMT 1993]**
(a) Ammonium sulphate
(b) Calcium cyanamide
(c) Urea
(d) Ammonium nitrate

13. Which of the following oxides will be the least acidic?
(a) As_4O_6 (b) As_4O_{10} **[CBSE PMT 1996]**
(c) P_4O_{10} (d) P_4O_6

14. Which of the following oxy-acids has the maximum number of hydrogens directly attached to phosphorus?
(a) $H_4P_2O_7$ (b) H_3PO_2 **[CBSE PMT 1999]**
(c) H_3PO_3 (d) H_3PO_4

15. Nitrogen forms N_2, but phosphorus is converted into P_4 from P, the reason is **[CBSE PMT 2001]**
(a) Triple bond is present between phosphorus atom
(b) $p\pi - p\pi$ bonding is strong
(c) $p\pi - p\pi$ bonding is weak
(d) Multiple bond is formed easily

16. Oxidation states of P in $H_4P_2O_5$, $H_4P_2O_6$, and $H_4P_2O_7$, are respectively: **[CBSE-PMT 2010]**
(a) $+3, +5, +4$ (b) $+5, +3, +4$
(c) $+5, +4, +3$ (d) $+3, +4, +5$

17. In which of the following compounds, nitrogen exhibits highest oxidation state ? **[CBSE-PMT 2012 S]**
(a) N_2H_4 (b) NH_3
(c) N_3H (d) NH_2OH

18. Which of the following statements is not valid for oxoacids of phosphorus? **[CBSE-PMT 2012 S]**
(a) Orthophosphoric acid is used in the manufacture of triple superphosphate.
(b) Hypophosphorous acid is a diprotic acid.
(c) All oxoacids contain tetrahedral four coordinated phosphorus.
(d) All oxoacids contain atleast one P = O and one P — OH group.

19. In case of nitrogen, NCl_3 is possible but not NCl_5 while in case of phosphorous, PCl_3 as well as PCl_5 are possible. It is due to **[AIEEE 2002]**
(a) availability of vacant *d* orbitals in P but not in N
(b) lower electronegativity of P than N
(c) lower tendency of H-bond formation in P than N
(d) occurrence of P in solid while N in gaseous state at room temperature.

20. Number of sigma bonds in P_4O_{10} is **[AIEEE 2002]**
(a) 6 (b) 7
(c) 17 (d) 16.

21. What may be expected to happen when phosphine gas is mixed with chlorine gas ? **[AIEEE 2003]**
(a) PCl_3 and HCl are formed and the mixture warms up
(b) PCl_5 and HCl are formed and the mixture cools down
(c) $PH_3 . Cl_2$ is formed with warming up
(d) The mixture only cools down

22. Which one of the following substances has the highest proton affinity? **[AIEEE 2003]**
(a) H_2S (b) NH_3
(c) PH_3 (d) H_2O

23. The number of hydrogen atom(s) attached to phosphorus atom in hypophosphorous acid is **[AIEEE 2005]**
(a) three (b) one
(c) two (d) zero

24. The decreasing values of bond angles from NH_3 (106°) to SbH_3 (101°) down group-15 of the periodic table is due to **[AIEEE 2006]**
(a) decreasing lp-bp repulsion
(b) decreasing electronegativity
(c) increasing bp-bp repulsion
(d) increasing p-orbital character in sp^3

25. Regular use of which of the the following fertilizers increases the acidity of soil? **[AIEEE 2007]**
(a) Ammonium sulphate
(b) Potassium nitrate
(c) Urea
(d) Superphosphate of lime.

26. The reaction of P_4 with **X** leads selectively to P_4O_6. The **X** is **[IIT-JEE 2009]**
(a) Dry O_2
(b) A mixture of O_2 and N_2
(c) Moist O_2
(d) O_2 in the presence of aqueous NaOH

27. Extra pure N_2 can be obtained by heating **[IIT-JEE 2011]**
(a) NH_3 with CuO (b) NH_4NO_3
(c) $(NH_4)_2Cr_2O_7$ (d) $Ba(N_3)_2$

28. Concentrated nitric acid, upon long standing, turns yellow brown due to the formation of **[JEE Advanced 2013]**
(a) NO (b) NO_2
(c) N_2O (d) N_2O_4

Exercise-4 | Applied MCQs

1. Phosphine on reaction with hydrobromic acid gives
(a) PBr_3 (b) PH_4Br
(c) PBr_5 (d) P_2H_4

2. An inorganic compound producing organic compound on heating is
(a) sodamide
(b) ammonium cyanate
(c) sodalime
(d) potassium cyanide

3. Which is not correct for N_2O ?
(a) It is laughing gas and is used as anaesthetic agent.
(b) It is nitrous oxide
(c) It is not a linear molecule.
(d) It is least reactive of all the oxides of nitrogen

4. An important method of fixation of atmospheric N_2 is
(a) Fisher- Tropsch's process
(b) Haber's process
(c) Frasch's process
(d) Solvay's process

5. The nitrate which when heated gives off a gas or a mixture of gases which cannot relight a glowing splinter is
(a) sodium nitrate (b) ammonium nitrate
(c) lead nitrate (d) potassium nitrate

6. Liquid ammonia bottles are opened after cooling them in ice for sometime. It is because liquid NH_3
(a) Brings tears to the eyes
(b) Has a high vapour pressure
(c) Is a corrosive liquid
(d) Is a mild explosive

7. Ammonia is generally manufactured for fertilizers by the reaction
(a) $2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O + 2NH_3$
(b) By passing an electric discharge in a mixture of N_2 and H_2
(c) By passing a mixture of N_2 and H_2 under high pressure and moderate temperature over a catalyst
(d) None of these

8. Nitrogen can be purified from the impurities of oxides of nitrogen and ammonia by passing through
(a) conc. HCl
(b) alkaline solution of pyrogallol
(c) a solution of $K_2Cr_2O_7$ acidified with H_2SO_4
(d) a solution of KOH

9. Ammonium dichromate is used in some fire works. The green coloured powder blown is
(a) CrO_3 (b) Cr_2O_3
(c) Cr (d) $CrO(O_2)$

10. Phosphine is not obtained by which of the following reaction
(a) White P is heated with NaOH
(b) Red P is heated with NaOH
(c) Ca_3P_2 reacts with water
(d) Phosphorus trioxide is boiled with water

11. Phosphine is not evolved when
(a) white phosphorus is boiled with a strong solution of $Ba(OH)_2$
(b) phosphorus acid is heated
(c) calcium hypophosphite is heated
(d) metaphosphoric acid is heated.

12. Pure phosphine is not combustible while impure phosphine is combustible, this combustibility is due to presence of
(a) P_2H_4 (b) N_2
(c) PH_5 (d) P_2O_5

13. A white precipitate is obtained on hydrolysis of
(a) PCl_5 (b) NCl_3
(c) $BiCl_3$ (d) $AsCl_3$

14. Calcium cyanamide on treatment with steam under pressure gives NH_3 and
(a) $CaCO_3$ (b) $Ca(OH)_2$
(c) CaO (d) $CaHCO_3$

15. Which of the following statements is not true ?
(a) NO_2 can be prepared by heating $Pb(NO_3)_2$
(b) NO_2 is red - brown gas
(c) NO_2 is diamagnetic
(d) NO_2 readily dimerises to N_2O_4

16. Hydrolysis of PI_3 yields
(a) monobasic acid and a salt
(b) monobasic acid and dibasic acid
(c) dibasic acid and tribasic acid
(d) monobasic acid and tribasic acid

17. If 20% nitrogen is present in a compound its minimum molecular weight can be
(a) 144 (b) 70
(c) 100 (d) 140

18. Blasting of TNT is done by mixing it with
(a) NH_4Cl (b) NH_4NO_3
(c) NH_4NO_2 (d) $(NH_4)_2SO_4$

19. Ammonia, on reaction with hypochlorite anion, can form
(a) NO (b) NH_4Cl
(c) N_2H_4 (d) HNO_2

20. The catalyst used in the manufacture of HNO_3 by Ostwald's process is :
(a) platinum gauze (b) vanadium pentoxide
(c) finely divided nickel (d) platinum black .

21. The deep blue colour produced on adding excess of ammonia to copper sulphate is due to presence of
(a) Cu^{2+} (b) $Cu(NH_3)_4^{2+}$
(c) $Cu(NH_3)_6^{2+}$ (d) $Cu(NH_3)_2^{2+}$

22. Ammonia on catalytic oxidation gives an oxide from which nitric acid is obtained. The oxide is :
(a) N_2O_3 (b) NO
(c) NO_2 (d) N_2O_5

23. The dipole moment of NF_3 is less than NH_3 because
(a) NH_3 forms associated molecules.
(b) F is more reactive than H.
(c) The resultant of bond polarity is less.
(d) The resultant of individual polarities is opposed by the polarity of lone pair.

24. Which property of white phosphorus is common to red P
(a) It burns when heated in air.
(b) It reacts with hot caustic soda solution to give phosphine.
(c) It shows chemiluminescence.
(d) It is soluble in carbon disulphide.

25. Fixation of nitrogen means :
(a) reaction of nitrogen with oxygen.
(b) conversion of free atmospheric nitrogen into nitrogen compounds.
(c) the action of denitrifying bacteria on nitrogen compounds.
(d) decomposition of nitrogenous compounds to yield free nitrogen.

26. Conc. HNO_3 is heated with P_2O_5 to form :
(a) NO_2 (b) NO
(c) N_2O_5 (d) N_2O

27. Superphosphate of lime is obtained from the reaction of :
(a) Bones with gypsum
(b) Calcium phosphate with sulphuric acid
(c) Calcium phosphate with HCl
(d) Calcium carbonate with phosphoric acid

28. Orthophosphoric acid on heating gives :
(a) metaphosphoric acid (b) phosphine
(c) phosphorus pentoxide (d) phosphorus acid

Hints & Solutions

EXERCISE 1

1. This is because PH_3 is much weaker base than NH_3. NH_3 dissolves in water forming NH_4OH.
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
2. In H_3PO_3, there is $p\pi - d\pi$ bond whereas in HNO_3 there is $p\pi - p\pi$ bond. $p\pi - p\pi$ bond in HNO_3 is stronger than $p\pi - d\pi$ bond in H_3PO_3.
3. NO_2 has unpaired electron and due to this, it has brown colour. N_2O_4 does not have unpaired electron and thus it is colourless.
4. N atom does not have d-orbitals and thus it cannot have all five valence electrons as unpaired.
5. F is highly electronegative and N – F bond energy is higher than N – Cl bond energy.
6. N_2O is laughing gas prepared by heating NH_4NO_3.
$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$
7. PCl_5 is ionic in the solid state because it exists as $[PCl_4]^+[PCl_6]^-$.

16. (d) **17.** (b) **18.** (b) **19.** (a) **20.** (a)
21. (a) **22.** (b) **23.** (a) **24.** (a) **25.** (d)
26. (c) **27.** (c)

EXERCISE 2

1. **(d)** Metallic character increases down the group, Bi is most metallic
2. **(c)** Basic nature
3. **(a)** Nitrogen; NH_3 is most basic
4. **(d)** Ionic radii increases down the group
5. **(a)** –3, +3, +5 (see text)
6. **(c)**
7. **(a)**
8. **(b)** With the decrease in the electronegativity of central atom the bond angle decreases
9. **(a)**
10. **(a)** Dipole moment decreases with decrease in electronegativity of central metal atom
11. **(a)**
12. **(c)** The lesser the electronegativity of halogen in NX_3 the more is the basic character. N can donate more electrons in that case.
13. **(a)** Nitrogen does not contain vacant d orbitals in valence shell hence cannot extend its coordination number more than 3
14. **(c)** Due to inert pair effect the lower O.S. is more common at the bottom of group
15. **(c)** Hybridisation in $PCl_5 = \frac{1}{2}(5+5+0-0) = 5$ sp^3d
16. **(a)** N_2O is soluble in cold and not in hot water
17. **(b)** $FeSO_4 + NO \rightarrow FeSO_4.NO$
18. **(a)** In N_2O_5 nitrogen is present in the highest O.S. and it is most electronegative in nature than others
19. **(a)** See preparation of N_2O_5
20. **(b)** N_2O (see text)
21. **(a)** N_2O is used as anaesthetic
22. **(c)** $[Fe(H_2O)_5NO]^{2+}$ ion is formed
23. **(c)** $2NO + O_2 \rightarrow 2NO_2$ brown
24. **(b)** N_2O_3 is blue solid
25. **(b)** P_2O_5 ;P is electronegative and present in highest O.S. of 5, hence P_2O_5 is most acidic
26. **(c)** $H_5P_5O_{15}$ $(HPO_3)_5$. It is metaphosphoric acid which is a cyclic phosphate.
27. **(b)** See structures of oxy acids of phosphorous
28. **(b)** $H_4P_2O_5$ is pyrophosphorous acid it contains P–O–P bond
29. **(c)** H_3PO_4 is tribasic
30. **(a)** Hypophosphorous acid is H_3PO_2 in which O.S. of P is +1
31. **(c)** See structure of metaphosphoric acid.
32. **(c)** One σ and two π
33. **(b)** It is $\ddot{N} \equiv \ddot{N}$
34. **(c)** Nitrogen can form NCl_3, N_2O_5 Ca_3N_2 and not NCl_5 since it has no d atomic orbitals in valence shell
35. **(c)** $CaC_2 + N_2 \rightarrow \underset{\text{Calcium cyanamide}}{(CaCN_2 + C)}$
36. **(d)** $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + 4H_2O + N_2$
37. **(d)** The cause of inert nature of N_2 is the presence of triple bond $\ddot{N} \equiv \ddot{N}$
38. **(b)** NH_3 is not used as anaesthetic
39. **(c)** Ammonia is dried over CaO. Others will react with it
40. **(b)** Ammonia has pyramidal shape with sp^3 hybridisation.
41. **(c)** $\underset{\text{Acidic}}{P_4O_{10}} + 2H_2O \longrightarrow \underset{\text{meta phosphoric acid}}{4HPO_3} \xrightarrow[\text{basic}]{NH_3} \underset{\text{meta ammonium phosphate}}{NH_4PO_3}$

42. (b) $3CuO + 2NH_3 \rightarrow 3Cu + 3H_2O + N_2$,

O.S. of N in NH_3 is –3 and in N_2 is zero. Hence loss of 3 electrons

43. (d) Nitric acid decomposes to give NO_2 which is brown

$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2$

When air is passed through acid the reaction proceeds towards left hand side and brown colour diminishes.

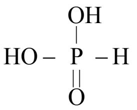
44. (d) In HNO_2 the O.S. of N is +3 which can be increased or decreased by gain or loss of electrons (O.S. of N varies from –3 to +5)

45. (b) White phosphorous is most reactive

46. (b) White phosphorous is P_4 and tetrahedral

47. (c) $\underset{\text{1 mole}}{Ca_3P_2} + 6H_2O \rightarrow 3Ca(OH)_2 + \underset{\text{2 moles}}{2PH_3}$

48. (d) PH_3 is covalent hydride

49. (b)


$HO-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle O}{||}}{P}}-H$ it can form two series of salts by replacement of H attached to oxygen

50. (d) $NaOH + H_3PO_4 \rightarrow NaH_2PO_4 + H_2O$. Since there is no change in O.N. of P hence its Mol. Wt. which is 98 will be equivalent weight also

51. (c) $2PCl_5 + 8H_2O \rightarrow 2H_3PO_4 + 10HCl$, the product formed is phosphoric acid

52. (d) NH_4Cl sublimes

53. (a) In BCl_3 there is sp^2 hybridisation (planar) in NCl_3 hybridisation is sp^3 hence shape is pyramidal

54. (c) The valence shell electronic configuration is $4s^24p^3$ similar to nitrogen $2s^2p^3$

55. (b) For this calculate the formal charge distributed on each P–H bond which is given by $= \dfrac{\text{Total charge}}{\text{No. of P – H bonds}}$.

The more the formal charge the lesser is the covalent character.

In

$$P_2H_6^{2+} = \frac{+2}{6} = +0.33; P_2H_5^+ = \frac{+1}{5} = +0.2;\ PH_4^+ = \frac{+1}{4} = +0.25$$

Hence lowest covalent character of P–H bond is in $P_2H_6^{2+}$

56. (c) In NF_3 and H_3O^+ the hybridisation is sp^3 and both are pyramidal. In NO_3^- and BF_3 the hybridisation is sp^2 and both are planar

57. (a) Formal charge on each oxygen $= \frac{-3}{4} = -0.75$ and

P–O bond order is $= \frac{5}{4} = 1.25$

(Here 5 is the number of P–O bonds and 4 is the number of resonating forms)

58. (c) The nitroprusside ion is $[Fe(CN)_6NO^+]^{2-}$. The magnetic moment measurements reveal the presence of 4 unpaired electrons in Fe which must be then in Fe^{++} ($3d^6$) and not Fe^{+++}($3d^5$)

59. (c) NO_3^- $(7+3\times8+1) = 32$ electrons

60. (d) In HNO_3 the O.S. of N is +5 and in N_2O it is +1. Hence change in O.S. is +4

61. (a) R_2NH hybridisation $= \frac{1}{2}(5+3+0-0) = 4\ sp^3$

62. (b) Hybridisation in $NO_2^+ = \frac{1}{2}(5+0+0-1) = 2\ (sp)$

$NO_3^- = \frac{1}{2}(5+0+1-0) = 3\ (sp^2)$; $NH_4^+ = \frac{1}{2}(5+4+0-1) = 4(sp^3)$

63. (a) N^{3-} ion has 7 protons and 10 electrons

64. (b) $NH_4NO_3 \xrightarrow{\Delta} N_2O\uparrow + 2H_2O\uparrow$

65. (b) In NO_2^+ hybridisation is, $\frac{1}{2}(5+0+0-1) = 2$, sp hence linear

66. (b) $3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2 \xrightarrow{6H_2O} 3Mg(OH)_2 + 2NH_3$;

$CuSO_4 + 4NH_3 \rightarrow \underset{\text{deep blue colour}}{[Cu(NH_3)_4]SO_4}$

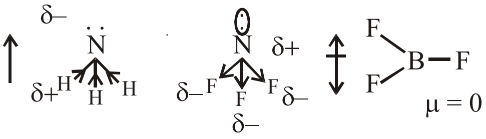
67. (c) PF_5 has trigonal pyramidal shape in which axial and equitorial bonds have different lengths

68. (b) Bond angle in NH_4^+ is 109°28' due to sp^3 hybridisation and symmetrical structure

69. (d) N_2O_4 is used as an oxidant with liquid propellants

70. (c) $FeSO_4 + NO \rightarrow FeSO_4.NO$

71. (d) $NH_3 > NF_3 > BF_3$. NH_3 and NF_3 have pyramidal shape. BF_3 is planar.

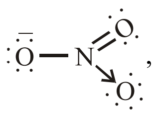


72. (a) It is calgon (Sodium hexametaphosphate)

73. (b) $H_2AsO_4^-$ $2(1) + x + 4(-2) = -1$, $\therefore x = +5$

74. (b) NCl_3 is explosive in nature.

75. (b) Inert pair effect (follow text)

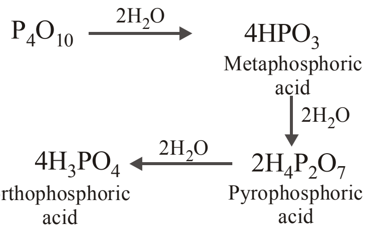
76. (d) 
, Bond pairs = 4, lone pair = 0

77. (b) Phosphorous can achieve coordination number 5 due to vacant d atomic orbitals in valence shell which is not possible in nitrogen

EXERCISE 3

1. **(c)** $N_2O_5 + H_2O \longrightarrow 2HNO_3$
2. **(a)** Magnesium and manganese are the metals that produce hydrogen with dilute nitric acid

   $Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$
3. **(a)** Both white and red phosphorus are not soluble in CS_2 only white P is soluble.
4. **(d)** $\underset{\text{ortho phosphoric acid}}{2H_3PO_4} \xrightarrow[-2H_2O]{600°C} \underset{\text{meta phosphoric acid}}{2HPO_3}$
5. **(b)** In case of nitrogen, d-orbitals are not available.
6. **(d)** P_2O_5 have great affinity for water. The final product is orthophosphoric acid.



7. **(b)** $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$
8. **(a)** $PH_4I + NaOH \rightarrow NaI + PH_3 + H_2O$
9. **(d)** Pure nitrogen in the lab can be obtained by heating ammonium nitrate. Ammonium nitrate is not a stable compound it dissociate to give nitrogen.

   $$NH_4Cl + NaNO_2 \xrightarrow{\text{Heat}} NH_4NO_2 \xrightarrow{\text{Heat}} N_2 + 2H_2O.$$
10. **(b)** Cane sugar is oxidised to oxalic acid

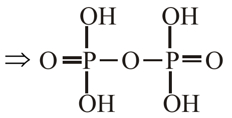
    $$(2HNO_3 \longrightarrow H_2O + 2NO_2 + O)18$$

    $$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + \underset{\text{From } HNO_3}{18[O]} \longrightarrow \underset{\text{Oxalic acid}}{6(COOH)_2} + 5H_2O.$$

    $$C_{12}H_{22}O_{11} + 36HNO_3 \longrightarrow 6(COOH)_2 + 36NO_2 + 23H_2O$$
11. **(c)** H_3PO_2 is named as hypophosphorous acid. As it contains only one P – OH group, its basicity is one.
12. **(c)** Urea (46.6%N). % of N in other compound are : $(NH_4)_2SO_4 = 21.2\%$;

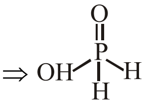
    $CaCN_2 = 35.0\%$ and $NH_4NO_3 = 35.0\%$
13. **(a)** As the O.N of the central atom of the compounds increases acidic strength of that compound also increases and on moving from top to bottom in groups acidic strength of oxides also decrease due to decreasing electronegativity in groups.

    $$\overset{+5}{P_4O_{10}} > \overset{+3}{P_4O_6} > \overset{+5}{As_4O_{10}} > \overset{+3}{As_4O_6}$$
14. **(b)**

(a) $H_4P_2O_7$ ⇒ 

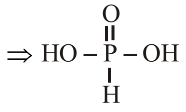
$$O{=}P(OH)_2{-}O{-}P(OH)_2{=}O$$

Pyrophosphoric acid

(b) H_3PO_2 ⇒ 

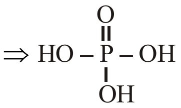
$$OH{-}\overset{\overset{\textstyle O}{\|}}{\underset{\textstyle H}{P}}{-}H$$

Hypophosphorous acid

(c) H_3PO_3 ⇒ 

$$HO-\overset{\overset{\textstyle O}{\|}}{\underset{\textstyle H}{P}}-OH$$

Phosphorous acid

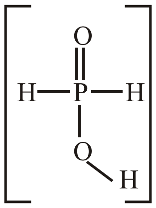
(d) H_3PO_4 ⇒ 

$$HO-\overset{\overset{\textstyle O}{\|}}{\underset{\textstyle OH}{P}}-OH$$

orthophosphoric acid

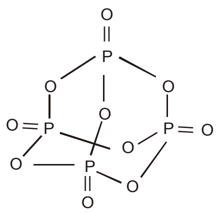
15. **(c)** Nitrogen form N_2 (i.e. $N \equiv N$) but phosphorus form P_4, because in P_2, p_π — p_π bonding is present which is a weaker bonding.
16. **(d)**
17. **(c)**

Compound	Oxidation number of nitrogen
N_2H_4	= –2
NH_3	= –3
N_3H	= –1/3
NH_2OH	= –1

18. **(b)** 
Hypophosphorous acid (H_3PO_2) is a monobasic acid. i.e., it has only one ionisable hydrogen atom or one OH is present.
19. **(a)** ${}_7N = 1s^2\, 2s^2\, 2p^3$; ${}_{15}P = 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^3$

    In phosphorous the 3 d- orbitals are available.

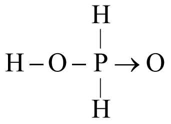
20. (d)



21. (a) $PH_3 + 3Cl_2 \longrightarrow PCl_3 + 3HCl$

22. (b) Among the given compounds, the $\ddot{N}H_3$ is most basic. Hence has highest proton affinity

23. (c) Hypophosphorous acid



$$H-O-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{P}}\rightarrow O$$

Two H-atoms are attached to P atom.

24 (b) The bond angle decreases on moving down the group due to decrease in bond pair-bond pair repulsion.

NH_3	PH_3	AsH_3	SbH_3	BiH_3
107°	94°	92°	91°	90°

This can also be explained by the fact that as the size of central atom increases sp^3 hybrid orbital becomes more distinct with increasing size of central atom i.e. pure p-orbitals are utilized in M–H bonding.

25. (a) $(NH_4)_2SO_4 + 2H_2O \longrightarrow 2H_2SO_4 + NH_4OH$

H_2SO_4 being strong acid increases the acidity of soil. In case of potassium nitrate and superphosphate of lime on hydrolysis strong base also form along with strong acid on hydrolysis results into neutralisation.

26. (b) $P_4 + 3O_2 \xrightarrow{\text{In presence of } N_2} P_4O_6$

Here N_2 acts as a diluent and thus retards further oxidation. Reaction of P_4 under other three conditions.

(a) $P_4 + 3O_2 \longrightarrow P_4O_6 \xrightarrow{2O_2} P_4O_{10}$

(c) In moist air, P_4O_6 is hydrolysed to form H_3PO_3

$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$

(d) In presence of NaOH,

$P_4 + 3OH^- + 3H_2O \longrightarrow PH_3 + 3H_2PO_2^-$

27. (d) Very pure N_2 can be obtainted by thermal decomposition of sodium or barium azide. $Ba(N_3)_2 \longrightarrow Ba + 3N_2$

28. (b) The slow decomposition of HNO_3 is represented by the eqn.

$$4HNO_3 \rightarrow \underset{\text{(yellow-brown)}}{4NO_2} + 2H_2O + O_2$$

EXERCISE 4

1. (b) $PH_3 + HBr \rightarrow PH_4Br$ Phosphorium bromide

2. (b) $NH_4CNO \xrightarrow{\Delta} NH_2CONH_2$. Urea is an organic compound

3. (c) N_2O has linear structure (see structure)

4. (b) By Haber's Process atmospheric nitrogen is converted into NH_3.

5. (b) $NH_4NO_3 \rightarrow N_2O + 2H_2O.$

N_2O is non combustible and non supporter of combustion. Other nitrates give O_2 which supports combustion.

6. (b) Liquid ammonia has high vapour pressure which is lowered down by cooling, otherwise the liquid will bump.

7. (c) By Haber's process

8. (d) The oxides of nitrogen being acidic in nature are soluble in KOH which is an alkali.

9. (b) $(NH_4)_2Cr_2O_7 \rightarrow N_2 + \underset{\text{green}}{Cr_2O_3} + 4H_2O$

10. (b) Red P does not react with NaOH to give PH_3.

11. (d) PH_3 is not obtained when metaphosphoric acid is heated.

12. (a) The combustibility of PH_3 is due to presence of P_2H_4. The pure PH_3 is not combustible.

13. (c) $BiCl_3 + H_2O \rightarrow BiOCl + 2HCl$. BiOCl gives white ppt. which is used as white pigment, under the name of **pearl white.**

14. (a) $CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$

15. (c) NO_2 is paramagnetic and readily dimerises to N_2O_4 which is diamagnetic.

16. (b) $PI_3 + 3H_2O \rightarrow \underset{\text{Dibasic acid}}{H_3PO_3} + \underset{\text{Monobasic acid}}{3HI}$

17. (b) 20% nitrogen means if 20 g N then M.wt = 100

if 14 g N then M.wt $= \dfrac{100 \times 14}{20} = 70$

At least one N atom must be present in the molecule.

18. (b) TNT when mixed with NH_4NO_3, gives blasting mixture.

19. (c) $2NH_3 + OCl^- \rightarrow NH_2.NH_2 + H_2O + Cl^-$

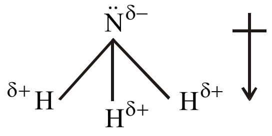
20. (a) $4NH_3 + 5O_2 \xrightarrow{\text{Pt. gauge}} 4NO + 6H_2O$

21. (b) $CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$

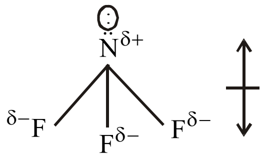
Blue complex due to $Cu(NH_3)_4^{2+}$

22. (b) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

23. (d) $\ddot{N}H_3$



$\ddot{N}F_3$



24. (a) Except (a) all other properties are shown by white phosphorous.

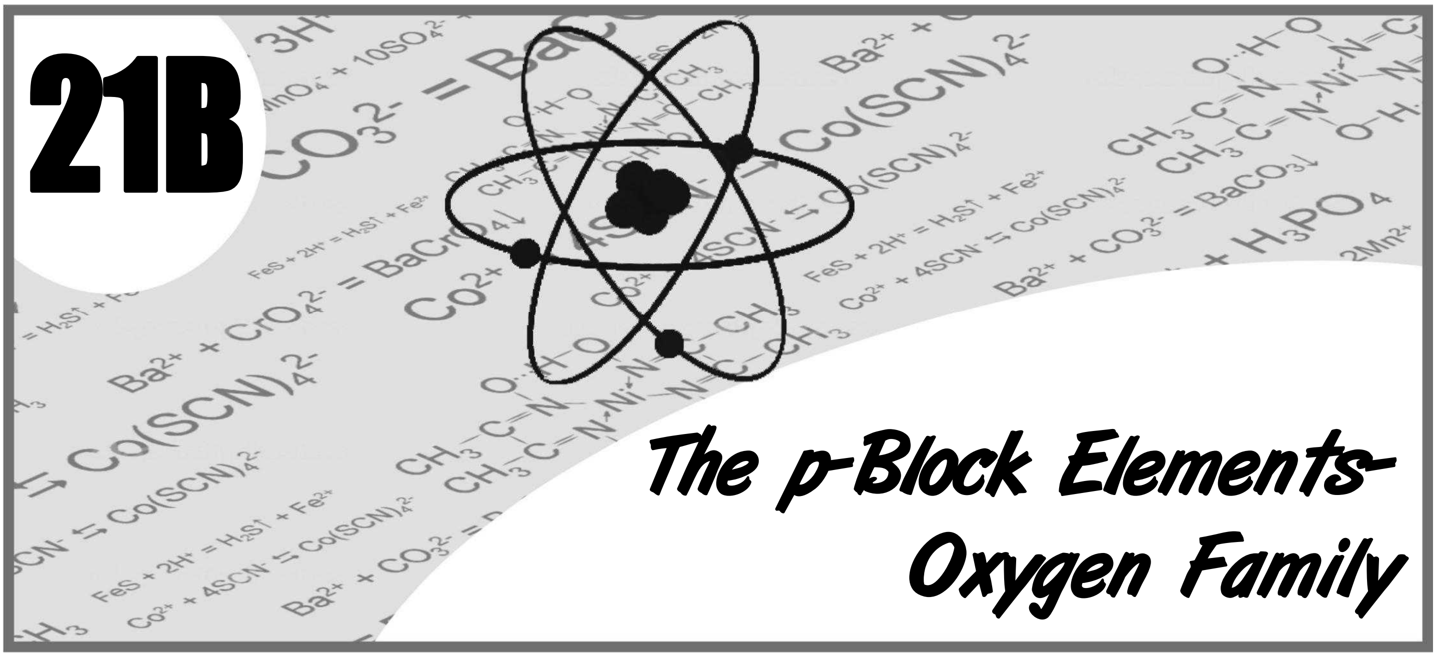
25. (b) The conversion of atmospheric nitrogen to nitrogen compounds is known as fixation of nitrogen.

26. (c) $P_2O_5 + 2HNO_3 \rightarrow N_2O_5 + 2HPO_3$

27. (b) $Ca_3(PO_4)_2 + 2H_2SO_4 + 5H_2O \rightarrow$

$$Ca(H_2PO_4)_2 . H_2O + 2CaSO_4.2H_2O$$

28. (b) $2H_3PO_4 \rightarrow \underset{\text{meta phosphoric acid}}{2HPO_3} + 2H_2O$



21B

The p-Block Elements- Oxygen Family

GENERAL CHARACTERISTICS :

The elements **oxygen, sulphur, selenium, tellurium** and **polonium** belong to group VIA or 16 group of periodic table.

These elements are known as **chalcogens** i.e. ore forming elements.

1. **Electronic configuration**

Elements	*At.No.*	*Electronic Confg.*	*Valence shell electronic confg.*
Oxygen	8	$[He]2s^2p^4$	$2s^2 2p^4$
Sulphur	16	$[Ne]3s^2 3p^4$	$3s^2 3p^4$
Selenium	34	$[Ar]4s^2 4p^4$	$4s^2 4p^4$
Tellurium	52	$[Kr]5s^2 5p^4$	$5s^2 5p^4$
Polonium	84	$[Xe]6s^2 6p^4$	$6s^2 6p^4$

The oxygen differs from the rest of the elements due to its (i) small size (ii) higher electronegativity (iii) absence of d atomic orbitals in valence shell (iv) tendency to form multiple bonding.

2. **Metallic and non metallic character**

$$\underbrace{O \qquad S}_{\text{Non metals}} \quad \underbrace{Se \qquad Te}_{\text{Metalloids}} \quad Po$$

Metal (Radio active) $t_{1/2}$ 138.4 days

3. **Abundance** O > S > Se > Te > Po

Oxygen is the most abundant element. It constitutes 46.6% of earth's crust, 21% of air and 89.1% of ocean by weight. Sulphur forms about 0.052% of earth's crust.

4. **Density** - Increases down the group regularly.

5. **Melting point and boiling point** - Both show a regular increase down the group due to increase in molecular weight and Van der Waal's forces of attraction.

6. **Oxidation state**

O	S	Se	Te	Po
–1,–2	–2 to +6	–2 to +6	–2 to +6	–2 to +6

In OF_2 the oxidation state of oxygen is +2

7. **Ionisation energy** - They possess a large amount of ionisation energy which decrease gradually from O to Po due to increase in size of atoms and increase in screening effect.

8. **Electron affinity** - They have high electron affinity which decrease from O to Po. As the size of the atom increases the extra added electron feels lesser attraction by nucleus and electron affinity decreases.

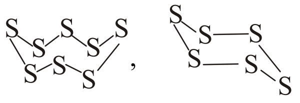
9. **Electronegativity** - It decreases down the group due to decrease in the effective nuclear charge down the group.

10. **Catenation** - The tendency to form chains of identical atoms is known as catenation. It follows the order

S-S	>	Se - Se	>	O - O	>	Te - Te
226		172		142		126 kJ/mole

The higher the bond strength, the higher is the catenation.

11. **Atomicity** - Oxygen is diatomic, sulphur and selenium octa atomic with puckered ring structure



Ring S_6

12. **Allotropy** - All the elements exhibit allotropy
- Oxygen - O_2 dioxygen and O_3 ozone
- Sulphur - Rhombic (or α) sulphur S_8
  Monoclinic (or β) sulphur S_8
  (most stable)
  Plastic (or λ) sulphur open chain
  Colloidal (or δ) sulphur

The S_R changes to S_M above 95.4°C.

- Selenium Rhombic Se_8
  Monoclinic Se_8
  Grey

Grey is the most stable consisting of regularly arranged spirals of Se atoms.

- Tellurium Non metallic
  Metallic (more stable)
- Polonium α and β both metallic

13. **Atomic radii** - Increases regularly from O to Po.
14. **Ionic radii** - Increases regularly from O to Po
15. **Atomic volume** - Increase regularly from O to Po.
16. **Multiple bond formation** - The tendency of these elements to form multiple bonds to C and N decreases down the group eg S = C = S is moderately stable.
    Se = C = Se decomposes readily and
    Te = C = Te not known

COMPOUNDS OF SIX GROUP ELEMENTS :

(i) ***Hydrides*** - All these elements form stable hydrides of the type H_2M either by directly combining with hydrogen or by the action of acids on metal sulphides, Selenides and tellurides

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

$$FeS + H_2SO_4 \rightarrow H_2S + FeSO_4$$

$$Na_2Se + H_2SO_4 \rightarrow H_2Se + Na_2SO_4$$

H_2O is a liquid due to hydrogen bonding. Others are colourless gases with unpleasant smell.

H_2O >	H_2S	>	H_2Se	>	H_2Te
104.5°	92.5°		91°		90°
					(all sp^3 hybridised)

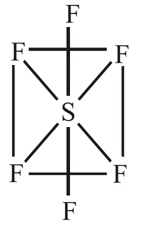
← Stability, volatile character (from H_2S to H_2Te)

→ Poisonous nature, acidic character, raducing character.

The weakening of M – H bond with the increase in the size of M (not the electronegativity) explains the acid character of hydrides.

(ii) ***Halides*** - All these elements form a number of halides. The halides of oxygen are not very stable eg OF_2, Cl_2O_7, I_2O_5 etc

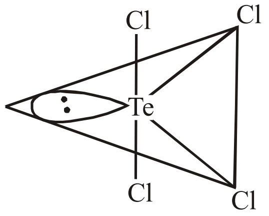
(a) ***Hexahalides*** - These are formed by fluorine only (not by Cl, Br, I) where elements exhibit maximum valency of +6. SF_6, SeF_6, TeF_6 are colourless gases with sp^3d^2 hybridisation and octahedral structure. These are covalent in nature. Due to bigger size of Cl, Br and I the coordination number of 6 is not achieved.



(b) ***Tetrahalides*** - With the exception of SBr_4, SI_4 and SeI_4 all tetrahalides are known. SF_4 is gaseous, SeF_4 is liquid and TeF_4 is solid. SCl_4 is unstable liquid. These have lewis acid character

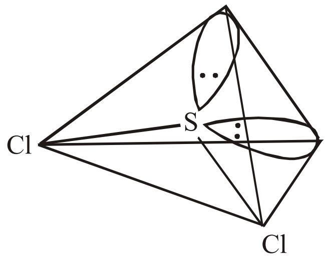
$$SF_4 + F_2 \rightarrow SF_6$$

They have trigonal bipyramidal shape with sp^3d hybridiation.



(c) ***Dihalides*** - The dihalides eg SCl_2, OF_2, $TeBr_2$ are sp^3, hybridised and have distorted bond angles due to electron pair repulsions

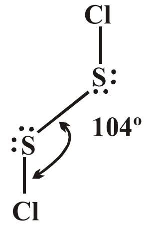
SCl_2	OF_2	$TeBr_2$
104°	101.5°	98°



(d) ***Dimeric monohalides*** - The dimeric monohalides are given by sulphur and selenium eg S_2F_2, S_2Cl_2, Se_2Cl_2 S_2Br_2, Se_2Br_2. These are slowly hydrolysed and undergo disproportionation.

$$2S_2Cl_2 + 2H_2O \rightarrow 4HCl + SO_2 + 3S$$

$$2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$$

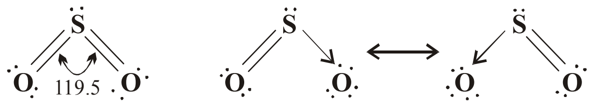


The monohalides have structure similar to H_2O_2 with distorted bond angle of sp^3 hybridisation

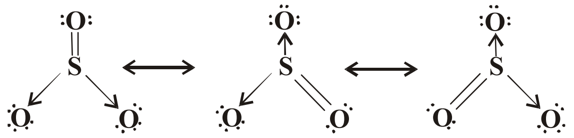
(iii) **Oxides -** Ozone is considered as oxide of oxygen O. Oxides of other elements are as follows

Element	***Mono Oxide***	***Dioxide***	***Tri Oxide***
S	SO	SO_2	SO_3
Se	-	SeO_2	SeO_3
Te	TeO	TeO_2	TeO_3
Po	PoO	PoO_2	-

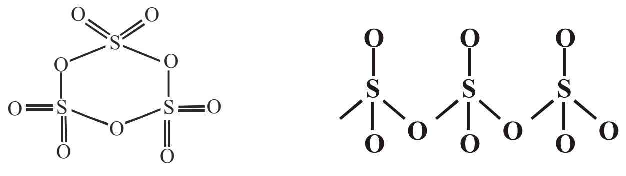
SO_2 is a gas having sp^2 hybridisation and V-shape.



SO_3. is a gas, sp^2 hybridised and planar in nature.

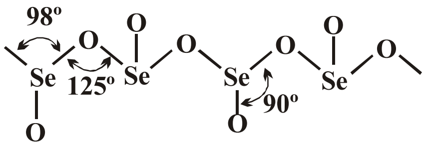


In solid state it exist as a **cyclic trimer** $\mathbf{(SO_3)_3}$ α-form or as a **linear** chain cross linked sheets

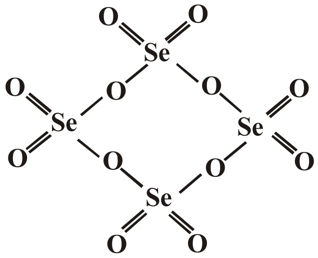


α-form β- and γ- form

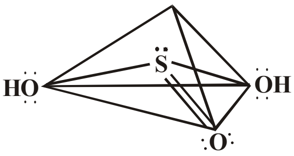
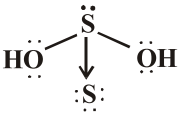
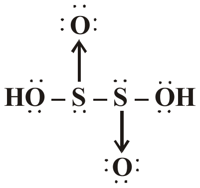
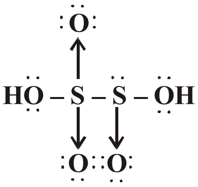
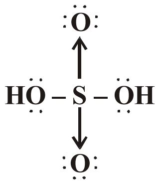
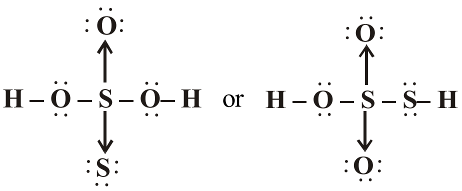
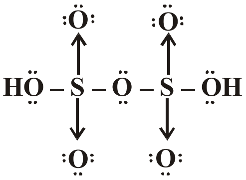
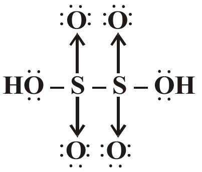
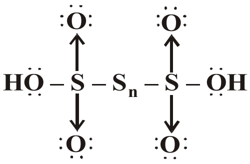
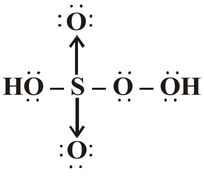
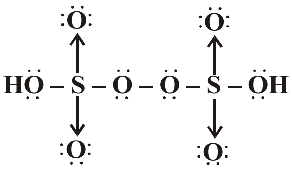
$\mathbf{SeO_2}$ volatile solid consists of non planar infinite chains



$\mathbf{SeO_3}$ has tetrameric cyclic structure



Oxy acids - Sulphur forms four series of oxy acids

Name	***Formula***	***Structure***
1. *Sulphurous acid series*		
(i) Sulpurous acid	H_2SO_3	
(ii) Thiosulphurous acid	$H_2S_2O_2$	 $HO-\underset{\underset{S}{\downarrow}}{S}-OH$
(iii) Hyposulphurous acid	$H_2S_2O_4$	 $HO-\overset{\overset{O}{\uparrow}}{S}-\underset{\underset{O}{\downarrow}}{S}-OH$
(iv) Pyrosulphurous acid	$H_2S_2O_5$	 $HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-\underset{\underset{O}{\downarrow}}{S}-OH$
2. *Sulphuric acid series*		
(i) Sulphuric acid	H_2SO_4	 $HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-OH$
(ii) Thiosulphuric acid	$H_2S_2O_3$	 $H-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{S}{\downarrow}}{S}}-O-H$ or $H-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-S-H$
(iii) Pyrosulphuric acid	$H_2S_2O_7$	 $HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-OH$
3. *Thionic acid series*		
(i) Dithionic acid	$H_2S_2O_6$	 $HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-OH$
(ii) Polythionic acid	$H_2S_nO_6$	 $HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-S_n-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-OH$ (n=3, 4, 5, 6)
4. *Peroxy acid series*		
(i) Peroxomonosulphuric acid	H_2SO_5	 $HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O-OH$ (Caro's Acid)
(ii) Peroxodisulphuric acid	$H_2S_2O_8$	 $HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-OH$ (Marshall's acid)

Oxy acids of selenium - Selenous acid H_2SeO_3, Selenic acid H_2SeO_4

Oxy acids of Tellurium Tellurous acid H_2TeO_3; Telluric acid H_2TeO_4

OZONE (O_3) :

Discovered by **Van Marum** by passing electric discharge through air, named by **Schonbien** (azo - I smell) and **Sorret** established the formula O_3 as allotrope of oxygen

It is formed in atmosphere by action of UV rays on O_2. It is also formed by (i) slow oxidation of phosphorous in air (ii) Reaction of fluorine with water at low temperature (iii) Electrolysis of water (iv) SO_2 reacts with H_2O_2

Preparation lab method *:* By passing silent electric discharge through cold, dry oxygen in ozoniser

$$3O_2 \rightleftharpoons 2O_3 + 284.5\ \text{kJ}$$

The ozonisers used are

1. **Siemen's ozoniser**
2. **Brodie's ozoniser**

Manufacture. For the manufacture of ozonised air *Siemen and Halske's* ozoniser is employed.

Electrolytic method. When acidified water, using high current density and Pt. anode, is electrolysed 95% O_3 is obtained at anode rest being O_2.

Properties - Pale blue gas, dark blue liquid and violet black solid with characteristic strong smell, slightly soluble in water but more soluble in turpentine oil, glacial **acetic acid** and carbon tetrachloride.

Decomposition

$$2O_3 \xrightarrow{573K} 3O_2 \qquad \Delta H = 284\ \text{kJ/mole}$$

Oxidising action

$O_3 \rightarrow O_2 + O$ (nascent oxygen hence powerfully oxidising)

$$PbS + 4O \rightarrow PbSO_4$$

$$H_2S + O \rightarrow H_2O + S$$

$$2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O$$

$$2K_4[Fe(CN)_6] + H_2O + O \rightarrow 2K_3[Fe(CN)_6] + 2KOH$$

$$2I_2 + 9O \rightarrow I_4O_9 \qquad [I_2, P, S, As] + O_3 \rightarrow \text{ic acid}$$

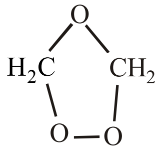
Reducing action

$$H_2O_2 + O_3 \rightarrow H_2O + 2O_2 \qquad BaO_2 + O_3 \rightarrow BaO + 2O_2$$

$$NaOCl + O_3 \rightarrow NaCl + 2O_2$$

$$K_3[Fe(CN)_6] \xrightarrow{\text{Alkaline}} K_4[Fe(CN)_6]$$

Addition reactions $CH_2 = CH_2 + O_3 \rightarrow$



Ozonide

Uses:-

(1) Bleaching ivory, oils, flour etc.

(2) As germicide and disinfectant, for sterilising water

(3) For improving atmosphere in crowded places

(4) Manufacture of $KMnO_4$ and artificial silk.

Tests:-

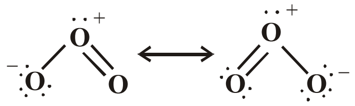
(1) Turns starch iodine paper blue.

(2) **Tailing of Hg**. Mercury loses its meniscus in contact with O_3 and sticks to the surface of glass due to formation of Hg_2O

(3) Clean silver foil blackened by O_3

(4) It turns benzidene paper brown and tetramethyl base violet

Structure



Oxidation state of O is +1 and –1

Oxides: Oxides are the binary compounds of oxygen with metals and non metals. Based on their oxygen content they have been classified as

(1) Normal oxides - Oxides containing oxygen according to normal oxidation number of M eg. H_2O, MgO, Al_2O_3.

(2) Polyoxides - These contain more oxygen than normal oxidation number of M and M – O and O – O bonds. They are further classified as

(i) ***Peroxides*** - They contain O_2^{2-} ion, produce hydrogen peroxide with dil. acids and O_2 with concentrated acids eg BaO_2, Na_2O_2

$$BaO_2 + H_2SO_4 \xrightarrow{\text{(dil.)}} BaSO_4 + H_2O_2$$

$$2BaO_2 + 2H_2SO_4 \xrightarrow{\text{(Conc)}} 2BaSO_4 + 2H_2O + O_2$$

(ii) ***Super oxides*** - They contain O_2^- ion. With water they give hydrogen peroxide and oxygen

$$2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2 + O_2$$

(iii) ***Dioxides*** - They give chlorine with conc HCl and oxygen with Conc H_2SO_4 eg MnO_2, PbO_2 etc.

$$2MnO_2 + 4HCl(\text{Conc}) \rightarrow MnCl_2 + 2H_2O + Cl_2$$

$$2MnO_2 + 2H_2SO_4(\text{Conc}) \rightarrow 2MnSO_4 + 2H_2O + O_2$$

(iv) ***Suboxides*** - They contain lower percentage of oxygen eg N_2O, C_3O_2

They have M – M and M – O bonds. For example O = C = C = C = O (carbon suboxide)

(v) ***Mixed oxides*** - Formed by the combination of two simple oxides eg Red lead, Pb_3O_4 ($PbO_2.2PbO$), Fe_3O_4 ($FeO+Fe_2O_3$)

Classification on the basis of chemicals behaviour

(i) Acidic oxides - Oxides of non metals which give acids when dissolved in water are called acidic oxides eg.

CO_2, NO_2, P_2O_5, SO_2, SO_3, Cl_2O_7 etc.

$CO_2 + H_2O \rightarrow H_2CO_3$ carbonic acid

The metallic oxides of high oxidation state eg Mn_2O_7, V_2O_5 and CrO_3

(ii) Basic oxides

(a) ***Ionic in nature***. Oxides of alkali and alkaline earth

metals eg Na_2O, CaO, BaO. In water they give basic solutions

$$Na_2O + H_2O \rightarrow 2NaOH$$

(b) ***Covalent oxides*** - Oxides of transition metals are covalent in nature eg CuO, FeO. Insoluble in water.

(iii) Amphoteric oxides - The oxides which react with both acids and alkalies are known as amphoteric oxides eg ZnO, Al_2O_3, SnO etc.

$$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$$

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$$

(iv) Neutral oxides - Such oxides do not combine with an acid or a base eg NO, N_2O, CO, H_2O etc.

OXYGEN :

Chinese observed the presence of oxygen in air. **Priestly & Scheely** prepared oxygen by heating suitable oxygen compounds.

Occurrence - About $\frac{1}{5}$th of the atmosphere is free of elemental oxygen. In the combined state it is present in water 89% by weight, earth's crust about 50% and plants and animal tissues 50–70%.

Preparation -

(1) By action of heat on oxygen rich compounds

(i) ***From oxides***

$$2HgO \xrightarrow{\Delta} 2Hg + O_2 \uparrow$$

$$2Ag_2O \rightarrow 4Ag + O_2 \uparrow$$

(ii) ***From peroxides and other oxides***

$$2H_2O_2 \xrightarrow{MnO_2} 2H_2O + O_2$$

$$2BaO_2 \xrightarrow{\Delta} 2BaO + O_2$$

$$2PbO_2 \xrightarrow{\Delta} 2PbO + O_2$$

$$2Pb_3O_4 \xrightarrow{\Delta} 6PbO + O_2$$

$$3MnO_4 \xrightarrow{\Delta} Mn_3O_4 + O_2$$

(iii) ***From certain compounds***

$$2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$$

$$2KNO_3 \rightarrow 2KNO_2 + O_2$$

$$2CaOCl_2 \rightarrow 2CaCl_2 + O_2$$

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

(2) By the action of some chemical reagent on compound rich in O_2.

$$2Na_2O_2 + 2H_2O \rightarrow 2NaOH + O_2$$

$$2K_2Cr_2O_7 + 8H_2SO_4(conc) \rightarrow$$

$$2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

(3) By electrolysis of water either acidified with H_2SO_4 using platinum electrodes or by making it alkaline with NaOH or $Ba(OH)_2$ using nickel electrodes.

$$2H_2O \rightleftharpoons 2H + 2OH^- \xrightarrow{-2\bar{e}} 2OH \rightleftharpoons H_2O + \frac{1}{2}O_2$$

(4) By decomposition of steam by chlorine.

$$2H_2O + 2Cl_2 \rightarrow 4HCl + O_2$$

Manufacture - By fractional distillation of liquid air

Properties - It is colourless, odourless, tasteless slightly heavier than air, sparingly soluble in water, soluble in pyrogallol.

Chemical properties - On heating it combines directly with metals and non metals.

$$C + O_2 \rightarrow CO_2$$

$$P_4 + 5O_2 \rightarrow 2P_2O_5$$

$$S + O_2 \rightarrow SO_2$$

$$N_2 + O_2 \xrightarrow{3000^\circ C} 2NO$$

$$2Mg + O_2 \rightarrow 2MgO \qquad 3Fe + 2O_2 \rightarrow Fe_3O_4$$

$$4Na + O_2 \rightarrow 2Na_2O \rightarrow Na_2O_2$$

$$Pb + O_2 \rightarrow PbO_2$$

Combination with O_2 is accelerated by using catalyst. Platinum is particularly active.

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O \quad \textbf{(Ostwald's process)}$$

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3 \quad \textbf{(Contact process)}$$

$$2CH_3OH + O_2 \rightarrow 2HCHO + 2H_2O$$

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O \quad \textbf{(Deacon's process)}$$

Uses

(1) For breathing

(2) In welding and cutting – oxy-hydrogen or oxy - acetylene torch is used.

(3) In iron and steel industry – to increase the content of blast in the Bessemer and open hearth process.

(4) As a fuel in rockets.

Tests

(1) With NO it gives reddish brown fumes of NO_2.

(2) Absorbed by alkaline pyrogallol.

(3) A smouldering wood splinter bursts into flames in a jar of O_2.

Structure

It is paramagnetic with following electronic configuration

$$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi^* 2p_x^1 = \pi^* 2p_y^1$$

Atomic oxygen : $O_2 \xrightarrow[\text{1 mm pressure}]{\text{discharge tube}} O + O \quad \Delta H = 489.6\text{kJ}$

Isotopes	O^{16}	O^{17}	O^{18}
	10000:	1:	8

SULPHUR :

Occurence - It occurs free in volcanic regions. In combined state it occurs as

(i) Gypsum $CaSO_4.2H_2O$

(ii) S-Celesite $SrSO_4$

(iii) Galena PbS

(iv) Zinc blende ZnS

(v) Copper pyrites $Cu_2SFe_2S_3$

(vi) Iron pyrites FeS_2

Properties - Ordinary sulphur is pale yellow, insoluble in water but dissolves in CS_2, C_6H_6 and turpentine

Allotrophic forms - Its important allotrophic forms are

Crystalline - Rhombic, monoclinic

Amorphous - Plastic, milk of sulphur, colloidal sulphur.

COMPOUNDS OF SULPHUR :

1. Sulphuric acid - It is also known as ***oil of vitriol*** and ***king of chemicals.***

Manufactures of sulphuric acid

(1) ***Lead chamber process*** - The various steps involved are

(a) ***Production of SO_2*** : By burning S or iron pyrites.

$$S + O_2 \xrightarrow{\Delta} SO_2$$

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

(b) ***Production of catalyst*** - Oxides of nitrogen

$$2NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_3$$

$$2HNO_3 \rightarrow H_2O + NO + NO_2 + O_2$$

(c) ***Reaction in lead chamber***

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$2NO + O_2 \rightarrow 2NO_2 \quad \text{(used again)}$$

Gay-Lussac Tower : The residual gases (mainly air + oxides of nitrogen) from lead chambers + conc. H_2SO_4 from glover tower give nitrated acid.

$$2H_2SO_4 + NO + O_2 \rightarrow 2NO.HSO_4 + H_2O$$

Glover Tower : The nitrated acid from Gay-Lussac tower is denitrated in this tower.

$$\underset{\substack{\text{Nitroso}\\ \text{sulphuric acid}}}{2NO.HSO_4} + H_2O \rightarrow 2H_2SO_4 + NO + NO_2$$

(d) ***Conditions*** - Temperature 50ºC, excess of steam, lead chamber since lead is not attacked H_2SO_4.

(e) ***Purification*** - The acid obtained contains the impurities of $PbSO_4$, AS_2O_3, NO and NO_2 which are removed as follows

As_2O_3 is precipitated as As_2S_3 by passing H_2S

$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$$

$PbSO_4$ is insoluble in water and settles down on dilution and filtered off.

NO and NO_2 are removed by heating with $(NH_4)_2SO_4$

$$(NH_4)_2SO_4 + NO + NO_2 \rightarrow 3H_2O + H_2SO_4 + 2N_2$$

(f) ***Concentration*** - The sulphuric acid is concentrated by evaporation

(2) ***Contact process*** - The steps involved are

(i) **Production of SO_2** - It is produced by burning sulphur and iron pyrites and purified by treating with steam to remove dust particles. The arsenic is removed by ferric hydroxide, water vapour removed by conc H_2SO_4. The gases are filtered through coke filters and purity is tested by Tyndal box.

(ii) **Conversion of SO_2 to SO_3 -** It is done in contact or catalyst chamber after being preheated to 450ºC.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + x \text{ cal}$$

450° - 500ºC 1.6 to 1.7 atm Pressure

Catalyst - Formerly platinised asbestose was used which is costly and easily poisoned. Now a days V_2O_5 is used.

(iii) SO_3 is absorbed by conc H_2SO_4 and then water is added to produce the acid of desired concentration

$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$$

(oleium or pyrosulphuric acid)

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

If SO_3 is absorbed by water it liberates large amount of heat producing acid fog.

Properties - Its specific gravity is 1.8 and it is 98% by weight normality is 36N.

Chemical properties

(i) **Action of heat** $H_2SO_4 \rightarrow H_2O + SO_2 + O$

Hence it acts as oxidising agent

Non metals are oxidised to their oxides

$$C + 2O \rightarrow CO_2 \quad S + 2O \rightarrow SO_2$$

$$2P + 5O \rightarrow P_2O_5$$

$$2KI + 2H_2SO_4 \rightarrow K_2SO_4 + SO_2 + I_2 + 2H_2O$$

$$2KBr + 2H_2SO_4 \rightarrow K_2SO_4 + SO_2 + Br_2 + 2H_2O$$

(ii) ***Displacement reactions*** - It displaces volatile acids from their salts.

$$Na_2S + H_2SO_4 \rightarrow H_2S + Na_2SO_4$$

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$$

$$NaNO_3 + H_2SO_4 \rightarrow HNO_3 + NaHSO_4$$

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4$$

Metals above hydrogen in ECS react with dil. H_2SO_4 with evolution of H_2.

$M(Fe, Sn, Zn, Al, Mn, Mg) + H_2SO_4 \rightarrow MSO_4 + H_2$

Conc. H_2SO_4 reacts with all metals except Au and Pt with evolution of SO_2.

$Metal + Conc.\ H_2SO_4 \rightarrow MSO_4 + SO_2 + H_2O$

(iii) ***Dehydrating agent -*** It is strong dehydrating in nature

$$C_{12}H_{22}O_{11} \rightarrow 12C + H_2SO_4.11H_2O$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2SO_4.H_2O$$

$$HCOOH \rightarrow CO + H_2SO_4.H_2O$$

$$(COOH)_2 \rightarrow CO + CO_2 + H_2SO_4.H_2O$$

(iv) ***Reaction with PCl_5***

$$HO.SO_2.OH + PCl_5 \rightarrow \underset{\text{Chlorosulphonic acid}}{Cl.SO_2.OH} + POCl_3 + HCl$$

$$HO.SO_2.OH + 2PCl_5 \rightarrow \underset{\text{Sulphuryl Chloride}}{Cl.SO_2.Cl} + 2POCl_3 + 2HCl$$

(v) ***Sulphonation of aromatic compounds***

$$C_6H_6 + H_2SO_4 \rightarrow \underset{\text{Benzene sulphonic acid}}{C_6H_5.SO_2OH} + H_2O$$

(vi) ***Precipitation*** - Barium and lead are precipitated as sulphates

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$$

$$Pb(NO_3)_2 + H_2SO_4 \rightarrow PbSO_4 + 2HNO_3$$

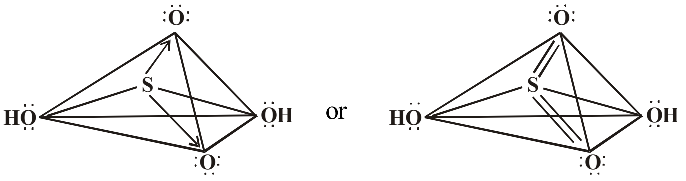
Hence these are gravimetrically estimated

Fuming sulphuric acid $[H_2SO_4.SO_3]$

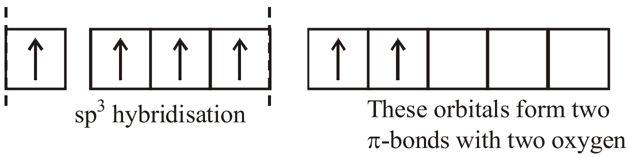
With ammonia it forms $(NH_4)_2SO_4$ hence NH_3 can not be dried over H_2SO_4

Uses - It is used as oxidising, dehydrating agent and for the preparation of dyes, drugs, explosives, volatile acids etc.

Structure - It has tetrahedral structure



S- in doubly excited state



SULPHUR DIOXIDE (SO_2)

Preparation

(i) ***By heating sulphur in air*** $S + O_2 \xrightarrow{\Delta} SO_2$

(ii) ***Roasting iron pyrites in excess of air***

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

(iii) ***Lab method :*** By heating Cu with conc H_2SO_4

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

Properties -

(i) ***As reducing agent***

$$SO_2 + Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$$

$$SO_2 + 2FeCl_3 + 2H_2O \rightarrow H_2SO_4 + 2FeCl_2 + 2HCl$$

$$2KIO_3 + 5SO_2 + 4H_2O \rightarrow 2KHSO_4 + 3H_2SO_4 + I_2$$

$$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

It decolorises the solution of $KMnO_4$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + \underset{\text{green}}{Cr_2(SO_4)_3} + H_2O$$

(ii) ***As oxidising agent***

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S\downarrow$$

$$SO_2 + 2Mg(\text{burning}) \rightarrow 2MgO + S\downarrow$$

$$3Fe + SO_2 \rightarrow 2FeO + FeS$$

$$PbO_2 + SO_2 \rightarrow PbSO_4$$

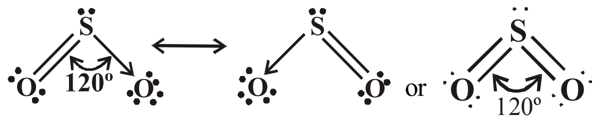
(iii) ***Burning of potassium*** - Potassium burns in SO_2 giving sulphate and thiosulphate

$$4K + 3SO_2 \rightarrow K_2SO_3 + K_2S_2O_3$$

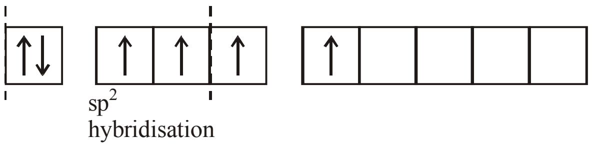
(iv) ***Bleaching action*** - Its bleaching action is due to reduction

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$$

Structure : It is sp^2 hybridised and has V- shape.



S- in excited state



σ bond from sp^2-p overlap

one π bond from pπ-pπ bond overlap

other π bond from pπ-dπ overlap

SULPHUR TRIOXIDE (SO_3) :

Preparation

(i) **By heating** conc H_2SO_4 with P_2O_5

$$H_2SO_4 + P_2O_5 \rightarrow SO_3 + 2HPO_3$$

(ii) ***Manufacture*** : It is done by contact process

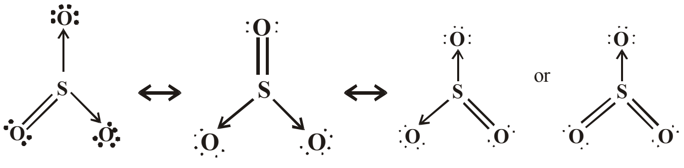
$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

Properties - It dissolves in water with loud hissing sound and evolution of heat

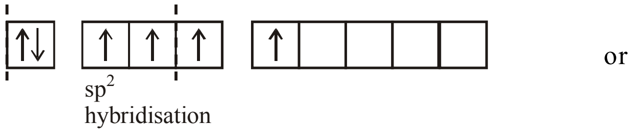
Chemical properties

1. Action of heat $2SO_3 \rightleftharpoons 2SO_2 + O_2$
2. Water $SO_3 + H_2O \rightleftharpoons H_2SO_4$
3. With H_2SO_4(Conc) : $\underset{\text{(oleum)}}{H_2SO_4 + SO_3 \rightarrow H_2S_2O_7}$
4. Acidic nature: $CaO + SO_3 \rightarrow CaSO_4$
5. With HCl : $SO_3 + HCl \rightarrow Cl.SO_2OH$
   (Chloro Sulphonic acid)
6. Oxidising agent - It is powerful oxidising agent
   $SO_3 + 2HBr \rightarrow H_2O + Br_2 + SO_2$

Structure - It has planar triagonal structure due to sp^2 hybridisation

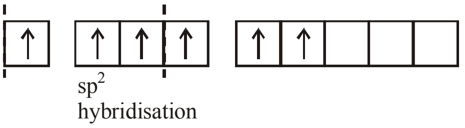


S- in excited state

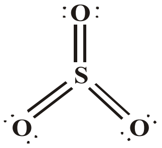


σ bond from sp^2-p overlap
π bonds from pπ-pπ and pπ-dπ overlap

or doubly excited state



Structure :



Allotropic forms - It has three allotropic forms α , β and γ

Uses *:* In the manufacture of H_2SO_4 and drying agent.

HYDROGEN SULPHIDE (H_2S)

Preparation : Lab Method -

By action of dil. H_2SO_4 or HCl on iron sulphide

$FeS + 2H_2SO_4 \rightarrow FeSO_4 + H_2S$

Properties - Colourless poisonous gas with odour of rotten eggs fairly soluble in water

(i) ***Combustibility*** - $2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$

(ii) ***Reducing nature***

$$2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

$$H_2S + Cl_2 \rightarrow 2HCl + S\ ,\ H_2O_2 + H_2S \rightarrow 2H_2O + S$$

Uses - In qualitative analysis

SODIUM THIOSULPHATE - $Na_2S_2O_3.5H_2O$:

Preparation

(i) By boiling Na_2SO_3 with flowers of sulphur in absence of air

$Na_2SO_3 + S \rightarrow Na_2S_2O_3$

(ii) By heating sodium hydrogen sulphide and sodium hydrogen sulphite together

$2NaHS + 4NaHSO_3 \rightarrow 3Na_2S_2O_3 + 3H_2O$

Properties - It is also known as hypo

1. ***Complexing*** - It dissolves silver halides forming complex

$AgX + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaX$

Sodium argento thiosulphate (soluble complex)

2. ***It absorbs halogens*** -

$Cl_2 + H_2O + Na_2S_2O_3 \rightarrow Na_2SO_4 + 2HCl + S$

Hence used to remove last traces of chlorine

$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$

used for estimation of iodine

3. ***Reaction with $AgNO_3$***

$2AgNO_3 + Na_2S_2O_3 \rightarrow \underset{\text{Silver thiosulphate (white precipitate)}}{Ag_2S_2O_3} + 2NaNO_3$

$Ag_2S_2O_3 + H_2O \rightarrow \underset{\text{Blue precipitate}}{Ag_2S} + H_2SO_4$

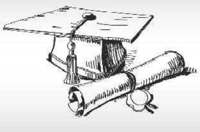
4. ***Action of dil. H_2SO_4***

$Na_2S_2O_3 + dil.H_2SO_4 \rightarrow Na_2SO_4 + SO_2 + \underset{\text{yellow precipitate}}{S} + H_2O$

Uses -

(i) It is used as an antichlor compound.
(ii) Fixer in photography to remove AgBr left.
(iii) In the metallurgy for extraction of Ag and Au.

Exercise-1 | NCERT BASED QUESTIONS



Very Short/Short Answer Questions

1. Why does the tendency to show –2 oxidation state diminishes from S to Po?

2. Why does oxygen not show an oxidation state of + 4 and + 6 like sulphur?

3. Sulphur forms SF_6 while oxygen does not form OF_6. Why?

4. Name allotropes of oxygen.

5. H_2S is acidic while H_2O is neutral. Why?

6. Compare the structure of SO_3 and SeO_3

7. H_2S has a stronger reducing behaviour in comparison to that of water. Explain.

8. Oxygen shows covalency of two whereas sulphur shows covalency upto six. Why?

9. Why do hydrides of oxygen and sulphur differ in physical state?

10. Why do sulphurous acid a reducing agent?

11. Among following, which has highest bond angle:

H_2O, H_2S, H_2Se or H_2Te

12. S in vapour state exhibits paramagnetism. Why?

13. Thermal stability of water is much higher than that of H_2S. Explain.

14. Why are group 16 elements called chalcogens?

Long Answer Questions

15. What is catenation illustrate it for oxygen group.

16. What is inert pair effect and what is its reason.

Multiple Choice Questions

17. Which one of the following property is not correct for ozone?

(a) It oxidises lead sulphide
(b) It oxidises potassium iodide
(c) It oxidises mercury
(d) It cannot act as bleaching agent.

18. Bleaching action of SO_2 is due to

(a) reduction (b) oxidation
(c) hydrolysis (d) its acidic nature

19. Difference between S and S^{2-} as S^{2-} has

(a) larger radii and large size
(b) smaller radii and large size
(c) larger radii and small size
(d) smaller radii and small size

20. Polyanion formation is maximum in

(a) nitrogen (b) oxygen (c) sulphur (d) boron

21. The acid which has a peroxy linkage is

(a) sulphurous acid (b) pyrosulphuric acid
(c) dithionic acid (d) caro's acid

22. Which compound is used in photography?

(a) Na_2SO_5 (b) $Na_2S_2O_8$
(c) $Na_2S_2O_6$ (d) $Na_2S_2O_3$

23. By passing H_2S gas in acidified $KMnO_4$ solution, we get

(a) S (b) K_2S
(c) MnO_2 (d) K_2SO_3

24. A gas that cannot be collected over water is :

(a) N_2 (b) O_2
(c) SO_2 (d) PH_3

25. On electrolysis of dilute sulphuric acid using platinum electrodes, the product obtained at the anode will be

(a) hydrogen (b) oxygen
(c) hydrogen sulphide (d) sulphur dioxide.

26. It is possible to obtain oxygen from air by fractional distillation because

(a) oxygen is in a different group of the periodic table from nitrogen
(b) oxygen is more reactive than nitrogen
(c) oxygen has higher b.p. than nitrogen
(d) oxygen has a lower density than nitrogen.

Exercise-2 | CONCEPTUAL MCQs

1. Electron affinity of sulphur is

(a) more than O and Se
(b) more than O but less than Se
(c) less than O but more than Se
(d) equal to O and Se

2. All the elements of oxygen family are

(a) non metals (b) metalloids
(c) radioactive (d) polymorphic

3. Which shows maximum catenation property ?

(a) S (b) Se
(c) Te (d) O

4. A group 16 element exists in monoatomic state in the metallic lattice. It also exists in two crystalline forms. The metals is

(a) Po
(b) S
(c) Se
(d) Te

5. Atomicity of sulphur in rhombic sulphur is

(a) 1
(b) 2
(c) 8
(d) 6

6. Which of the following hydrides has the lowest boiling point ?

(a) H_2O
(b) H_2S
(c) H_2Se
(d) H_2Te

7. Which of the following hydrides is most acidic ?

(a) H_2Te
(b) H_2Se
(c) H_2O
(d) H_2S

8. Which of the following hydrides shows the highest boiling point ?

(a) H_2O
(b) H_2S
(c) H_2Se
(d) H_2Te

9. Electronegativity of oxygen is more than sulphur yet H_2S is acidic while water is neutral. This is because

(a) water is highly associated compound
(b) molecular mass of H_2S is more than H_2O
(c) H_2S is gas while H_2O is a liquid
(d) H–S bond is weaker than H–O bond

10. What is the hybridization of S in SF_4 ?

(a) sp^3d^2
(b) sp^3d
(c) sp^3d^3
(d) sp^3

11. The shape of the molecule SF_3Cl_3 is

(a) trigonal bipyramidal
(b) cubic
(c) octahedral
(d) tetrahedral

12. States of hybridization of P in PF_5 and S in SF_6 are respectively?

(a) sp^3d^2, sp^3d
(b) sp^3d, sp^3d^2
(c) sp^3, sp^3d
(d) sp^2, d^3

13. Which of the following is not tetrahedral ?

(a) SCl_4
(b) SO_4^{2-}
(c) $Ni(CO)_4$
(d) $NiCl_4^{2-}$

14. In OF_2 molecule, the total number of bond pairs and lone pairs of electrons present respectively are

(a) 2, 6
(b) 2, 8
(c) 2, 10
(d) 2, 9

15. The type of hybridization in water molecule is

(a) sp
(b) sp^2
(c) sp^3
(d) None of these

16. Hybridization of S in SO_3 is

(a) sp^2
(b) sp^3
(c) sp^2d
(d) sp^3d^2

17. Permonosulphuric acid is known as

(a) Marshall's acid
(b) Caro's acid
(c) Sulphuric acid
(d) None of these

18. S – S bond is not present in

(a) $S_2O_4^{2-}$
(b) $S_2O_5^{2-}$
(c) $S_2O_3^{2-}$
(d) $S_2O_7^{2-}$

19. There is S – S bond in

(a) $H_2S_2O_7$
(b) $H_2S_2O_8$
(c) $H_2S_2O_6$
(d) H_2SO_5

20. Oleum is chemically known as

(a) H_2SO_3
(b) H_2SO_5
(c) $H_2S_2O_7$
(d) $H_2S_2O_8$

21. S - S bond is present in

(a) $S_2O_7^{2-}$
(b) S_3O_9
(c) $S_2O_4^{2-}$
(d) $S_2O_3^{2-}$

22. Which of the following has pπ- dπ bonding ?

(a) NO_3^-
(b) SO_3^{2-}
(c) BO_3^{3-}
(d) CO_3^{2-}

23. Caro's acid is

(a) H_2SO_3
(b) $H_3S_2O_5$
(c) H_2SO_5
(d) $H_2S_2O_8$

24. H_2S reacts with O_2 to form

(a) $H_2O + S$
(b) $H_2O + SO_2$
(c) $H_2O + SO_3$
(d) $H_2SO_4 + S$

25. Which is the best oxidising agent among the following ?

(a) S
(b) O
(c) Se
(d) Te

26. On heating $KClO_3$ we get

(a) $KClO_2 + O_2$
(b) $KCl + O_2$
(c) $KCl + O_3$
(d) $KCl + O_2 + O_3$

27. Oxygen molecule is

(a) diamagnetic with no-unpaired electron(s)
(b) diamagnetic with two unpaired electrons
(c) paramagnetic with two unpaired electrons
(d) paramagnetic with no unpaired electron(s)

28. The number of electrons that are paired in oxygen molecule are

(a) 16
(b) 12
(c) 14
(d) 7

29. Which of the following is incorrect ?

(a) O_2 is weaker oxidant than O_3
(b) O_2 has larger bond length than O_3
(c) Both O_2 and O_3 are paramagnetic
(d) O_2 is linear and O_3 is angular in shape

30. Which of the following species possesses the highest bond order ?

(a) O_2
(b) O_2^+
(c) O_2^-
(d) O_2^{2-}

31. In the species O_2, O_2^+, O_2^- and O_2^{2-}, the correct decreasing order of bond strength is

(a) $O_2 > O_2^+ > O_2^- > O_2^{2-}$
(b) $O_2^+ > O_2 > O_2^- > O_2^{2-}$
(c) $O_2^{2-} > O_2^- > O_2^+ > O_2$
(d) $O_2^- > O_2^{2-} > O_2 > O_2^+$

32. Which is most acidic in nature ?
(a) Na_2O (b) MgO
(c) Al_2O_3 (d) CaO

33. Which of the following oxides reacts with both HCl and NaOH ?
(a) CaO (b) ZnO
(c) N_2O_5 (d) CO_2

34. Which of the following is formed by the action of water on sodium peroxide ?
(a) H_2 (b) N_2
(c) O_2 (d) CO_2

35. Sulphuric acid reacts with PCl_5 to give
(a) thionyl chloride (b) sulphur monochloride
(c) sulphuryl chloride (d) sulphur tetrachloride

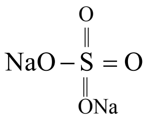
36. Which one of the following reacts with conc. H_2SO_4?
(a) Au (b) Ag
(c) Pt (d) Pb

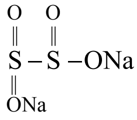
37. HCOOH reacts with conc. H_2SO_4 to produce
(a) CO (b) CO_2
(c) NO (d) NO_2

38. The number of dative bonds in sulphuric acid molecule is
(a) 0 (b) 1
(c) 2 (d) 4

39. What is the number of sigma (σ) and pi (π) bonds present in sulphuric acid molecule ?
(a) $6\sigma, 2\pi$ (b) $6\sigma, 0\pi$
(c) $2\sigma, 4\pi$ (d) $2\sigma, 2\pi$

40. The oxidation number of sulphur is –1 in
(a) FeS (b) FeS_2

(c) 
$\mathrm{NaO-\overset{\overset{O}{\|}}{\underset{\underset{ONa}{\|}}{S}}=O}$

(d) 
$\mathrm{\overset{\overset{O}{\|}}{\underset{\underset{ONa}{\|}}{S}}-\overset{\overset{O}{\|}}{S}-ONa}$

41. Bromine water reacts with SO_2 to form ?
(a) H_2O and HBr (b) $H_2SO_4 + HBr$
(c) HBr and S (d) S and H_2O

42. Which of the following behaves as both oxidising as well as reducing agent ?
(a) H_2SO_4 (b) SO_2
(c) H_2S (d) HNO_3

43. By which of the following SO_2 is formed ?
(a) Reaction of dil. H_2SO_4 with O_2
(b) Hydrolysis of dil. H_2SO_4
(c) Reaction of conc. H_2SO_4 with Cu
(d) None of these

44. The compound of sulphur that can be used as refrigerant is
(a) SO_2 (b) SO_3
(c) S_2Cl_2 (d) H_2SO_4

45. Which of the following causes damage to the building containing calcium and responsible for cough and choking in human?
(a) Sulphur (b) Carbon
(c) Nitrogen dioxide (d) Sulphur dioxide

46. Number of bonds in SO_2 are
(a) two σ and two π (b) two σ and one π
(c) two σ and three π (d) None of these

47. Bleaching action of SO_2 is due to its
(a) oxidising property (b) acidic property
(c) reducing property (d) basic property

48. H_2S does not produce metallic sulphide with
(a) $CdCl_2$ (b) $ZnCl_2$
(c) $COCl_2$ (d) $CuCl_2$

49. By passing H_2S gas in acidified $KMnO_4$ solution, we get
(a) K_2S (b) S
(c) K_2SO_3 (d) MnO_2

50. $Na_2S_2O_3$ is prepared by
(a) reacting $H_2S_2O_3$ with NaOH
(b) reducing Na_2SO_4 with S in alkaline medium
(c) heating NaOH and S
(d) reducing Na_2SO_4 with S in acidic medium

51. What are the products formed when chlorine is passed through aqueous hypo solution?
(a) $Na_2SO_3 + HCl + S$ (b) $Na_2SO_3 + SO_3 + HCl$
(c) $Na_2SO_4 + HCl + S$ (d) $Na_2SO_4 + HCl + SO_2$

52. What is the oxidation number of sulphur in $Na_2S_4O_6$?
(a) $\frac{2}{3}$ (b) $\frac{3}{2}$
(c) $\frac{3}{5}$ (d) $\frac{5}{2}$

53. The metal with highest electrical resistance at room temperature is
(a) Pb (b) Te
(c) Po (d) Fe

54. The compound containing coordinate bond is
(a) O_3 (b) SO_3
(c) H_2SO_4 (d) All of these

55. Which of the following is not a reducing agent ?
(a) SO_2 (b) H_2O_2
(c) CO_2 (d) NO_2

56. When potassium ferrocyanide crystals are heated with conc. H_2SO_4, the gas evolved is
(a) SO_2 (b) NH_3
(c) CO_2 (d) CO

57. Correct order of O – O bond length (increasing) in O_2, H_2O_2 and O_3 is
(a) $H_2O_2 < O_3 < O_2$ (b) $O_2 < O_3 < H_2O_2$
(c) $O_3 < O_2 < H_2O_2$ (d) $O_3 < H_2O_2 < O_2$

58. Which of the following does not exhibit sp^3 hybridisation?
(a) SO_2 (b) CH_4
(c) NH_3 (d) SO_4^{2-}

59. Which of the following species is basic & reducing?
(a) SO_3^{2-} (b) SO_4^{2-}
(c) $S_2O_4^{2-}$ (d) HSO_4^-

60. Iron sulphide is heated in air to form A, an oxide of sulphur. A is dissolved in water to give an acid. The basicity of this acid is
(a) 2 (b) 3
(c) 1 (d) zero

Exercise-3 | PAST COMPETITION MCQs

1. Hypo is used in photography to **[CBSE-PMT1988]**
   (a) Reduce AgBr grains to metallic silver
   (b) Convert metallic silver to silver salt
   (c) Remove undecomposed silver bromide as a soluble complex
   (d) Remove reduced silver
2. Oxygen will directly react with each of the following elements except **[CBSE-PMT 1989]**
   (a) P (b) Cl (c) Na (d) S.
3. The gases respectively absorbed by alkaline pyrogallol and oil of cinnamon are **[CBSE-PMT 1989]**
   (a) O_3, CH_4 (b) O_2, O_3 (c) SO_2, CH_4 (d) N_2O, O_3.
4. It is possible to obtain oxygen from air by fractional distillation because **[CBSE-PMT 1989]**
   (a) oxygen is in a different group of the periodic table from nitrogen
   (b) oxygen is more reactive than nitrogen
   (c) oxygen has higher b.p. than nitrogen
   (d) oxygen has a lower density than nitrogen.
5. Which would quickly absorb oxygen ? **[CBSE-PMT1991, 92]**
   (a) Alkaline solution of pyrogallol
   (b) Conc. H_2SO_4
   (c) Lime water
   (d) Alkaline solution of $CuSO_4$
6. Oleum is **[CBSE-PMT 1991]**
   (a) Castor Oil (b) Oil of vitriol
   (c) Fuming H_2SO_4 (d) None of them
7. A certain compound (X) when treated with copper sulphate solution yields a brown precipitate. On adding hypo solution, the precipitate turns white. The compound is
   (a) K_2CO_3 (b) KI **[CBSE-PMT 1994]**
   (c) KBr (d) K_3PO_4
8. Polyanion formation is maximum in **[CBSE-PMT 1994]**
   (a) Nitrogen (b) Oxygen
   (c) Sulphur (d) Boron
9. The acid which has a peroxy linkage is **[CBSE-PMT 1994]**
   (a) Sulphurous acid (b) Pyrosulphuric acid
   (c) Dithionic acid (d) Caro's acid
10. About 20 km above the earth, there is an ozone layer. Which one of the following statements about ozone and ozone layer is true? **[CBSE-PMT 1995]**
    (a) ozone has a triatomic linear molecule
    (b) it is harmful as it stops useful radiation
    (c) it is beneficial to us as it stops U.V radiation
    (d) conversion of O_3 to O_2 is an endothermic reaction
11. By passing H_2S gas in acidified $KMnO_4$ solution, we get **[CBSE-PMT 1995]**
    (a) S (b) K_2S
    (c) MnO_2 (d) K_2SO_3
12. Oxidation of thiosulphate by iodine gives **[CBSE-PMT 1996]**
    (a) tetrathionate ion (b) sulphide ion
    (c) sulphate ion (d) sulphite ion
13. During its reactions, ozone **[CBSE-PMT 1999]**
    (a) can only combine with hydrogen atoms
    (b) accepts electrons
    (c) loses electrons
    (d) shows the role of electrons to be irrelevant
14. Which of the following is the most basic oxide?
    (a) Sb_2O_3 (b) Bi_2O_3 **[CBSE-PMT 2006]**
    (c) SeO_2 (d) Al_2O_3
15. Which one of the following compounds is a peroxide ? **[CBSE-PMT 2010]**
    (a) KO_2 (b) BaO_2
    (c) MnO_2 (d) NO_2
16. Match List - I (substances) with List - II (processes) employed in the manufacture of the substances and select the correct option. **[CBSE-PMT 2010]**

List - I **Substances**	**List - II** **Processes**
(A) Sulphuric acid	(i) Haber's process
(B) Steel	(ii) Bessemer's process
(C) Sodium hydroxide	(iii) Leblanc process
(D) Ammonia	(iv) Contact process

Options:

	(A)	(B)	(C)	(D)
(a)	(iv)	(ii)	(iii)	(i)
(b)	(i)	(iv)	(ii)	(iii)
(c)	(i)	(ii)	(iii)	(iv)
(d)	(iv)	(iii)	(ii)	(i)

17. Which of the following oxide is amphoteric ? **[CBSE-PMT 2011 M]**
    (a) SnO_2 (b) CaO (c) SiO_2 (d) CO_2
18. Sulphur trioxide can be obtained by which of the following reaction : **[CBSE-PMT 2012 S]**
    (a) $CaSO_4 + C \xrightarrow{\Delta}$ (b) $Fe_2(SO_4)_3 \xrightarrow{\Delta}$
    (c) $S + H_2SO_4 \xrightarrow{\Delta}$ (d) $H_2SO_4 + PCl_5 \xrightarrow{\Delta}$

19. Roasting of sulphides gives the gas X as a by product. This is colorless gas with choking smell of burnt sulphur and caused great damage to respiratory organs as a result of acid rain. Its aqueous solution is acidic, acts as a reducing agent and its acid has never been isolated. The gas X is :
(a) SO_2 (b) CO_2 **[NEET 2013]**
(c) SO_3 (d) H_2S

20. Which of the following does not give oxygen on heating?
(a) $Zn(ClO_3)_2$ (b) $K_2Cr_2O_7$ **[NEET 2013]**
(c) $(NH_4)_2Cr_2O_7$ (d) $KClO_3$

21. Which one of the following is an amphoteric oxide ? **[AIEEE 2003]**
(a) Na_2O (b) SO_2
(c) B_2O_3 (d) ZnO

22. KO_2 (potassium super oxide) is used in oxygen cylinders in space and submarines because it **[AIEEE 2002]**
(a) absorbs CO_2 and increases O_2 content
(b) eliminates moisture
(c) absorbs CO_2
(d) produces ozone.

23. Excess of KI reacts with $CuSO_4$ solution and then $Na_2S_2O_3$ solution is added to it. Which of the statements is incorrect for this reaction ? **[AIEEE 2004]**
(a) $Na_2S_2O_3$ is oxidised
(b) CuI_2 is formed
(c) Cu_2I_2 is formed
(d) Evolved I_2 is reduced

24. Which of the following statements regarding sulphur is incorrect? **[AIEEE 2011]**
(a) S_2 molecule is paramagnetic.
(b) The vapours at 200°C consists mostly of S_8 rings.
(c) At 600°C the gas mainly consists of S_2 molecules.
(d) The oxidation state of sulphur is never less than +4 in its compounds.

25. Aqueous solution of $Na_2S_2O_3$ on reaction with Cl_2 gives – **[IIT-JEE 2008]**
(a) $Na_2S_4O_6$ (b) $NaHSO_4$ (c) NaCl (d) NaOH

Exercise-4 | Applied MCQs

1. When SO_2 gas is passed through an acidified solution of $K_2Cr_2O_7$
(a) the solution becomes blue
(b) the solution becomes colourless
(c) SO_2 is reduced
(d) green $Cr_2(SO_4)_3$ is formed

2. $FeCl_3$ solution on reaction with SO_2 changes to
(a) $FeCl_2$ (b) $Fe_2(SO_4)_3$
(c) $Fe_2(SO_3)_3$ (d) $FeSO_4$

3. A considerable part of the harmful ultraviolet radiation of the sun does not reach the surface of the earth . This is because high above the earth's atmosphere there is a layer of
(a) CO_2 (b) hydrogen
(c) ozone (d) ammonia

4. On passing H_2S through acidified $FeCl_3$ solution $FeCl_3$ is converted into
(a) $FeCl_2$ (b) $Fe_2(SO_4)_3$
(c) FeS (d) $FeSO_4$

5. H_2SO_4 is added while preparing a standard solution of Mohr's salt to prevent
(a) hydration (b) reduction
(c) hydrolysis (d) complex formation

6. Concentrated H_2SO_4 is not used to prepare HBr from KBr because it
(a) oxidizes HBr
(b) reduces HBr
(c) causes disproportionation of HBr
(d) reacts too slowly with KBr

7. Which reaction represents the oxidizing behaviour of H_2SO_4
(a) $2PCl_5 + H_2SO_4 \rightarrow 2POCl_3 + 2HCl + SO_2Cl_2$
(b) $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$
(c) $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$
(d) $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$

8. Which characteristic is not correct about H_2SO_4 ?
(a) Reducing agent (b) Oxidising agent
(c) Sulphonating agent (d) Highly viscous

9. Which of the following is a saline oxide ?
(a) Na_2O_2 (b) BaO_2
(c) Na_2O (d) Fe_2O_3

10. In the manufacture of H_2SO_4 the nitrated acid from the Gay-Lussac's tower is chemically
(a) $H_2SO_4.NO_2$ (b) $H_2SO_4.NO$
(c) $H_2SO_4.2NO$ (d) $HSO_4.NO$

11. Potassium chlorate on heating with conc H_2SO_4 gives
(a) chlorine dioxide (b) $HClO_4$
(c) $KHSO_4$ (d) All of these

12. Sulphur forms the chlorides S_2Cl_2 and SCl_2. The equivalent mass of sulphur in SCl_2 is 16g /mol . Therefore the equivalent mass of sulphur in S_2Cl_2 is
(a) 32 g / mol (b) 16 g /mol
(c) 64 g/mol (d) 8 g/ mol

13. Reagent used to distinguish H_2O_2 and O_3 is
(a) PbS (b) starch and iodine
(c) $KMnO_4$ (d) bleaching powder

14. Which of the following does not react with AgCl

(a) $Na_2S_2O_3$ (b) NH_4OH
(c) $NaNO_3$ (d) Na_2CO_3

15. When KBr is treated with conc. H_2SO_4 reddish brown gas is evolved . The gas is

(a) Br_2 (b) $Br_2 + HBr$
(c) NO_2 (d) H_2O_2

16. One gas bleaches the colour of the flowers by reduction while the other by oxidation. The gases are

(a) CO and CO_2 (b) H_2S and Br_2
(c) SO_2 and Cl_2 (d) NH_3 and SO_3

17. Which oxide is of different type than others

(a) MnO_2 (b) PbO_2
(c) TiO_2 (d) Na_2O_2

18. In which reaction does SO_2 act as oxidising agent

(a) Acidified $KMnO_4$ (b) Acidified $K_2Cr_2O_7$
(c) Acidified C_2H_5OH (d) H_2S

19. Hydrogen sulphide reacts with lead acetate forming a black compound which reacts with H_2O_2 to form another compound . The colour of the compound is

(a) black (b) yellow
(c) white (d) pink

20. Hydrolysis of one mole of peroxodisulphuric acid produces

(a) two moles of sulphuric acid
(b) two moles of peroxomonosulphuric acid
(c) one mole of sulphuric acid and one mole of peroxomonosulphuric acid
(d) one mole of sulphuric acid, one mole of peroxomonosulphuric acid and one mole of hydrogen peroxide.

21. Oxygen gas can be prepared from solid $KMnO_4$ by :

(a) treating the solid with H_2 gas
(b) strongly heating the solid
(c) dissolving the solid in dil. H_2SO_4
(d) dissolving solid in dil. HCl

22. Which of the following statements is correct :

(a) Ozone is a resonance hybrid of oxygen
(b) Ozone is an isomer of oxygen
(c) Ozone has no relationship with oxygen
(d) Ozone is an allotropic modification of oxygen

23. The crystals of ferrous sulphate on heating give :

(a) $FeO + SO_2 + H_2O$
(b) $FeO + SO_3 + H_2SO_4 + H_2O$
(c) $Fe_2O_3 + SO_2 + H_2SO_4 + H_2O$
(d) $Fe_2O_3 + H_2SO_4 + H_2O$

24. In the upper layers of atmosphere ozone is formed by the

(a) action of ultraviolet rays on oxygen
(b) action of electric discharge on oxygen molecules
(c) combination of oxygen molecules
(d) None of these

25. When sugar is treated with conc. sulphuric acid, the sugar is charred. In this process, sugar is

(a) reduced (b) oxidized
(c) sulphonated (d) dehydrated

26. H_2SO_4 and H_2SO_3 can be distinguished by the addition of :

(a) magnesium powder (b) $NaHSO_4$ solution
(c) $FeCl_3$ solution (d) litmus solution

27. Yellow ammonium sulphide is

(a) $(NH_4)_2S_8$ (b) $(NH_4)_2S$
(c) $(NH_4)_2S_x$ (d) $(NH_4)_2S_4$

Hints & Solutions

EXERCISE 1

2. Because oxygen do not have vacant d-orbitals.

4. Dioxygen (O_2) and ozone (O_3).

7. H_2S is a stronger reducing agent as compared to water. This is because S – H bond is weaker than O – H bond.

11. Bond angle is highest in H_2O (104.5) and minimum in H_2Te (90°)

13. This is because of O – H bond energy being higher than that of S – H bond energy.

14. The elements of group 16 are called chalcogens because many metals are found as oxides and sulphides and a few as selenides and tellurides.

17. **(d)** **18.** **(a)** **19.** **(a)** **20.** **(c)** **21.** **(d)** **22.** **(d)**
23. **(a)** **24.** **(c)** **25.** **(b)** **26.** **(c)**

EXERCISE 2

1. (a) Electron affinity increases from left to right in period and decreases from top to bottom in a group but electron affinity of O is less than S due to small size.

2. (d) All exhibit polymorphism

3. (a) Sulphur (see text)

4. (a) Po is monoatomic and has α and β metallic forms

5. (c) It is 8 (see general discussion).

6. (b) H_2S (see text)

7. (a) H_2Te (see text)

8. (a) H_2O (due to intermolecular H - bonding)

9. (d) SH–bond is weaker than, O–H bond. Hence H_2S will furnish more H^+ ions

10. (b) For hybridisation = $\frac{1}{2}$ (Number of valence electrons of central metal atom + Monovalent atoms + Negative charge – Positive charge) = $\frac{1}{2}(6 + 4 + 0 - 0) = 5$ (hence sp^3d.)

11. (c) Hybridisation is sp^3d^2, hence octahedral

12. (b)

13. (a) Hybridisation in $SCl_4 = \frac{1}{2}(6+4+0-0) = 5$ sp^3d, similarly SO_4^{--} is sp^3 hybridised $Ni(CO)_4$ O.S. of Ni is 0. Electronic configuration $[Ar]3d^84s^2$ CO strong ligand hence $[Ar]3d^{10}$ $\therefore$ Hybridisation sp^3 and $Ni(Cl)_4^{2-}$ is sp^3.

14. (b) $:\ddot{\underset{..}{F}} - \ddot{\underset{..}{O}} - \ddot{\underset{..}{F}}:$ Number of bond pairs = 2, Number of lone pairs = 8.

15. (c) H_2O is sp^3 hybridised

16. (a) In SO_3, sp^2 hybridisation

17. (b) It is Caro's acid

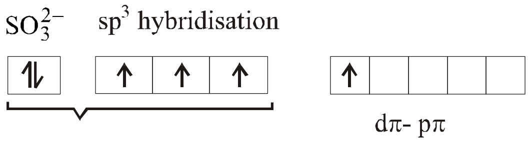
18. (d) See oxy acids of sulphur

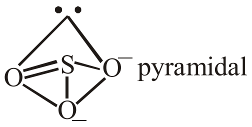
19. (c) See oxy acids of sulphur

20. (c) O. N. of S in $H_2S_2O_8$ is + 6 (see structure and calculate)

21. (c) See structures of oxy acids of sulphur

22. (b) $p\pi - d\pi$ bonding is present in SO_3^{2-}, N, B, C have no vacant d atomic arbitals.





pyramidal

23. (c) It is H_2SO_5 (see text)

24. (a) $2H_2S + O_2 \rightarrow 2H_2O + 2S$

25. (b) Oxygen being more electronegative

26. (b) $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$

27. (c) See text it is paramagnetic with two unpaired electrons

28. (c) Total number of electrons in O_2 is 16. It has 2 unpaired electrons, the rest 14 are paired.

29. (c) O_2 is paramagnetic and O_3 is diamagnetic

30. (b) Bond order = $\frac{1}{2}$(Number of bonding electrons – antibonding electrons)

$$O_2 = \frac{10-6}{2} = 2; O_2^+ = \frac{10-5}{2} = 2.5; O_2^- = \frac{10-7}{2} = 1.5;$$

$$O_2^{2-} = \frac{10-8}{2} = 1$$

Highest bond order 2.5 O_2^+

31. (b)

32. (c) Oxides of alkali and alkaline earth metals are basic Al_2O_3 is amphoteric hence acidic in comparision to others.

33. (b) ZnO is amphoteric (see oxides).

34. (c) $2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$

35. (c) $HO.SO_2OH + 2PCl_5 \rightarrow ClSO_2Cl + 2POCl_3 + 2HCl$

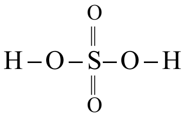
Sulphuryl chloride

36. (b) $2Ag + 2H_2SO_4 \rightarrow 2H_2O + SO_2 + Ag_2SO_4$.

Au, Pt does not react. Pb forms insoluble $PbSO_4$

37. (a) $HCOOH \rightarrow H_2O + CO$ (Dehydration)

38. (c) See structure of acids

39. (a) 

$H-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-H$; 6σ & 2π

40. (b) In $\overset{2+}{Fe}|\overset{2-}{S_2}$ O.N of S is -1

41. (b) $Br_2 + SO_2 + 2H_2O \rightarrow 2HBr + H_2SO_4$

42. (b) In SO_2, S is in +4 O.S. which can be increased or decreased by gain or loss of electrons. Hence SO_2 can act as both oxidising and reducing agent.

43. (c) $Cu + 2H_2SO_4(conc) \rightarrow CuSO_4 + SO_2 + 2H_2O$

44. (a) Due to large enthalpy of vaporisation SO_2 can be used as refrigerant

45. (d) $2SO_2 + 2H_2O + O_2 \rightarrow 2H_2SO_4$. It reacts with marble ($CaCO_3$) causing damage.

46. (b) 2σ, one π see structure

47. (c) $SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$. Bleaching action is due to reduction.

48. (c) $COCl_2$ does not contain metal others give ZnS, CdS CuS

49. (b) $2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow$

$K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$

50. (c) See preparation

$6NaOH + 4S \rightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$

51. (c) $Na_2S_2O_3 + Cl_2 + H_2O \rightarrow 2HCl + S + Na_2SO_4$

52. (d) $Na_2S_4O_6$

Let O.N. of S be x; $2 \times (+1) + 4 \times (x) + 6 \times (-2) = 0$

$\therefore x = \frac{5}{2}$

53. (b) Ans is (Te)

54. (d) All (see text)

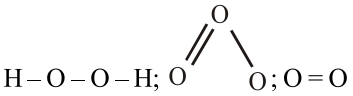
55. (c) CO_2 in which C cannot increase its O.N.

56. (d) $K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \rightarrow$

$2K_2SO_4 + FeSO_4 + 6CO + 3(NH_4)_2SO_4$

57. (b) $H_2O_2 > O_3 > O_2$

B. O. is 1, 1.5 and 2 respectively.



$H-O-O-H;\ O\overset{O}{\diagup\!\!\diagup\;\diagdown}O;\ O=O$

58. (a) SO_2 is sp^2 hybridised whereas others are sp^3 hybridised.

59. (a) A base can donote electrons hence all are bases but SO_3^{2-} can be oxidised to SO_4^{2-} hence it is reducing also.

60. (a) $4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2$

$SO_2 + H_2O \rightarrow H_2SO_3 \rightleftharpoons 2H^+ + SO_3^{2-}$

It is dibasic

EXERCISE 3

1. **(c)** Undecomposed AgBr forms a soluble complex with hypo

$AgBr + 2Na_2S_2O_3 \rightarrow \underset{\text{soluble complex}}{Na_3[Ag(S_2O_3)_2]} + NaBr$

It is washed with water and the image is fixed

2. **(b)** $S + O_2 \xrightarrow{\quad} SO_2$ (burns with blue light)

$4Na + O_2 \xrightarrow{\quad} 2NaO$

(burns with yellow light)

$P_4 + 3O_2 \xrightarrow{\quad} P_4O_6$

$P_4 + 5O_2 \xrightarrow{\quad} P_4O_{10}$

$Cl + O_2 \xrightarrow{\quad}$ No reaction

Chlorine does not react directly with oxygen.

3. **(b)** Alkaline pyrogallol absorbs O_2 and oil of cinnamon absorbs O_3.

4. **(c)** Air is liquified by making use of the joule-Thomson effect (cooling by expansion of the gas). Water vapour and CO_2 are removed by solidification. The remaining constituents of liquid air i.e., liquid oxygen and liquid nitrogen are separated by means of fractional distillation (b.p. of $O_2 = -183°C$: b. P. of $N_2 = -195.8°C$).

5. **(a)** Alkaline solution of pyrogallol absorbs oxygen quickly.

6. **(c)** Oleum is $H_2S_2O_7$ ($H_2SO_4 + SO_3$) which is obtained by dissolving SO_3 in H_2SO_4 and is called fuming sulphuric acid.

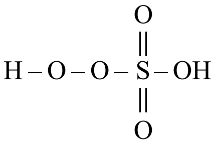
7. **(b)** KI reacts with $CuSO_4$ solution to produce cuprous iodide (white precipitate) and I_2 (which gives brown colour) Iodine reacts with hypo ($Na_2S_2O_35H_2O$) solution. Decolourisaiton of solution shows the appearance of white precipitate.

$2CuSO_4 + 4KI \rightarrow 2K_2SO_4 + \underset{\substack{\text{Cuprous iodide}\\\text{(White ppt.)}}}{2CuI} + \underset{\substack{\text{(Brown colour}\\\text{in solution)}}}{I_2}$

$2Na_2S_2O_3 + I_2 \xrightarrow{\quad} \underset{\substack{\text{Sod. tetra}\\\text{thionate}\\\text{(colourless)}}}{Na_2S_4O_6} + 2NaI$

8. **(c)** Due to greater tendency for catenation, sulphur shows property of polyanion formation to a greater extent. For example, in polysulphides such as $S_3^{2-}, S_4^{2-}, S_5^{2-}$

9. **(d)** Caro's acid is H_2SO_5 which contains one $S-O-O-H$ peroxy linkage. It is also known as permonosulphuric acids.



$$H-O-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OH$$

Caro's acid

10. **(c)** Ozone layer is beneficial to us, because it stops harmful ultraviolet radiations to reach the earth.

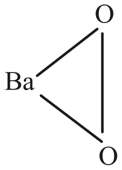
11. **(a)** $2KMnO_4 + 5H_2S + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5S + 8H_2O.$
Thus in this reaction sulphur (S) is produced.

12. **(a)** $2S_2O_3^{-2} + I_2 \rightarrow \underset{\text{Tetrathionate}}{S_4O_6^{-2}} + 2I^-$

13. **(a)** Since ozone can easily lose oxygen atom (nascent oxygen), it acts as a powerful oxidising agent, and hence reacts with hydrogen atoms.

14. **(b)** More the oxidation state of the central atom (metal) more is its acidity. Hence SeO_2 (O. S. of Se = +4) is acidic. Further for a given O.S., the basic character of the oxides increases with the increasing size of the central atom. Thus Al_2O_3 and Sb_2O_3 are amphoteric and Bi_2O_3 is basic.

15. **(b)**



16. **(a)**

(A) Sulphuric acid	(iv) Contact process
(B) Steel	(ii) Bessemer's process
(C) Sodium hydroxide	(iii) Leblanc process
(D) Ammonia	(i) Haber's process

17. **(a)** SnO_2 is an amphoteric oxide because it reacts with acids as well as with bases to form corresponding salts.
$SnO_2 + 2H_2SO_4(\text{conc}) \longrightarrow Sn(SO_4)_2 + 2H_2O$
$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$

18. **(b)** $Fe_2(SO_4)_3 \xrightarrow[\Delta]{} Fe_2O_3 + 3SO_3$

19. **(a)** Based on the features given above the gas must be SO_2.

20. **(c)** $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

$Zn(ClO_3)_2 \xrightarrow{\Delta} ZnCl_2 + 3O_2$

$2\,KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$

$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$

21. **(d)** Na_2O (basic), SO_2 and B_2O_3 (acidic) and ZnO is amphoteric

22. **(a)** $2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2 + O_2$ eliminates moisture.

23. **(b)** $4K\overset{-1}{I} + 2CuSO_4 \rightarrow \overset{0}{I_2} + Cu_2I_2 + 2K_2SO_4$

$\overset{0}{I_2} + 2Na_2\overset{2+}{S_2}O_3 \rightarrow Na_2\overset{-2.5}{S_4}O_6 + 2Na\overset{-1}{I}$

In this CuI_2 is not formed.

24. **(d)** Oxidation state of sulphur varies from – 2 to + 6 in its various compounds.

25. **(b)** The following reaction occurs
$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2\,NaHSO_4 + 8HCl.$

EXERCISE 4

1. **(d)** $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + H_2O$

2. **(a)** $2FeCl_3 + SO_2 + 2H_2O \rightarrow 2FeCl_2 + H_2SO_4 + 2HCl$

3. **(c)** U.V rays are absorbed by O_3

4. **(a)** $2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S$

5. **(c)** $FeSO_4$ is hydrolysed to Fe $(OH)_2$ which is converted back to $FeSO_4$

$FeSO_4 + 2H_2O \rightarrow Fe(OH)_2 + H_2SO_4$

6. **(a)** $2HBr + H_2SO_4 \rightarrow Br_2 + 2H_2O + SO_2$ HBr is oxidised to Br_2

7. **(d)** $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$ (HI is oxidised to I_2) (H_2SO_4 is reduced to SO_2)

8. **(a)** In H_2SO_4, the S atom is present in its highest oxidation state of +6. Hence H_2SO_4 can act an oxidant only by gain of electrons

9. **(c)** Oxides which are more ionic in nature (salt - like) are known as saline oxides e.g. oxides of alkali metals

10. **(d)** $2H_2SO_4 + NO + O_2 \rightarrow \underset{\text{Nitrated acid}}{2NO.HSO_4} + H_2O$

11. **(d)** $3KClO_3 + 3H_2SO_4 \rightarrow 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$

12. **(a)** Apply the formula $\frac{W_A}{E_A} = \frac{W_B}{E_B}; \frac{64}{E} = \frac{71}{35.5}, \therefore E = 32$

13. **(c)** The pink colour of $KMnO_4$ is decolorised by H_2O_2 and not by O_3

$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$

$H_2O_2 + O \rightarrow H_2O + O_2$

14. **(c)** There is no reaction with $NaNO_3$ and AgCl while all other react to give $Ag_2S_2O_3$, $[Ag(NH_3)_2]Cl$ and Ag respectively

15. (a) $2KBr + 3H_2SO_4 \rightarrow 2KHSO_4 + SO_2 + Br_2 + 2H_2O$

16. (c) SO_2 bleaches by reduction and Cl_2 by oxidation

17. (d) N_2O_2 is peroxide while others are dioxides

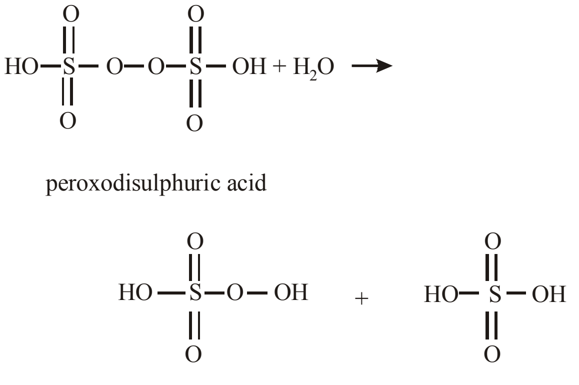
18. (d) $SO_2 + 2H_2S \rightarrow 2H_2O + 3S.$

The O.S of S changes from – 2 to 0 by loss of electrons.
Hence SO_2 is oxidising

19. (c) $(CH_3COO)_2Pb + H_2S \rightarrow PbS + 2CH_3COOH$

$PbS + 4H_2O_2 \rightarrow \underset{\text{White}}{PbSO_4} + 4H_2O$

20. (c)



$HO-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}}-O-O-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}}-OH + H_2O \longrightarrow$

peroxodisulphuric acid

$HO-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}}-O-OH + HO-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}}-OH$

peroxomonosulphuric acid sulphuric acid

21. (b) $2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + 4MnO_2 + O_2$

22. (d) Ozone is an allotrope of oxygen.

23. (c) $FeSO_4.7H_2O \rightarrow FeSO_4 + 7H_2O$

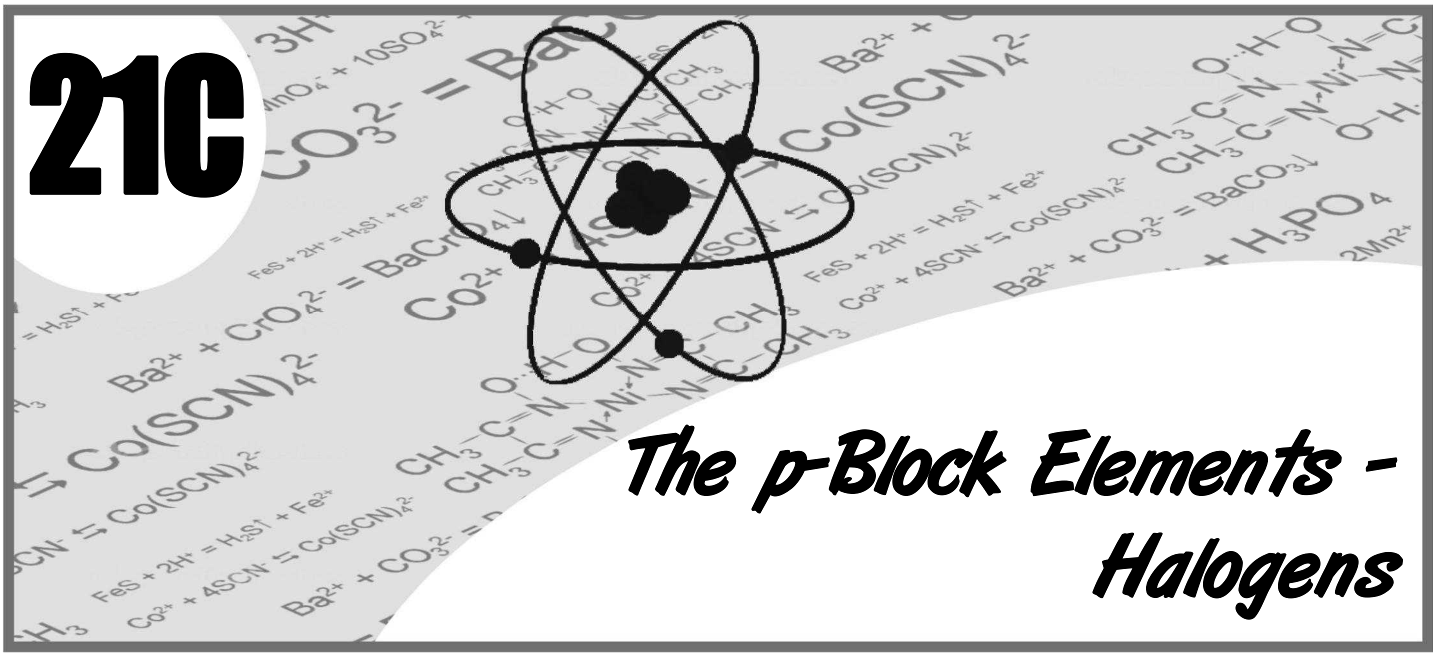
$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$

24. (a) $3O_2 \xrightarrow{UV} 2O_3$

25. (d) $C_{12}H_{22}O_{11} \xrightarrow[\Delta]{H_2SO_4} \underset{\text{black}}{12C} + 11H_2O$

26. (c) $FeCl_3$ acts as oxidant and H_2SO_3 as reductant.

27. (c) Yellow ammonium sulphide is $(NH_4)_2S_x$



21C

The p-Block Elements - Halogens

GENERAL CHARACTERISTICS :

The group 17 of periodic table consists of five elements **fluorine, chlorine, bromine, iodine** and **astatine** and are known as halogens (sea salt forming elements). Astatine is artificially prepared by radioactive element.

1. **Electronic configuration -**

Element	*Symbol*	*At No.*	*Valence shell electronic configration*
Fluorine	F	9	$[\mathrm{He}]\,2s^2 2p^5$
Chlorine	Cl	17	$[\mathrm{Ne}]\,3s^2 3p^5$
Bromine	Br	35	$[\mathrm{Ar}]\,3d^{10},4s^2 4p^5$
Iodine	I	53	$[\mathrm{Kr}]4d^{10},5s^2 5p^5$
Astatine	At	85	$[\mathrm{Xe}]\,4f^{14},3d^{10},6s^2 6p^5$

2. **Physical State** - Intermolecular forces in halogens are weak and increase down the group. Thus F_2, Cl_2 are **gases,** Br_2 ***volatite liquid*** and I_2 ***volatile solid.***
3. **Atomicity** - All halogens are diatomic in nature.
4. **Abundance -** Being very reactive in nature they are not found free in nature. Their presence in earth's crust follows the order.

   $F_2 > Cl_2 > Br_2 > I_2 > At$
5. **Colour -** They absorb light in the visible range forming excited states and thus they are coloured in nature.

F_2	Cl_2	Br_2	I_2
Pale yellow	yellowish green	reddish brown	deep violet

6. **Metallic Character -** All the elements are non metals and metallic character increases down the group.
7. **Oxidation State -**

F_2	Cl_2	Br_2	I_2	At
-1	-1 to + 6	-1 to +6	-1 to +7	-1,+1,+5

8. **Bond energy and bond length -** The bond length increases from fluorine to iodine

	F-F	*Cl-Cl*	*Br-Br*	*I-I*
Bond length (Å)	1.42	1.99	2.28	2.67
Bond energy (kJ mol^{-1})	158.8	242.6	192.8	151.1

   Due to small size the interelectronic repulsions between non bonding electrons are high in case of fluorine which results in weakening of F-F bond.
9. **Density** - It increases down the group in a regular fashion and follows the order F > Cl > Br > I

   (i) Atomic radii ***(ii) Ionic radii***

   (iii) atomic volume ***(iv) density***

   (v) Electronegativity ***(vi) Oxidising power***

   (vii) Reactivity ***(viii) Affinity for hydrogen***

   (ix) Reduction potential

   (x) Solubility, all follow the above given order.
10. **Ionisation potential -** The ionisation potential of halogens is very high and value decreases down the group. Thus iodine also forms I^+ and I^{3+} and forms compounds like ICl, ICN, IPO_4. In molten state these compounds conduct electricity and show ionic character.
11. **Electron affinity -** The halogens have the high values for electron affinity following the order.

    Cl > F > Br > I

    Due to small size of fluorine (hence high electron density) the extra electron to be added feels more electron - electron repulsion. Therefore fluorine has less value for electron affinity than chlorine.
12. **Solubility** - Halogens are soluble in water which follow the order

$F_2 > Cl_2 > Br_2 > I_2$

The solubility of iodine in water is enhanced in presence of KI

$KI + I_2 \rightleftharpoons KI_3 \rightleftharpoons K^+ + I_3^-$

In organic solvents like CS_2, $CHCl_3$ and CCl_4 the Cl_2, Br_2 and I_2 are more soluble and give coloured solutions. Thus Cl_2 gives yellow, Br_2 gives brown and I_2 gives violet solution.

13. **Properties of halide ions (X^-) -** Some properties of halide ions follow the following order

$F^- > Cl^- > Br^- > I^-$

← Basic character

← Reducing character

← Heat of hydration

14. **Nature of bonds with other elements -** Halogens with metals of low ionisation potentials form ionic bonds. The ionic character follows the order

M - F > M - Cl > M - Br > M - I

The more the ionic character, the more is the mp and bp of halides .

Halogens with metals of high ionisation potentials (transition metals) and non metals form covalent bond.

COMPOUNDS OF HALOGENS :

1. **Hydracids (HX) -** All halogens directly combine with hydrogen to form HX known as hydracid.

$H_2 + X_2 \rightarrow 2HX$

HF and HCl can be obtained by heating fluorides and chlorides with conc. H_2SO_4

$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$

$2\,NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$

HBr and HI are strong reducing agents in nature and reduce conc. H_2SO_4 and cannot be prepared by this method.

$2HBr\ (\text{or } 2HI) + H_2SO_4 \rightarrow Br_2\ (\text{or } I_2) + 2H_2O + SO_2$

Hence they are prepared by hydrolysis of phosphorous halides

$PX_3 + 3H_2O \rightarrow H_3PO_3 + 3HX\ (X = Br, I)$

Properties - HF is a low boiling liquid due to intermolecular hydrogen bonding, while HCl, HBr, HI are gases. The bpt follows the trend HF > HI > HBr > HCl

Some other properties observe the following trend :

HI > HBr > HCl > HF

← Acid Strength

← Reducing character

← Bond length

Trend for following properties : HI < HBr < HCl < HF

Thermal stability →

Dipole moment →

Bond strength →

Stability →

Itching of glass : Glass contains silica which reacts with HF.

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O + 2HF \rightarrow \underset{\text{Hydro fluorosilicic acid}}{H_2SiF_6}$$

2. ***Oxy acids -*** All form oxy acids of the type HOX, HXO_2, HXO_3 and HXO_4 as shown below

Name	*O. N. of X*	*Fluorine*	*Chlorine*	*Bromine*	*Iodine*	*Salt's name*
Hypohalous acid, HXO	+1	HOF	HOCl	HOBr	HOI	Hypohalite
Halous acid, HXO_2	+3	-	$HClO_2$	-	-	Halite
Halic acid, HXO_3	+5	-	$HClO_3$	$HBrO_3$	HIO_3	Halate
Perhalic acid, HXO_4	+7	-	$HClO_4$	$HBrO_4$	HIO_4	Perhalate

Trend for following properties

$HXO_4 > HXO_3 > HXO_2 > HXO$

← Thermal stability

← Acid strength

Oxidising nature →

The conjugate bases obtained from above acids are XO^-, XO_2^-, XO_3^- and XO_4^-. Their stability increases with the increase of oxygen atoms due to greater chances of dispersal of negative charge. The more is the stability of conjugate base, the more is the acid character.

$XO_4^- > XO_3^- > XO_2^- > XO^-$

(i) ***Hypohalous acids** (HOX)* - They are formed in aqueous solution by disproportionation of halogens

$X_2 + H_2O \rightleftharpoons HOX + HX$

Acid character and thermal stability follows the order

HClO > HBrO > HIO

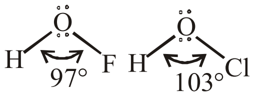
Hypohalites disproportionate in aqs. solution to halides and halates.

$3\,^-OX \rightleftharpoons 2X^- + XO_3^-$

Rate of disproportionation

$IO^- > BrO^- > ClO^-$

The structure of HClO and HFO are



Bleaching powder $CaOCl_2$ is a mixed salt of HOCl and HCl

(ii) ***Halic acids*** - $HClO_3$ and $HBrO_3$ exist in aqueous solution and HIO_3 is a white solid. The stability follows the order

$HIO_3 > HBrO_3 > HClO_3 \rightarrow$ Acid strength

They are strong oxidising in nature

$XO_3^- + 5X^- + 6H^+ \rightarrow 3X_2 + 3H_2O$

Their salts, $NaClO_3$ is a powerful weed killer and $KClO_3$ ***(Berthelot's salt)*** is used in fire works and matches as oxidising agent.

(iii) ***Perhalic acids*** - Perhalates are obtained by electrolytic oxidation of halates

$$4ClO_3^- \rightarrow Cl^- + 3ClO_4^-,\quad 4IO_3^- \rightarrow I^- + 3IO_4^-$$

Perborate is obtained by oxidation with F_2 in basic solution

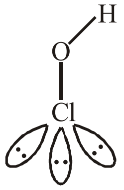
$$BrO_3^- + F_2 + 2OH^- \rightarrow BrO_4^- + 2F^- + H_2O$$

They are strong oxidising agents following the order

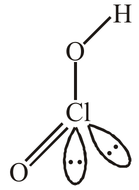
$$ClO_4^- < BrO_4^- > IO_4^-$$

Structure of oxyacids

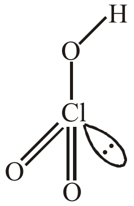
(a) Hypochlorous acid ($HOCl$)



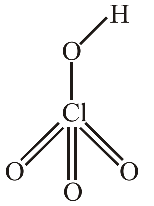
(b) Chlorous acid ($HClO_2$)



(c) Chloric acid ($HClO_3$)



(d) Perchloric acid ($HClO_4$)



3. ***Oxides -*** All form oxides of different types. Halogens do not combine directly with oxygen hence they are prepared by indirect methods. They are

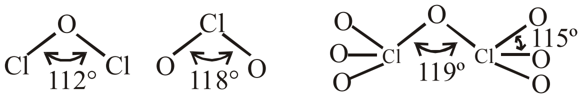
OF_2
O_2F_2

Cl_2O
Cl_2O_3
ClO_2
Cl_2O_6
Cl_2O_7

Br_2O
BrO_2
BrO_3

I_2O_4
I_2O_5

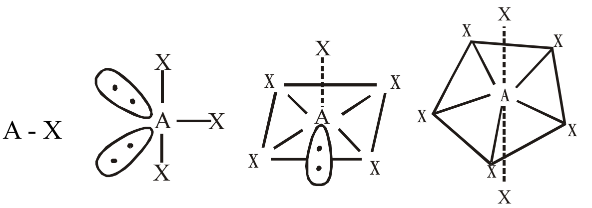
Structure of some oxides



All oxides are powerful oxidising agents and decompose with explosion when heated or hit.

4. ***Interhalogen compounds -*** Halogens combine among themselves to form compounds known as interhalogens or interhalogen compounds of the type AX, AX_3, AX_5 and AX_7. Their structure and hybridisation is as follows:

AX type sp^3	*AX_3 sp^3d*	*AX_5 sp^3d^2*	*AX_7 sp^3d^3*
Linear	*T-shaped*	*Square pyramidal*	*Pentagonal bipyramidal*



Examples IBr, BrCl, ClF_3, BrF_3, ICl_3 BrF_5, IF_5, IF_7 ClF, BrF, ICl

Properties - They are covalent, more reactive, strong oxidising and diamagnetic in nature.

Preparation - The are prepared by direct combination of halogens

$$Cl_2 + F_2 \xrightarrow{500K} 2ClF$$

By the action of halogens on lower interhalogen

$$ClF_3 + F_2 \rightarrow ClF_5$$

Polyhalide ions - The ions containing more than two halogen atoms are known as polyhalide ions eg.

$$KI + I_2 \rightarrow KI_3 \rightleftharpoons K^+ + I_3^-$$

Other examples are

$$Br_3^-, Cl_3^-, ICl_2^-, IBr_2^-, ICl_4^-, BrF_4^-, I_5^-, IF_6^-$$

Iodine Cation - Iodine also forms I^+ and I^{3+} cations due to less ionisation energy as $(CH_3COO)_3I$, $I(ClO_4)_3$ and IPO_4 have been isolated.

Pseudohalogens and pseudohalides - The substances behaving like halogens are known as pseudohalides.

Some examples are

Pseudo halogen	***Pseudohalide ion***
$(CN)_2$ Cyanogen	CN^- Cyanide
$(OCN)_2$ Oxycyanogen	OCN^- Cyanate
$(SCN)_2$ Thiocyanogen	SCN^- Thiocyanate
$(SeCN)_2$ Selenocynogen	$SeCN^-$ Selenocyanide
	NCN^- Cyanamide
	N_3^- Azide

FLUORINE (SUPER HALOGEN) :

Discovered by *Moisson* 1886

Occurrence - In combined state it occurs as

1. Fluorspar CaF_2
2. Cryolite Na_3AlF_6 and
3. Fluorapatite $CaF_2.3Ca_3(PO_4)_2$.

It is present in small amounts in soil, river water, bones and teeth of animals.

Preparation

(1) ***Dennis method*** - By electrolysis of fused sodium or potassium hydrogen fluoride (dry) between graphite electrodes . (KHF_2 is known as **Fremy salt**)

$$KHF_2 \rightarrow KF + HF \qquad HF \rightarrow H^+ + F^-$$

$$2H^+ + 2e^- \rightarrow H_2 \text{ (At cathode)}$$

$$2F^- - 2e^- \rightarrow F_2 \text{ (At anode)}$$

(2) ***Whytlaw Gray's method*** - Electrolysis of fused KHF_2 is carried out in Cu cell (electrically heated) which serves the purpose of cathode, Anode is of graphite

(3) ***Modern method*** - Electrolysis of fused mixture of KF and HF is carried out in steel vessel (cathode). Anode is of graphite

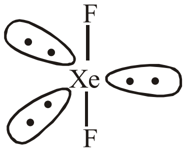
Properties **-** It is pale greenish yellow gas can be condensed to pale yellow liquid and then pale yellow solid. It is very reactive.

(1) ***Most active*** - It directly combines with metals and non metals eg Al, Mg, C, P, S, As, Sb, Br_2, I_2 etc to from fluorides, Cu and Hg form a protective coating of fluoride.

(2) ***Reaction with Xe*** - With Xenon it forms three definite halides

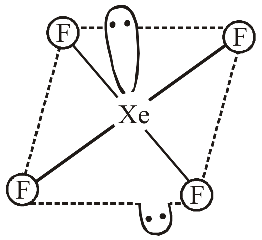
XeF_2, XeF_4 and XeF_6 having the following structure

XeF_2 hybridisation sp^3d



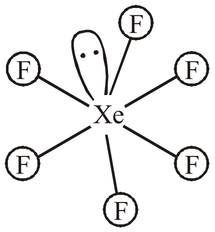
Linear symmetrical

XeF_4 hybridisation sp^3d^2



Square planar

XeF_6 sp^3d^3 hybridisation



Distorted octahedral

(3) ***With hydrogen even in dark*** -

$H_2 + F_2 \rightarrow 2HF \qquad \Delta H = -536\ kJ$

(4) ***With water*** - $2F_2 + 2H_2O \rightarrow 4HF + O_2$

$3F_2 + 3H_2O \rightarrow 6HF + O_3$

(5) ***Oxidising nature*** -

$KClO_3 + F_2 + H_2O \rightarrow KClO_4 + H_2F_2$

$2KCl + F_2 \rightarrow 2KF + Cl_2$

(6) ***With alkali*** - dil $2NaOH + 2F_2 \rightarrow F_2O + 2NaF + H_2O$

Conc. $4NaOH + 2F_2 \rightarrow O_2 + 4NaF + 2H_2O$

(7) ***With NH_3*** - $2NH_3 + 3F_2 \rightarrow N_2 + 6HF$ and some NF_3 (**not explosive**)

(8) ***With H_2S*** - $H_2S + 4F_2 \rightarrow SF_6 + 2HF$

(9) ***With hydrocarbons*** - It reacts with hydrocarbons violently eg CH_4

$CH_4 + 4F_2 \rightarrow 4HF + CF_4$

Hence fluorination is carried out in presence of N_2 (it dilutes F_2) and calalyst copper gauge.

Uses

(1) Fluoro derivatives are solvents, lubricants, refrigerants, fire extinguishers, fungicides, germicides, dyes and plastics etc.

(2) For separation of U^{235} by forming UF_6 from natural uranium

(3) Preparation of Teflon $(C_2F_4)_n$

FREONS :

Chlorofluoro compounds of methane and ethane are known as freons. They are extremely, unreactive, non corrosive, easily liquefiable compounds. Freon-12 (CCl_2F_2) is most common and prepared as

$$3CCl_4 + 2SbF_3 \xrightarrow{\Delta} 3CCl_2F_2 + 2SbCl_3$$

They are used as refrigerants and propellants .

Magic acid - $FSO_3H\ SbF_5$ is strongest acid and known as magic acid.

Chlorine :

It was discovered by *Scheele* by heating HCl acid (muriatic acid) with MnO_2 and named it oxymuriatic gas. *Davy* established its nature and called it chlorine.

Occurrence - Being very reactive does not occur free in nature. It is widely distributed as chlorides. Common salt NaCl is most important chloride present in sea water and as rock salt.

Preparation - By oxidation of Conc HCl

$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$

$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 2H_2O + 3Cl_2$

$CaOCl_2 + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2$

$NaOCl + 2HCl \rightarrow NaCl + H_2O + Cl_2$

$PbO_2 + 4HCl \rightarrow PbCl_2 + 2H_2O + Cl_2$

$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + 4H_2O + Cl_2$

In place of HCl mixture of (NaCl + Conc.H_2SO_4) can be used

$$2NaCl + MnO_2 + 3H_2SO_4 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2$$

Manufacture

(i) ***Weldon's process*** - By heating pyrolusite with Conc HCl

$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$

(ii) ***Deacon's process*** - In this process HCl is oxidised by O_2 in presence of $CuCl_2$ as catalyst at 400° C

$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$$

(iii) ***Electrolytic process*** - By the electrolysis of brine solution in Nelson cell

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$2Na^+ + 2\bar{e} \rightarrow 2Na + 2H_2O \rightarrow 2NaOH + H_2 \text{ (at cathode)}$$

$$2Cl^- - 2e^- \rightarrow 2Cl \rightarrow Cl_2 \text{ (at anode)}$$

Pure Chlorine **-** By heating $AuCl_3$ or $PtCl_4$ in hard glass tube

$$2AuCl_3 \xrightarrow{448K} \left[2AuCl + 2Cl_2\right] \xrightarrow{463K} 2Au + 3Cl_2$$

$$PtCl_4 \xrightarrow{873K} Pt + 2Cl_2$$

Properties **-** It is yellowish green gas. Collected by upward displacement of air, poisonous in nature, soluble in water. It's aqueous solution is known as chlorine water which on careful cooling gives chlorine hydrate $Cl_2.8H_2O$

(1) ***Action of water*** - $Cl_2 + H_2O \rightarrow HOCl + HCl$

$HOCl \rightarrow HCl + O$

Coloured matter + nascent O → colourless matter

The bleaching action of chlorine is due to oxidation by nascent [O].

(2) ***Action of Hydrogen*** - $H_2 + Cl_2 \xrightarrow[\text{Charcoal catalyst}]{\text{U.V light}} 2HCl$

They combine explosively but in presence of charcoal catalyst combination is smooth at room temperature

(3) ***Displacement reactions*** -

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

(4) ***Action of NaOH Cold*** -

$$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$$

Aqeous solution of NaOCl is called Javelle water. It is used as bleaching agent.hot and Conc.

$$6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

(5) ***Action of H_2S*** - $H_2S + Cl_2 \rightarrow 2HCl + S$

(6) ***Action of dry SO_2*** - $SO_2 + Cl_2 \rightarrow SO_2Cl_2$

(7) ***Action of CO*** - $CO + Cl_2 \rightarrow COCl_2$

(8) ***Oxidising properties*** - In aqueous solution Cl_2 acts as oxidising agent

$$SO_2 + Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$$

$$2FeSO_4 + Cl_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2HCl$$

$$Na_2S_2O_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl + S$$

(9) ***Reaction with ammonia*** -

(i) When ammonia is in excess

$$8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$$

(ii) When chlorine is in excess

$$NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$$

Uses **-** It is used as a (i) bleaching agent (ii) disinfectant (iii) in the manufacture of $CHCl_3$, CCl_4, DDT anti knock compounds, bleaching powder, poisonous gas phosgene ($COCl_2$), tear gas CCl_3NO_2 and mustard gas $ClC_2H_4SC_2H_4Cl$.

Euchlorine **-** It is a mixture of chlorine and chlorine dioxide and obtained by heating $KClO_3$ with conc. HCl

$$2KClO_3 + 4HCl \rightarrow 2KCl + Cl_2 + 2ClO_2 + 2H_2O$$

BROMINE :

It was discovered by Balard (1826)

Occurrence - In nature it occurs in combined state only as bromides of Na, K and Mg in sea water. Carnallite $KCl.MgCl_2.6H_2O$ contains some bromo carnallite $KBr.MgBr_2.6H_2O$ in Germany (Stass furt). In Chile and Mexico in silver mines as AgBr.

Preparation **-** Lab method -

(i) By heating mixture of potassium bromide maganese dioxide and conc H_2SO_4

$$2KBr + 3H_2SO_4 + MnO_2 \rightarrow$$
$$2KHSO_4 + MnSO_4 + 2H_2O + Br_2$$

(ii) By passing chlorine through solution of a bromide.

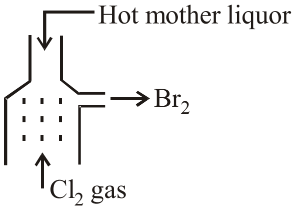
$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$

Manufacture -

(1) ***From carnallite*** - The mother liquor left after the crystallisation of chlorides from carnallite ($KCl.MgCl_2.6H_2O$) contains bromides of Na, K and Mg and is known as ***bittern***.

$$2KBr + Cl_2 \rightarrow KCl + Br_2$$

$$MgBr_2 + Cl_2 \rightarrow MgCl_2 + Br_2$$



Uncondensed vapour passed through tower packed with moist iron fillings when these are absorbed and yield ferrosoferric bromide.

$$3Fe + 4Br_2 \rightarrow Fe_3Br_8$$

Alternative method - By electrolysis of above mother liquor

$$MgBr_2 \rightarrow Mg^{++} + \left(2B\bar{r}\right) \rightarrow Br_2 + 2e^-$$

Even if some $MgCl_2$ is decomposed, the Cl_2 evolved reacts with $MgBr_2$ to liberate Br_2

(2) ***From sea water*** - The sea water is concentrated when salts separate as crystals. The mother liquor contains $MgBr_2$ and is treated as above to get bromine.

In America sea water is acidified with 0.1%H_2SO_4 and chlorine is passed through it. The vapours liberated is passed in Na_2CO_3 solution.

$$MgBr_2 + Cl_2 \rightarrow MgCl_2 + Br_2$$

$$3Br_2 + 3Na_2CO_3 \rightarrow 5NaBr + NaBrO_3 + 3CO_2$$

$$5NaBr + NaBrO_3 + 6HCl \rightarrow 6NaCl + 3H_2O + 3Br_2$$

Properties - Bromine is a heavy dark brown liquid gives irritating vapour. Density 3.2g/ml bpt 58.5°C and fpt- 7°C. It is soluble in water and gives bromine water about 3.6% at 20° C.

Saturated solution of bromine on cooling gives bromine hydrate $Br_2.8H_2O$.

Chemical properties -

(i) ***Combination with hydrogen*** -

$$H_2 + Br_2 \xrightarrow[\text{or at }200°C]{\text{Pt at room temp.}} 2HBr$$

(ii) ***Oxidising nature*** - Under ordinary conditions it does not react with water but in presence of an oxidisable substance it gives HBr.

$$Br_2 + H_2O \rightarrow 2HBr + O$$

Thus it oxidises SO_2 to H_2SO_4

$$SO_2 + H_2 + O \rightarrow H_2SO_4$$

Sodium sulphite to sulphate

$$Na_2SO_3 + O \rightarrow Na_2SO_4$$

Thiosulphite to sulphate

$$Na_2S_2O_3 + O \rightarrow Na_2SO_4 + S$$

Arsenite to arsenate

$$Na_3AsO_3 + O \rightarrow Na_3AsO_4$$

Hydrogen sulphide to sulphur

$$H_2S + O \rightarrow H_2O + S$$

(iii) ***Reaction with alkali***

(a) In cold $2NaOH + Br_2 \rightarrow NaBr + NaBrO + H_2O$

(b) In hot $6NaOH + 3Br_2 \rightarrow 5NaBr + NaBrO_3 + 3H_2O$

(iv) ***Displacement reaction*** - $2KI + Br_2 \rightarrow 2KBr + I_2$

(v) ***Action of ammonia*** - $8NH_3 + 3Br_2 \rightarrow 6NH_4Br + N_2$

(vi) ***Action of organic Compounds*** -

$$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$$

$$C_2H_6 + Br_2 \rightarrow C_2H_5Br + HBr$$

(vii) Br_2 + moist starch paper = brown colour or Br_2 + moist starch $\rightarrow$ KI paper = violet

Uses-

(i) In the manufacture of tetraethyl lead an important antiknock compound

$$4C_2H_5Br + \underset{\text{sodium-lead alloy}}{4Na.Pb} \rightarrow (C_2H_5)_4Pb + 4NaBr + Pb$$

(ii) NaBr and KBr are used as sedatives

(iii) AgBr is used in photography

(iv) Ethylene bromide increases efficiency of TEL.

(v) NaBr and KBr are used as sedatives.

IODINE :

Iodine was discovered by *Courtios*.

Occurrence - It is not found in free state. It occurs in sea weeds as NaI. In Caliche (Chile saltpeter) as $NaIO_3$.

Preparation - Lab method : By heating of a mixture of MnO_2, H_2SO_4 and KI,

$$2KI + 3H_2SO_4 + MnO_2 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2$$

Manufacture -

(i) ***From sea weeds***

$$2NaI + MnO_2 + 3H_2SO_4 \xrightarrow{\Delta} 2NaHSO_4 + MnSO_4 + 2H_2O + I_2$$

(ii) ***From Caliche*** -

$$2NaIO_3 + 5NaHSO_3 \rightarrow 2Na_2SO_4 + 3NaHSO_4 + H_2O + I_2$$

Exact amount of $NaHSO_3$ is to be added since it reacts with I_2, if present in excess.

$$NaHSO_3 + I_2 + H_2O \rightarrow NaHSO_4 + 2HI$$

Purification - It contains the impurities of Cl_2, Br_2 and H_2O. Cl_2 and Br_2 are removed by distillation with KI.

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

$$2KI + Br_2 \rightarrow 2KBr + I_2$$

Water is removed by distillation over concentrated H_2SO_4. Further it is purified by sublimation.

Properties - It is black (dark violet) shining solid with metallic lustre. It sublimes on heating (mpt 114°C). It is metallic in character and forms I^+ and I_3^+ ions.

Chemical properties -

(i) ***Solubility*** - It is slightly soluble in water but dissolves in presence of KI

$$KI + I_2 \rightleftharpoons KI_3$$

(ii) ***Combination with elements*** -

$$H_2 + I_2 \xrightarrow[\Delta]{Pt} 2HI$$

$$2P + 3I_2 \xrightarrow{\Delta} 2PI_3$$

(iii) ***Displacement reactions*** -

$$2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl_2$$

$$2KBrO_3 + I_2 \rightarrow 2KIO_3 + Br_2$$

(iv) ***Reaction with alkalies***

(a) dilute and cold NaOH

$$2NaOH + I_2 \rightarrow NaI + NaOI + H_2O$$

(b) Concentrated and hot NaOH

$$6NaOH + I_2 \rightarrow 5NaI + NaIO_3 + 3H_2O$$

Hypoiodite decomposes even at room temperature.

$$3NaOI \rightarrow 2NaI + NaIO_3$$

(v) ***Action of ammonia*** - $2NH_3 + 3I_2 \rightarrow \underset{\text{Explosive compound}}{NH_3.NI_3} + 3HI$

$$8NI_3.NH_3 \rightarrow 5N_2 + 9I_2 + 6NH_4I$$

(vi) ***Reaction with hypo*** -

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

(vii) ***Action of strong oxidising agents,*** eg conc HNO_3, O_3 and Cl_2 They produce iodic acid.

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

Uses

(i) In medicines eg as tincture of iodine, iodex, iodoform

(ii) Solution of KI and I_2 used in the treatment of goitre.

Tincture of iodine - It is mixture of

$\frac{1}{2}O_Z$. Iodine$+\frac{1}{4}O_Z.KI+1$ pint rectified spirit.

BLEACHING POWDER - $CaOCl_2.H_2O$:

The composition of bleaching powder is

$$Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$$

Manufacture - It is manufactured by the action of chlorine on slaked lime. $Ca(OH)_2$

$$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$$

The manufacture is carried out in ***Hosenclever*** plant or ***Bachmann's plant*** - (Modern process)

Properties - It is yellowish powder with strong smell of chlorine.

1. By the action of dilute acids or carbon dioxide it loses its chlorine

   $$CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2$$

   $$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$$

   The chlorine thus obtained as known as "***available chlorine***" A good sample of bleaching powder contains 35-40% available chlorine the value of which goes on decreasing on keeping the powder due to the following change

   $$6CaOCl_2 \rightarrow Ca(ClO_3)_2 + 5CaCl_2$$

2. It give O_2 in presence of cobalt chloride solution

   $$2CaOCl_2 \xrightarrow{CoCl_2} 2CaCl_2 + O_2$$

3. In presence of slight amount of dilute acid it loses oxygen.

   $$2CaOCl_2 + H_2SO_4 \rightarrow CaCl_2 + CaSO_4 + 2HClO$$

   $$HClO \rightarrow HCl + O$$

   The evolution of nascent oxygen makes it oxidising and bleaching agent.

4. It reacts with ethyl alcohol or acetone to form chloroform

   $$CH_3CH_2OH \text{ or } CH_3COCH_3 \xrightarrow[\text{distill}]{CaOCl_2} CHCl_3$$

5. It does not form clear solution with water and aqueous solution contains $Ca^{2+}, \overline{Cl}$ and $\overline{OCl}$ ions.

Uses

(i) It is used as disinfectant and germicide

(ii) For the manufacture chloroform

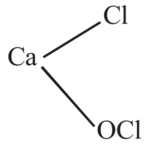
(iii) For the sterlisation of drinking water

(iv) For making unshrinkable wool

(v) For bleaching cotton, wood pulp.

Structure

(i) Due to ***Odling***



(ii) According to ***Bunn, Clark*** **and** ***Clifford***, it is a mixture of calcium hypochlorite $Ca(OCl)_2.4H_2O$ and basic calcium chloride $CaCl_2Ca(OH)_2.2H_2O$.

ABNORMAL PROPERTIES OF HYDROFLUORIC ACID:

1. It is highly poisonous and has corrosive action on skin
2. It is exist as H_2F_2 even in gaseous state and forms two series of salts KHF_2 (FREMY'S SALT) and K_2F_2.
3. It is not oxidised even by strong oxidising agents.
4. It reacts with silica and glass

   $$SiO_2 + 2H_2F_2 \rightarrow SiF_4 + 2H_2O$$

   $$SiF_4 + H_2F_2 \rightarrow \underset{\text{Hydrofluorosilicic acid}}{H_2SiF_6}$$

   $$Na_2SiO_3 + 3H_2F_2 \rightarrow Na_2SiF_6 + 3H_2O$$

   $$CaSiO_3 + 3H_2F_2 \rightarrow CaSiF_6 + 3H_2O$$

   Hence it is used for etching glass

5. On heating with MnO_2 and H_2SO_4 it does not give F_2 while other hydrogen halides (HX) give X_2

   $$MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O + O$$

   $$2HX + O \rightarrow H_2O + X_2$$

6. AgF and PbF_2 are soluble in water while chlorides, bromides and iodides of silver (Ag) and lead (Pb) are insoluble in water.
7. CaF_2 and SrF_2 are insoluble in water while chlorides, bromides and iodides af Ca and Sr are soluble.
8. ***Azeotropes of hydracids***

Hydrogen	*halide Composition*	*Boiling point °C*
H_2F_2	36%	120
HCl	20.4%	110
HBr	47.0%	126
HI	57.0%	127

Exercise-1 | NCERT BASED QUESTIONS

Very Short/Short Answer Questions

1. Why is HF the weakest acids among hydrohaloacids inspite of the fact that F is most electronegative?
2. Why are the interhalogens compounds more reactive than the halogens (except F_2)?
3. Show that Cl_2 gas can be obtained from bleaching powder.
4. Why is fluorine most reactive among halogens?
5. Why is HF stored in wax-coated glass bottles?
6. Name a halogen which does not exhibit positive oxidation state.
7. Arrange the following in the decreasing order of property indicated.
   (*i*) F_2, Cl_2, Br, I_2 – Bond energy
   (*ii*) HF, HCl, HBr, HI – Acid strength (in water)
   (*iii*) M – F, M – Cl, M – Br, M – I – Ionic character of the bond.
   (*iv*) ClO_4^-, BrO_4^-, IO_4^- – Oxidizing power
8. Compare the acidic strengths of HF and HCl & explain the difference.
9. Which of the following is regarded as the weakest acid and why?
   HF, HCl, HBr or HI.
10. HF has higher boiling point than HCl. Why?
11. Iodine forms I_3^- but F_2 does not form F_3^- ions. Why?
12. Why is perchloric acid, $HClO_4$ a stronger acid than sulphuric acid?
13. Fluorine does not undergo disproportionation reactions but other halogens do. Explain why?

Long Answer Questions

14. Arrange the following in order of property indicated for each set:
    (*i*) F_2, Cl_2, Br_2, I_2 – increasing bond dissociation enthalpy.
    (*ii*) NH_3 , PH_3, AsH_3, SbH_3, BiH_3 – increasing base strength
    (*iii*) $HClO_4$, $HClO_3$, $HClO_2$, HClO – increasing acidic strength
    (*iv*) HOCl, HOBr, HOI – increasing acidic strength.

Multiple Choice Questions

15. The correct order of acidic strength is
    (a) HF < HCl < HBr < HI
    (b) HBr < HCl < HI < HF
    (c) HCl < HBr < HF < HI
    (d) HI < HBr < HCl < HF
16. The order of reactivity of halogens is
    (a) F > Cl > Br > I (b) F < Cl < Br < I
    (c) F < Cl > Br < I (d) F < Cl < Br > I
17. Which of the following statements is correct ?
    (a) only iodine forms oxy acid
    (b) only chlorine and bromine form oxy acid
    (c) All the halogens form oxy acid
    (d) All the halogens form oxy acids except fluorine
18. Of the four elements, the one having maximum electron affinity is :
    (a) Fluorine (b) Chlorine
    (c) Bromine (d) Iodine
19. Which one of the following orders is not in accordance with the property stated against is ?
    (a) HI > HBr > HCl > HF : Acidic property in water
    (b) $F_2 > Cl_2 > Br_2 > I_2$: Electronegativity
    (c) $F_2 > Cl_2 > Br_2 > I_2$: Bond dissociation energy
    (d) $F_2 > Cl_2 > Br_2 > I_2$: Oxidising power

20. Which of the following species has four lone pairs of electrons?
    (a) I (b) O^-
    (c) Cl^- (d) He

21. Which one is the correct order of the size of iodine species?
    (a) $I > I^+ > I^-$ (b) $I > I^- > I^+$
    (c) $I^+ > I^- > I$ (d) $I^- > I > I^+$

22. Cl_2 reacts with hot and conc. NaOH to give –
    (a) NaClO (b) $NaClO_3$
    (c) $NaClO_2$ (d) $NaClO_4$

23. Which one is most stable to heat –
    (a) HClO (b) $HClO_2$
    (c) $HClO_3$ (d) $HClO_4$

24. Conc. HNO_3 reacts with I_2 to form :
    (a) HI (b) HOI
    (c) HIO_2 (d) HIO_3

25. Which of the following has maximum bond energy?
    (a) Cl_2 (b) F_2
    (c) Br_2 (d) I_2

26. Iodine is a :
    (a) electrovalent solid (b) atomic solid
    (c) molecular solid (d) covalent solid

27. Fluorine exhibits an oxidation state of only –1 because
    (a) it can readily accept an electron
    (b) it is very strongly electronegative
    (c) it is a non-metal
    (d) it belongs to halogen family

Exercise-2 | CONCEPTUAL MCQs

1. Among F, Cl, Br and I the lowest ionization potential will be of
(a) fluorine
(b) chlorine
(c) bromine
(d) iodine

2. The electron affinity of the halogens follows the order
(a) $F > Cl > Br > I$
(b) $F < Cl < Br < I$
(c) $F < Cl > Br > I$
(d) $F < Cl < Br > I$

3. The electronegativity follows the order
(a) $F > O > Cl > Br$
(b) $F > Cl > Br > O$
(c) $O > F > Cl > Br$
(d) $Cl > F > O > Br$

4. The bond energies of F_2, Cl_2, Br_2 and I_2 are 155, 244, 193 and 151 kJ mol^{-1} respectively. The weakest bond will be in
(a) Br_2
(b) Cl_2
(c) F_2
(d) I_2

5. The correct order of reactivity of halogens with alkalies is
(a) $F > Cl > Br > I$
(b) $F < Cl > Br < I$
(c) $F < Cl < Br < I$
(d) $F < Cl < Br > I$

6. The correct order of increasing oxidising power is
(a) $F_2 > Br_2 > Cl_2 > I_2$
(b) $F_2 < Cl_2 < Br_2 < I_2$
(c) $Cl_2 > Br_2 > F_2 > I_2$
(d) $I_2 < Br_2 < Cl_2 < F_2$

7. Which of the following halogen does not exhibit positive oxidation state in its compounds?
(a) Cl
(b) Br
(c) I
(d) F

8. The halogen that is most easily reduced is
(a) F_2
(b) Cl_2
(c) Br_2
(d) I_2

9. The bond energies of F_2, Cl_2, Br_2 and I_2 are 37, 58, 46 and 36 kcal mol^{-1} respectively. The strongest bond is present in
(a) Br_2
(b) I_2
(c) Cl_2
(d) F_2

10. Which one of the following order is correct for the bond energies of halogen molecules ?
(a) $I_2 > Cl_2 > Br_2$
(b) $Br_2 > Cl_2 > I_2$
(c) $I_2 > Br_2 > Cl_2$
(d) $Cl_2 > Br_2 > I_2$

11. Which one of the following elements shows different oxidation states ?
(a) Sodium
(b) Fluorine
(c) Chlorine
(d) Potassium

12. Which of the following halogens exhibit only one oxidation state in its compounds ?
(a) Bromine
(b) Chlorine
(c) Fluorine
(d) Iodine

13. Which has the highest bond energy ?
(a) F_2
(b) Cl_2
(c) Br_2
(d) I_2

14. Which is the weakest out of HF, HCl, HBr and HI?
(a) HF
(b) HCl
(c) HBr
(d) HI

15. Hydrochloric acid at 25ºC is
(a) ionic and liquid
(b) covalent and liquid
(c) ionic and gas
(d) None of these

16. Which of the following is most volatile ?
(a) HI
(b) HBr
(c) HCl
(d) HF

17. Which of the following sets gives the correct arrangement of the compounds involved based on their bond strengths ?
(a) $HF > HCl > HBr > HI$
(b) $HI > HBr > HCl > HF$
(c) $HF > HBr > HCl > HI$
(d) $HCl > HF > HBr > HI$

18. At room temperature, HCl is a gas while HF is a low boiling liquid. This is because
(a) H- F bond is covalent
(b) H- F bond is ionic
(c) HF has metallic bond
(d) HF has hydrogen bond

19. Which of the following has the highest bond strength?
(a) HI
(b) HCl
(c) HF
(d) HBr

20. Which of the following is the strongest acid ?
(a) HOCl
(b) $HOClO_2$
(c) $HOClO_3$
(d) HOClO

21. The geometry of ClO_3^- according to valence shell electron pair repulsion (VSEPR) theory will be
(a) planar triangle
(b) pyramidal
(c) tetrahedral
(d) square planar

22. Oxidation state of chlorine in hypochlorous acid is
(a) $+1$
(b) $+2$
(c) -1
(d) -2

23. The correct decreasing order of acidic character is
(a) $HClO > HBrO > HIO$
(b) $HIO > HBrO > HClO$
(c) $HBrO > HIO > HClO$
(d) $HClO > HIO > HBrO$

24. The element which never acts as reducing agent in a chemical reaction is
(a) O
(b) Li
(c) F
(d) C

25. Unlike other halogens, fluorine does not show higher oxidation states because
(a) it is highly electronegative
(b) it has no *d*- orbitals
(c) its atomic radius is very small
(d) the F^- ion is stable and isoelectronic with neon

26. An element M has an atomic mass 19 and atomic number 9. Its ion is represented by
(a) M^+
(b) M^{2+}
(c) M^-
(d) M^{2-}

27. Which one of the following halogen liberates oxygen when passed through hot concentrated KOH solution ?
(a) I_2
(b) Cl_2
(c) Br_2
(d) F_2

28. One mole of fluorine is reacted with two moles of hot and concentrated KOH. The products formed are KF, H_2O and O_2. The molar ratio of KF, H_2O and O_2 respectively is

(a) 1 : 1 : 2 (b) 2 : 1 : 0.5
(c) 1 : 2 : 1 (d) 2 : 1 : 2

29. Fluorine oxidizes HSO_4^- to

(a) $S_2O_3^{2-}$ (b) $S_2O_8^{2-}$
(c) $S_4O_6^{2-}$ (d) SO_2

30. Chlorine cannot displace

(a) Fluorine from NaF
(b) Iodine from NaI
(c) Bromine from NaBr
(d) None of these

31. Cl_2 gas is dried over

(a) CaO (b) NaOH
(c) KOH (d) conc. H_2SO_4

32. The outer electronic structure of $3s^2\,3p^5$ is possessed by

(a) O (b) Cl
(c) Br (d) Ar

33. Chlorine acts as a bleaching agent only in the presence of

(a) dry air (b) moisture
(c) sunlight (d) None of these

34. When chlorine reacts with cold and dilute solution of sodium hydroxide, the products obtained are

(a) $Cl^- + ClO^-$ (b) $Cl^- + ClO_2^-$
(c) $Cl^- + ClO_3^-$ (d) $Cl^- + ClO_4^-$

35. In the reaction

$2Br^- + X_2 \rightarrow Br_2, 2X^-, X_2$ is

(a) Cl_2 (b) Br_2
(c) I_2 (d) N_2

36. Chlorine is liberated when we heat

(a) $KMnO_4 + NaCl$ (b) $K_2Cr_2O_7 + MnO_2$
(c) $Pb(NO_3)_2 + MnO_2$ (d) $K_2Cr_2O_7 + HCl$

37. Which of the following is correct about the reaction?

$$3NaClO \xrightarrow{\text{heat}} NaClO_3 + 2NaCl$$

(a) It is disproportionation reaction
(b) Oxidation number of Cl decreases as well as increases in this reaction
(c) This reaction is used for the manufacture of halates
(d) All of these

38. Which of the following is used in the preparation of chlorine ?

(a) Only MnO_2 (b) Only $KMnO_4$
(c) Both MnO_2 and $KMnO_4$ (d) Either MnO_2 or $KMnO_4$

39. A greenish yellow gas reacts with an alkali metal hydroxide to form a halate which can be used in fire works safety matches. The gas and halate respectively are

(a) Br_2, $KBrO_3$ (b) Cl_2, $KClO_3$
(c) I_2, $NaIO_3$ (d) Cl_2, $NaClO_3$

40. The reaction of $KMnO_4$ and HCl results in

(a) oxidation of Mn in $KMnO_4$ and production of Cl_2
(b) reduction of Mn in $KMnO_4$ and production of H_2
(c) oxidation of Mn in $KMnO_4$ and production of H_2
(d) reduction of Mn in $KMnO_4$ and production of Cl_2

41. Chlorine acts as a bleaching agent only in

(a) dry air (b) sunlight
(c) moisture (d) oxygen

42. In the reaction

$$3Br_2 + 6CO_3^{2-} + 3H_2O \longrightarrow 5Br^- + BrO_3^- + 6HCO_3^-$$

(a) bromine is oxidised and carbonate is reduced
(b) bromine is both oxidised and reduced
(c) bromine is reduced and water is oxidised
(d) bromine is neither oxidised nor reduced

43. The solubility of I_2 increases in water in presence of

(a) KI (b) H_2SO_4
(c) $KMnO_4$ (d) H_2S

44. Oxidation of thiosulphate with iodine gives

(a) sulphate ion (b) sulphite ion
(c) tetrathionate ion (d) sulphide ion

45. Which of the following cannot work as oxidizing agent ?

(a) O_2 (b) $KMnO_4$
(c) H_2O_2 (d) I^-

46. On boiling an aqueous solution of $KClO_3$ with I_2 the products obtained are

(a) $KIO_3 + Cl_2$ (b) $KCl + I_2O_5$
(c) $KIO_4 + Cl_2$ (d) No reaction takes place

47. When KI and $CuSO_4$ solutions are mixed, it gives

(a) $K_2SO_4 + I_2$ (b) $Cu_2I_2 + K_2SO_4$
(c) $CuI_2 + K_2SO_4$ (d) $Na_2SO_4 + I_2$

48. When I_2 is passed through KCl, KF and KBr solutions

(a) Cl_2 and Br_2 are evolved
(b) Cl_2 is evolved
(c) Cl_2, Br_2 and F_2 are evolved
(d) None of these

49. Sea weeds are an important source of

(a) iodine (b) bromine
(c) chlorine (d) Both (a) and (b)

50. Which of the following elements exhibits the most basic properties ?

(a) F (b) Cl
(c) Br (d) I

51. Which of the following is used as an antiseptic?

(a) I (b) Br
(c) Cl (d) F

52. In the presence of cobalt chloride ($CoCl_2$), bleaching powder decomposes to form

(a) $CaCO_3$ and O_3 (b) ClO_2 and CaO
(c) Cl_2O and CaO (d) $CaCl_2$ and O_2

53. In the reaction

$$HNO_3 + HF \longrightarrow H_2^+NO_3 + F^- \text{ base is}$$

(a) HF (b) HNO_3
(c) HF and HNO_3 (d) None of these

54. The aqueous solution of which of the following has maximum pH ?
(a) NaClO (b) $NaClO_2$
(c) $NaClO_3$ (d) $NaClO_4$

55. Which of the following is not the characteristic of interhalogen compounds ?
(a) They are more reactive than halogens
(b) They are quite unstable but none of them is explosive
(c) They are covalent in nature
(d) They have low boiling points and are highly volatile.

56. Which bond is most polar ?
(a) Cl - F (b) Br - F
(c) I - F (d) F - F

57. On heating $KClO_3$ we get
(a) $KClO_2 + O_2$ (b) $KCl + O_2$
(c) $KCl + O_3$ (d) $KCl + O_2 + O_3$

58. The hybridization in ICl_7 is
(a) sp^3d^3 (b) d^2sp^3
(c) sp^3d (d) sp^3

59. Which of the following bond is strongest ?
(a) F – B (b) F – Cl
(c) F – Br (d) Cl–Br

60. "Fluorosis" disease is caused due to the reaction of .... with excess of fluoride in the body.
(a) Ca (b) Mg
(c) Fe (d) K

61. Hydrogen bond is strongest in
(a) F – H...........O
(b) F – H...........N
(c) F – H...........F
(d) All are equally strong

Exercise-3 | PAST COMPETITION MCQs

1. Which among the following is paramagnetic ? **[CBSE-PMT 1994]**
(a) Cl_2O (b) ClO_2
(c) Cl_2O_7 (d) Cl_2O_6

2. Which one of the following oxides of chlorine is obtained by passing dry chlorine over silver chlorate at 90°C ? **[CBSE-PMT 1994]**
(a) Cl_2O (b) ClO_3
(c) ClO_2 (d) ClO_4

3. The formula for calcium chlorite is **[CBSE-PMT 1994]**
(a) $Ca(ClO_4)_2$ (b) $Ca(ClO_3)_2$
(c) $CaClO_2$ (d) $Ca(ClO_2)_2$

4. Regarding F^- and Cl^- which of the following statements is/ are correct? **[CBSE-PMT1996]**
(i) Cl^- can give up an electron more easily than F^-
(ii) Cl^- is a better reducing agent than F^-
(iii) Cl^- is smaller in size than F^-
(iv) F^- can be oxidized more readily than Cl^-
(a) (i) and (ii) (b) (i), (ii) and (iv)
(c) (iii) and (iv) (d) only (i)

5. Which one is the correct order of the size of iodine species? **[CBSE-PMT 1997]**
(a) $I > I^+ > I^-$ (b) $I > I^- > I^+$
(c) $I^+ > I^- > I$ (d) $I^- > I > I^+$

6. Which of the following statements is **not** true ? **[CBSE-PMT 2003]**
(a) HF is a stronger acid than HCl
(b) Among halide ions, iodide is the most powerful reducing agent
(c) Fluorine is the only halogen that does not show a variable oxidation state
(d) HOCl is a stronger acid than HOBr

7. Which is the best description of the behaviour of bromine in the reaction given below ? **[CBSE-PMT2004]**

$$H_2O + Br_2 \rightarrow HOBr + HBr$$

(a) Proton acceptor only
(b) Both oxidized and reduced
(c) Oxidized only
(d) Reduced only

8. Which one of the following orders correctly represents the increasing acid strengths of the given acids? **[CBSE-PMT 2007]**
(a) $HOClO < HOCl < HOClO_3 < HOClO_2$
(b) $HOClO_2 < HOClO_3 < HOClO < HOCl$
(c) $HOClO_3 < HOClO_2 < HOClO < HOCl$
(d) $HOCl < HOClO < HOClO_2 < HOClO_3$

9. Which one of the following arrangements does not give the correct picture of the trends indicated against it ? **[CBSE-PMT 2008]**
(a) $F_2 > Cl_2 > Br_2 > I_2$: Oxidizing power
(b) $F_2 > Cl_2 > Br_2 > I_2$: Electron gain enthalpy
(c) $F_2 > Cl_2 > Br_2 > I_2$: Bond dissociation energy
(d) $F_2 > Cl_2 > Br_2 > I_2$: Electronegativity.

10. In the case of alkali metals, the covalent character decreases in the order: **[CBSE-PMT 2009]**
(a) MF > MCl > MBr > MI
(b) MF > MCl > MI > MBr
(c) MI > MBr > MCl > MF
(d) MCl > MI > MBr > MF

11. Among the following which is the strongest oxidising agent? **[CBSE-PMT 2009]**
(a) Br_2 (b) I_2
(c) Cl_2 (d) F_2

12. The correct order of increasing bond angles in the following species are : **[CBSE-PMT 2010]**

(a) $Cl_2O < ClO_2 < ClO_2^-$ (b) $ClO_2 < Cl_2O < ClO_2^-$

(c) $Cl_2O < ClO_2^- < ClO_2$ (d) $ClO_2^- < Cl_2O < ClO_2$

13. Which is the strongest acid in the following : **[NEET 2013]**

(a) $HClO_3$ (b) $HClO_4$

(c) H_2SO_3 (d) H_2SO_4

14. Which of the following is a polar molecule ? **[NEET 2013]**

(a) SF_4 (b) SiF_4

(c) XeF_4 (d) BF_3

15. Concentrated hydrochloric acid when kept in open air sometimes produces a cloud of white fumes. The explanation for it is that **[AIEEE 2003]**

(a) oxygen in air reacts with the emitted HCl gas to form a cloud of chlorine gas

(b) strong affinity of HCl gas for moisture in air results in forming of droplets of liquid solution which appears like a cloudy smoke.

(c) due to strong affinity for water, concentrated hydrochloric acid pulls moisture of air towards itself. This moisture forms droplets of water and hence the cloud.

(d) concentrated hydrochloric acid emits strongly smelling HCl gas all the time.

16. Which among the following factors is the most important in making fluorine the strongest oxidizing halogen ?

(a) Hydration enthalpy **[AIEEE 2004]**

(b) Ionization enthalpy

(c) Electron affinity

(d) Bond dissociation energy

17. Among the properties (a) reducing (b) oxidising (c) complexing, the set of properties shown by CN^- ion towards metal species is **[AIEEE 2004]**

(a) c, a (b) b, c

(c) a, b (d) a, b, c

18. The correct order of the thermal stability of hydrogen halides (H–X) is **[AIEEE 2005]**

(a) HI > HCl < HF > HBr

(b) HCl< HF > HBr < HI

(c) HF > HCl < HBr > HI

(d) HI < HBr > HCl < HF

19. Identify the incorrect statement among the following. **[AIEEE 2007]**

(a) Br_2 reacts with hot and strong NaOH solution to give NaBr and H_2O.

(b) Ozone reacts with SO_2 to give SO_3.

(c) Silicon reacts with NaOH(aq) in the presence of air to give Na_2SiO_3 and H_2O.

(d) Cl_2 reacts with excess of NH_3 to give N_2 and HCl.

Exercise-4 | Applied MCQs

1. Which of the following species is not a pseudo halide

(a) CNO^- (b) $RCOO^-$

(c) OCN^- (d) NNN^-

2. HBr and HI reduce sulphuric acid ; HCl can reduce $KMnO_4$ and HF reduces

(a) H_2SO_4 (b) $KMnO_4$

(c) $K_2Cr_2O_7$ (c) None of these

3. Gaseous HCl is a poor conductor of electricity while its aqueous solution is a good conductor this is because

(a) H_2O is a good conductor of electricity

(b) a gas cannot conduct electricity but a liquid can

(c) HCl gas does not obey Ohm's law, whereas the solution does

(d) HCl ionises in aqueous solution

4. When NaCl or KCl is heated with conc. H_2SO_4 and solid $K_2Cr_2O_7$,we get

(a) chromic chloride

(b) chromous chloride

(c) chromyl chloride CrO_2Cl_2

(d) chromic sulphate

5. Antichlor is a compound

(a) which absorbs chlorine

(b) which removes Cl_2 from a material

(c) which liberates Cl_2 from bleaching powder

(d) which acts as a catalyst in the manufacture of Cl_2

6. Which reaction cannot be used for the preparation of the halogen acid

(a) $2KBr + H_2SO_4(conc.) \rightarrow K_2SO_4 + 2HBr$

(b) $NaCl + H_2SO_4(conc.) \rightarrow NaHSO_4 + HCl$

(c) $NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl$

(d) $CaF_2 + H_2SO_4(conc.) \rightarrow CaSO_4 + 2HF$

7. When an aqueous solution of hypochlorites is heated

(a) chlorine is evolved

(b) chlorine is formed

(c) chlorate is formed

(d) chlorine peroxide is formed

8. Which of the following oxyacids of chlorine is formed on shaking chlorine water with freshly precipitated yellow oxide of mercury

(a) $HClO_3$ (b) $HClO_2$

(c) $HClO$ (d) $HClO_4$

9. By the action of concentrated HCl on potassium chlorate we get this mixture of gases

(a) $CO_2 + Cl_2$ (b) $O_2 + ClO_2$
(c) $Cl_2 + ClO_2$ (d) $O_2 + Cl_2 + ClO_2$

10. A gas reacts with CaO, but not with $NaHCO_3$ The gas is

(a) CO_2 (b) Cl_2
(d) N_2 (d) O_2

11. Bleaching powder slowly loses its activity when it stands in air .This is due to

(a) reaction with moisture to liberate O_2
(b) auto-oxidation
(c) loss of $CaCl_2$
(d) formation of $Ca(OH)_2$

12. The greater reactivity of fluorine is due to

(a) low energy of the F - F bond
(b) small size
(c) high heat of Hydration
(d) All of these

13. SO_2 reacts with chlorine to form

(a) sulphur monochloride (b) sulphur dichloride
(c) sulphuryl chloride (d) sulphur trichloride

14. HF present as impurity in gaseous F_2 can be removed by passing over

(a) P_2O_5 (b) NaF
(c) H_2SO_4 (d) $CaCl_2$

15. Which of the following statement is incorrect ?

(a) Chlorine can bleach a wet piece of cloth
(b) Iodine stain can be removed by hypo solution
(c) Bromine can be prepared from carnallite
(d) Bromine is liberated when iodine is passed through an acidified KBr solution

16. The ion that cannot undergo disproportionation is

(a) ClO_4^- (b) ClO_3^-
(c) ClO_2^- (d) ClO^-

17. Which acid can combine with its own salt again

(a) HF (b) HBr
(c) HCl (d) HI

18. If Cl_2 gas is passed into aqueous solution of KI containing some CCl_4 and the mixture is shaken then

(a) upper layer becomes violet
(b) lower layer becomes violet
(c) homogenous violet layer is formed
(d) None of these

19. Interhalogen compounds are more reactive than the individual halogen because

(a) two halogens are present in place of one
(b) they are more ionic
(c) their bond energy is less than the bond energy of the halogen molecule
(d) they carry more energy

20. When chlorine water is exposed to sunlight, O_2 is liberated. Hence

(a) hydrogen has little affinity to O_2
(b) hydrogen has more affinity to O_2
(c) hydrogen has more affinity to Cl_2
(d) hydrogen has little affinity to Cl_2

21. The correct order of acidic strength is

(a) $Cl_2O_7 > SO_2 > P_4O_{10}$
(b) $CO_2 > N_2O_5 > SO_3$
(c) $Na_2O > MgO > Al_2O_3$
(d) $K_2O > CaO > MgO$

22. Bleaching powder on standing forms mixture of :

(a) $CaO + Cl_2$ (b) $CaO + CaCl_2$
(c) $HOCl + Cl_2$ (d) $CaCl_2 + Ca(ClO_3)_2$

23. When Cl_2 water is added to an aqueous solution of potassium halide in presence of CCl_4 a violet colour is obtained. On adding more of Cl_2 water, the violet colour disappears and a colourless solution is obtained. This test confirms presence of which of the following in aqueous solution :

(a) Bromide (b) Chloride
(c) Iodide and bromide (d) Iodide

24. In a given sample of bleaching powder the percentage of available chlorine is 49. The volume of chlorine obtained if 10 g of the sample is treated with HCl at NTP is :

(a) 15 litre (b) 1.5 litre
(c) 3 litre (d) 150 litre

25. Most of the elementary gases are obtained by chemical reaction of their compounds. For example, chlorine is obtained by allowing $KMnO_4$ to react with HCl. Fluorine, however, can be obtained only by the electrolysis of a fluorides. This is because :

(a) it is easy to electrolyse a fluoride
(b) fluorine is highly poisonous
(c) fluorine is strongest chemical oxidising agent
(d) fluorine is a highly reactive gas

26. Which reaction yields greatest quantity of chlorine from given quantity of HCl :

(a) Warming conc. HCl with MnO_2
(b) Warming conc. HCl with PbO_2
(c) Mixing conc. HCl with $KMnO_4$
(d) Treating bleaching powder with HCl

27. Fluorine is a stronger oxidising agent than chlorine in aqueous solution. This is attributed to many factors except

(a) heat of dissociation (b) ionisation potential
(c) heat of hydration (d) electron affinity

28. Which pair gives Cl_2 at room temperature :

(a) NaCl + Conc. H_2SO_4 (b) Conc. HCl + $KMnO_4$
(c) NaCl + Conc. HNO_3 (d) NaCl + MnO_2

Hints & Solutions

EXERCISE 1

1. Due to widespread H-bonding in HF, H^+ is not easily formed. Due to small bond length of H – F, bond dissociation energy is high.
2. This is because A – X bond in interhalogens in weaker than the X – X bond in halogens.
3. $CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$.
4. It is most electronegative and is smallest in its atomic size, and has relatively less bond energy.
5. HF reacts with silica (SiO_2) present in glass and forms water soluble acid.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$SiF_4 + 2HF \longrightarrow \underset{\text{(Water soluble)}}{H_2SiF_4}$$

6. F being the most electronegative element does not show positive oxidation states.
7. (*i*) Cl – Cl > Br – Br > F – F > I – I
   (*ii*) HI > HBr > HCl > HF
   (*iii*) M – F > M– Cl > M – Br > M – I
   (*iv*) $BrO_4^- > ClO_4^- > IO_4^-$

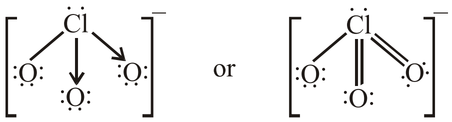
15. **(a)** **16.** **(a)** **17.** **(d)** **18.** **(b)** **19.** **(c)** **20.** **(c)**
21. **(d)** **22.** **(b)** **23.** **(d)** **24.** **(d)** **25.** **(a)** **26.** **(c)**
27. **(b)**

EXERCISE 2

1. **(d)** Ionisation potential decreases down the group.
2. **(c)** Since fluorine has small size the electron affinity of Cl is more than F
3. **(a)** Follow text
4. **(d)** The lesser the bond energy, the weaker is the bond
5. **(a)** (See text) Reactivity follows the order F > Cl > Br > I
6. **(d)** See text
7. **(d)** Fluorine exhibit -ve oxidation state
8. **(a)** Since F_2 is most oxidising, it is easily reduced
9. **(c)** The more the bond energy the stronger is the bond
10. **(d)** See text
11. **(c)** Chlorine shows O.S. from –1,+1 to +7, whereas others show O.S. as Na→ +1 ; K→ +1 ; F→ –1
12. **(c)** Fluorine always –1
13. **(b)** See text
14. **(a)** HF, due to intermolecular H-bonding is weakest among HX acids
15. **(d)** HCl acid at 25° C is a gas and polar in nature
16. **(c)** Volatile character HCl > HBr >HI > HF
17. **(a)** See text
18. **(d)** Due to hydrogen bonding HF is a liquid
19. **(c)** Follow text
20. **(c)** Oxy acids having higher + O.S for halogen are more stronger in nature . Hence the order

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

21. **(b)** Hybridisation is sp^3 and shape pyramidal



22. **(a)** In HClO the O.S of Cl is + ve (+1)
23. **(a)** Since the electronegativity of halogens follow the order Cl > Br > I the strength of acids follow the order HClO > HBr > HIO
24. **(c)** Fluorine has highest reduction potential hence it is strongest oxidising agent in nature
25. **(b)** Due to absence of d atomic orbitals the fluorine does not exhibit higher O.S.
26. **(c)** The element is F and ion is represented by M^-
27. **(d)** F_2 reacts with KOH to give O_2 and O_3 (see text)
28. **(b)** $2F_2 + 4KOH \rightarrow 4KF + O_2 + 2H_2O$ for 1 mole of F_2 the molar ratio.

F_2	KOH	KF	O_2	H_2O
1	2	2	$\frac{1}{2}$	1

29. **(b)** $HSO_4^- - \bar{e} \rightarrow HSO_4 \rightarrow H_2S_2O_8 \rightarrow S_2O_8{}^{2-}$
30. **(a)** Chlorine cannot displace F from NaF. The reactivity follows the order F > Cl > Br > I
31. **(d)** Cl_2 will react with CaO, NaOH and KOH (See text). It will not react with conc. H_2SO_4 hence can be dried over it.
32. **(b)** $3s^2 3p^5$ is electronic configuration of Cl
33. **(b)** In presence of moisture only, chlorine will give O;

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

34. **(a)** $2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$

hence Cl^- and OCl^-

35. **(a)** $2\bar{Br} + Cl_2 \rightarrow Br_2 + 2\bar{Cl}$ Chlorine is more oxidising is nature
36. **(d)** $K_2Cr_2O_7 + \text{Conc HCl} \rightarrow Cl_2$ See text
37. **(d)** $\overset{+1}{NaClO} \rightarrow \overset{+5}{NaClO_3} + 2\overset{-1}{NaCl}$ All statements are correct as evident from the reaction
38. **(d)** MnO_2 or $KMnO_4$ with conc HCl give Cl_2 (see text)
39. **(b)** $3Cl_2 + 6KOH \rightarrow KClO_3 + 5KCl + 3H_2O$

$KClO_3$ is used in fire works and safety matches and Cl_2 is greenish yellow gas

40. **(d)** $2\overset{+7}{KMnO4} + 16HCl \rightarrow 2\overset{+2}{MnCl2} + 2KCl + 8H_2O + 5Cl_2$

O.S of Mn changes from +7 to +2 hence reduction occurs and Cl_2 is formed.

41. (c) $Cl_2 + H_2O \to HCl + HOCl$

42. (b) $3Br_2 + 6CO_3^{2-} + 3H_2O \to 5Br^- + BrO_3^- + 6HCO_3^-$
O.S. of Br_2 changes from 0 to –1 and +5 which is reduction as well as oxidation.

43. (a) $KI + I_2 \to KI_3$ (Soluble complex)

44. (c) $2Na_2S_2O_3 + I_2 \to \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6} + 2NaI$

45. (d) I^- can act as reducing agent only and not oxidising since its O.S. can change from 0 to +7 only

46. (a) $2KClO_3 + I_2 \to 2KIO_3 + Cl_2$
+5 O.S. of iodine is more stable than chlorine

47. (b) $2KI + CuSO_4 \to K_2SO_4 + CuI_2$
$2CuI_2 \to Cu_2I_2 + I_2$

48. (d) Reactivity follows the order F > Cl > Br > I

49. (a) See text

50. (d) Basic character increases down the group

51. (a) Iodine is used as an antiseptic

52. (d) $2CaOCl_2 \xrightarrow{CoCl_2} 2CaCl_2 + O_2$ (see text)

53. (b) In $HNO_3 + HF \to H_2\overset{+}{N}O_3 + F^-$ HNO_3 accepts H^+ hence it is a base

54. (a) NaClO is a salt of strong base and weak acid hence on hydrolysis the solution will be most basic, therefore maximum pH.

55. (d) Interhalogen compounds are not highly volatile

56. (c) I – F is most polar. The more the electronegativity difference, the more is polar character of bond

57. (b) $2KClO_3 \to 2KCl + 3O_2$

58. (a) ICl_7. The hybridisation is $\frac{1}{2}(7 + 7 + 0 - 0) = 7$ (sp^3d^3)

59. (a) When atomic orbitals present in the same principle energy level overlap, a strong bond is formed. In case of F and B, atomic orbitals are from second principle energy levels.

60. (a) Fluorosis is caused due to reaction of Ca with excess of fluoride in the body

61. (c) The strength of H- bonding follows the order F > O > N

EXERCISE 3

1. (b) ClO_2 contains 7 + 12 i.e. 19 electrons (valence) which is an odd number, i.e. there is (are) free electron(s). Hence it is paramagnetic in nature.

2. (c) Pure ClO_2 is obtained by passing dry Cl_2 over $AgClO_3$ at 90°C.

$$2AgClO_3 + Cl_2(\text{dry}) \xrightarrow{90°C} 2AgCl + 2ClO_2 + O_2$$

3. (d) Calcium chlorite is $Ca(ClO_2)_2$

4. (d) The halide ions act as reducing agents . F^- ion does not show any reducing nature but Cl^-, Br^- & I^- ion act as reducing agents and their reducing nature is in increasing order

$$\xrightarrow[\text{Reducing nature increases}]{Cl^- \quad Br^- \quad I^-}$$

5. (d) We know that positive ion is always smaller and negative ion is always larger than the corresponding atom. Therefore the correct order of the size is $I^- > I > I^+$

6. (a) F is more electronegative than Cl therefore HF bond is stronger than HCl and hence proton is not given off easily and hence HF is a weakest acid.

7. (b) $H_2O + \overset{0}{Br_2} \longrightarrow HO\overset{+1}{Br} + H\overset{-1}{Br}$

Thus here oxidation number of Br increases from 0 to +1 and also decreases from 0 to –1. Thus it is oxidised as well as reduced.

8. (d) $HO\underset{+1}{Cl} < HO\underset{+3}{Cl}O < HO\underset{+5}{Cl}O_2 < HO\underset{+7}{Cl}O_3$

In case of oxyacids of similar element as the oxidation number of the central atom increases, strength of acid also increases.

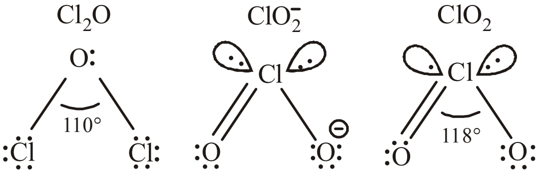
9. (b, c) From the given options we find option (a) is correct. The oxidising power of halogens follow the order $F_2 > Cl_2 > Br_2 > I_2$. Option (b) is incorrect because it in not the correct order of electron gain enthalpy of halogens.
The correct order is $Cl_2 > F_2 > Br_2 > I_2$. The low value of F_2 than Cl_2 is due to its small size.
Option (c) is incorrect. The correct order of bond dissociation energies of halogens is
$Cl_2 > Br_2 > F_2 > I_2$.
Option (d) is correct. It is the correct order of electronegativity values of halogens. Thus option (b) and (c) are incorrect.

10. (c) MI > MBr > MCl > MF. As the size of the anion decreases covalent character also decreases.

11. (d) Since all the halogens have a strong tendency to accept electrons. Therefore halogens act as strong oxidising agents and their oxidising power decreases from fluorine to iodine.

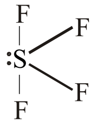
12. (c) The correct order of increasing bond angle is

$Cl_2O < ClO_2^- < ClO_2$



* In ClO_2^- there are 2 lone pairs of electrons present on the central chlorine atom. Therefore the bond angle in ClO_2^- is less than 118° which is the bond angle in ClO_2 which has less number of electrons on central chlorine atom.

13. (b) $HClO_4$ is the strongest acid amongst all because the oxidation state or Cl is maximum (+7).

14. (a) SF_4 has 4 bond pairs and 1 lone pair of electrons, sp^3d hybridisation leads to irregular shape  and resultant $\mu \neq 0$.

15. (a) $4HCl + O_2 \rightarrow \underset{\text{cloud of white fumes}}{2Cl_2 + 2H_2O}$

16. (d) The fluorine has low dissociation energy of F - F bond and reaction of atomic fluorine is exothermic in nature

17. (a) CN^- ion acts good complexing as well as reducing agent.

18. (c) The H–X bond strength decreases from HF to HI. i.e. $HF > HCl > HBr > HI$. Thus HF is most stable while HI is least stable. This is evident from their decomposition reactions. The decreasing stability of the hydrogen halide is also reflected in the values of dissociation energy of the H–X bond

H–F	H–Cl	H–Br	H–I
$135\ kcal\ mol^{-1}$	$103\ kcal\ mol^{-1}$	$87\ kcal\ mol^{-1}$	$71\ kcal\ mol^{-1}$

19. (d) Chlorine reacts with excess of ammonia to produce ammonium chloride and nitrogen.
$3Cl_2 + 8NH_3\ (excess) \longrightarrow 6NH_4Cl + N_2$

EXERCISE 4

1. (b) $RCOO^-$ is not pseudo halide . See list of pseudo halides

2. (d) HF does not act as reducing agent

3. (d) In gaseous state the HCl is covalent in nature while in aqueous solution it ionises to give H^+ and $C\bar{l}$ ions

4. (c) $2NaCl + K_2Cr_2O_7 + 4H_2SO_4 \rightarrow$

$$Na_2SO_4 + 2KHSO_4 + \underset{\text{Chromyl Chloride}}{CrO_2Cl_2} + H_2O$$

5. (b) Antichlor is a compound which removes unreacted chlorine from a material. For example hypo

6. (a) HBr is oxidized to Br_2
$H_2SO_4 + 2HBr \rightarrow SO_2 + 2H_2O + Br_2$

7. (c) $\underset{\text{Hypochlorite}}{3NaOCl} \rightarrow \underset{\text{Chlorate}}{NaClO_3} + \underset{\text{Chloride}}{2NaCl}$ (disproportionation)

8. (c) $HgO + 2Cl_2 + H_2O \rightarrow HgCl_2 + 2HOCl$

9. (c) $2KClO_3 + 4HCl \rightarrow 2KCl + Cl_2 + 2ClO_2 + 2H_2O$
The mixture of $(Cl_2 + ClO_2)$ is known as 'euchlorine".

10 (b) $2CaO + 2Cl_2 \rightarrow CaCl_2 + Ca(ClO)_2$

11. (b) $6CaOCl_2 \rightarrow Ca(ClO_3)_2 + 5CaCl_2$
(disproportionation or auto oxidation)

12. (d) All the factors are responsible for the greater reactivity of F_2

13. (c) $SO_2 + Cl_2 \rightarrow \underset{\text{Sulphuryl chloride}}{SO_2Cl_2}$

14. (b) $NaF + HF \rightarrow NaHF_2$

15. (d) The reactivity of halogens follows the order $F_2 > Cl_2 > Br_2 > I_2$ Hence I_2 cannot replace Br_2 from KBr.

16. (a) In ClO_4^- the Cl is present in its highest O.S of +7 hence it can undergo reduction and not oxidation

17. (a) $KF + HF \rightarrow KHF_2$

18. (b) $2KI + Cl_2 \rightarrow 2KCl + I_2$
$I_2 + CCl_4 \rightarrow$ Violet Colour
Note: The excess of Cl_2 should be avoided. The layer may become colourless due to conversion of I_2 to HIO_3
$I_2 + 5Cl_2 + 6H_2O \rightarrow 2HIO_3 + 10HCl$
In case of Br_2 : $Br_2 + 2H_2O + Cl_2 \rightarrow 2HBrO + 2HCl$
The layer test is based upon distribution law

19. (c) The bond energy of interhalogen compounds is less than the bond energy of halogens

20. (c) $Cl_2 + H_2O \rightarrow 2HCl + \frac{1}{2}O_2$
Hydrogen has more affinity for chlorine.

21. (a) Non-metallic oxides are acidic and acidic character decreases with decreasing non-metallic character.

22. (d) $6CaOCl_2 \rightarrow Ca(ClO_3)_2 + 5CaCl_2$
It is auto oxidation.

23. (d) $2KI + Cl_2 \rightarrow I_2 + 2KCl$
$I_2 + CCl_4 \rightarrow$ violet
$I_2 + 5Cl_2(Excess) + 6H_2O \rightarrow 2HIO_3 + 10HCl$
violet colour disappear

24. (b) 10 g of $CaOCl_2$ will give

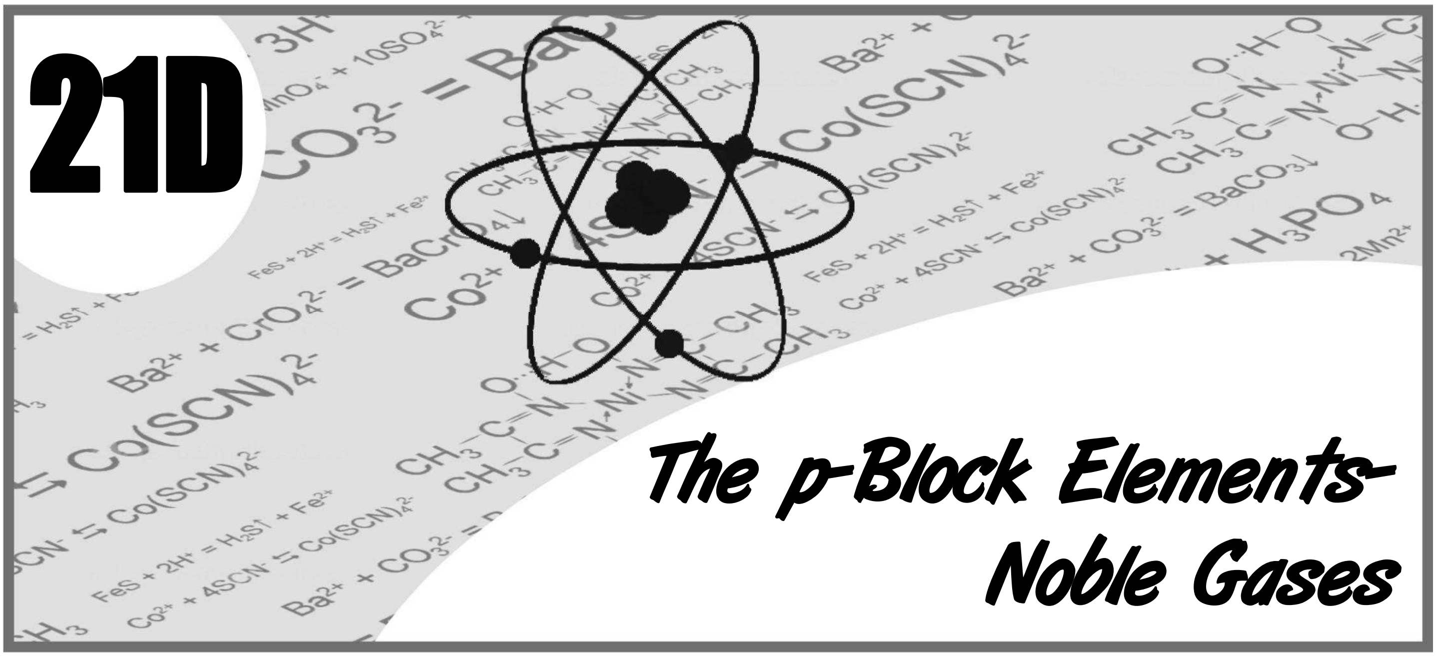
$$4.9\ g\ of\ Cl_2 = \frac{4.9 \times 22.4}{71} = 1.5\ litre$$

25. (c) Statement (c) is correct.

26. (d) Bleaching powder + HCl $\longrightarrow Cl_2$ (maximum)

27. (b) Except ionisation potential other factors are true to explain the oxidising (strong) behaviour of F_2 .

28. (b) $2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$



21D

The p-Block Elements- Noble Gases

INTRODUCTION :

The group 18 of the periodic table consists of colourless, odourless gases at room temperature, isolated by *William Ramsay and lord Rayleigh* in 1898 from air. They realized that a sample of nitrogen formed synthetically had a different density than obtained from air after removing oxygen, water vapour and carbon dioxide. The sample from air was heavier and it was found to contain 1.0% mixture of inert gases by volume (except Rn). Radon was obtained by radioactive disintegration of radium.

Helium is second most abundant element in the universe.

Argon is the most abundant of all the inert gases in the atmosphere.

GENERAL CHARACTERISTICS :

1. **Electronic configuration :**

Element	*Symbol*	*At No.*	*Valence shell electronic confg.*
Helium	He	2	$1s^2$
Neon	Ne	10	[He] $2s^2 2p^6$
Argon	Ar	18	[Ne] $3s^2 3p^6$
Krypton	Kr	36	[Ar] $3d^{10} 4s^2 4p^6$
Xenon	Xe	54	[Kr] $4d^{10}$, $5s^2 5p^6$
Radon	Rn	86	[Xe] $4f^{14}$, $3d^{10}$, $6s^2 6p^6$

2. **Physical state -** They are all gases under ordinary conditions of temperature and pressure.
3. **Presence -** Except Radon all occur in atmosphere in dry air 10% by volume. Main commercial source of helium is natural gas .
4. **Abundance-** In 1.0% air the abundance follows the order Ar> Ne>He>Kr> Xe
5. **Atomicity-** The $C_p/C_v = 1.67$ shows their monoatomic nature.
6. **Melting and boiling points-** Due to the increase in magnitude of Van der waals forces, the mpt and bpt increases from He to Rn.
7. **Atomic radii-** The atomic radii increases from He to Rn and it corresponds to the vander waals radii.
8. **Critical temperature/critical pressure-** The critical temperature (T_c) and Critical pressure (P_c) of noble gases increase down the group

Element	*He*	*Ne*	*Ar*	*Kr*	*Ye*	*Rn*
T_c(K)	5.1	44.3	150.6	211.0	256.4	373.5
P_c(Atm)	2.26	26.86	47.99	54.3	58.2	62.4

9. **Density-** The density of noble gases increases down the group.
10. **Heat of vaporisation** - They have very low values of heat of vaporisation due to weak van der waals forces of attraction. The value increases down the group.
11. **Solubility in water-** They are slightly soluble in water and solubility increases from He te Rn.
12. **Liquefication** - It is extremely difficult to liquefy inert gases due to weak van der waals forces of attraction among their molecules. Hence they possess low value of critical temperature also.
13. **Ionisation energy-** All noble gases possess very stable (ns^2 and ns^2p^6) electronic configuration. Therefore, ionisation energy of noble gases is very high and decreases down the group.
14. **Electron affinity-** Due to the presence of stable electronic configuration they have no tendency to accept additional electron. Therefore electron affinity is almost zero.

15. **Polarizability-** The polarizability increases with the size and hence follows the order.

    He< Ne< Ar< Kr< Xe

16. **Adsorption by charcoal-** Except helium all are adsorbed by coconut charcoal at low temperature. The extent of adsorption increases down the group.

DISCOVERY :

(i) ***Argon-*** It was isolated by *Rayleigh* and confirmed by *Ramsay*, from air (free from O_2, moisture and CO_2). Due to its inertness the gas was named as argon (meaning lazy).

(ii) ***Helium-*** It was observed in the spectrum of the sun hence name helium, from helios, which means sun, by *Lockyer and Frankland. Ramsay* obtained it from gases occluded in uranium minerals.

(iii) ***Neon, Krypton and Xenon-*** These were obtained by fractional distillation of liquid air under reduced pressure. These were named as neon means "***new***" krypton means "***hidden***" and Xenon means "***stranger or foreigner***".

(iv) ***Radon-*** Spectroscopically was noticed by *Dorn* and isolated by disintegration of radium by *Rutherford* and *Soddy*.

$$\underset{88}{Ra}^{226} \longrightarrow \underset{86}{Rn}^{222} + \underset{2}{He}^{4}$$

ISOLATION OF RARE GASES :

The following methods are employed for the isolation of Rare gas mixture.

(i) ***Ramsay and Rayleigh's first method-***

Air (dry and free from CO_2)

$$\xrightarrow[Cu]{\Delta} 2Cu + O_2 \longrightarrow CuO \xrightarrow[Mg]{\Delta}$$

$$2Mg + O_2 \rightarrow 2MgO \text{ and } 3Mg + N_2 \rightarrow Mg_3N_2$$

Residual gas - mixture of inert gases.

(ii) ***Ramsay and Rayleigh's second method***

$$Air + O_2 \xrightarrow[6000-8000V]{discharge} N_2 + O_2 \rightarrow 2NO \xrightarrow{NaOH} 2NO_2$$

$$2NO + O_2 \rightarrow 2NO_2$$

(CO_2 and NO_2 are absorbed by NaOH and O_2 if any is removed by alkaline pyrogallol)

(iii) ***Fischer and Ringe's method-***

$$Air \frac{90\%CaC_2}{10\%CaCl_2} \xrightarrow[373K]{\Delta} CaC_2 + N_2 \rightarrow [\underset{Nitrolium}{CaCN_2} + \underset{(C\ is\ graphite)}{C}]$$

$$C + O_2 \rightarrow CO_2$$

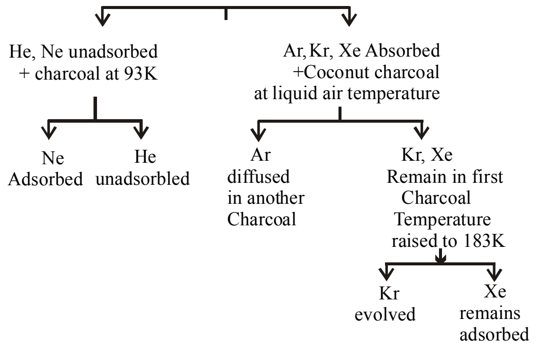
$$2CaC_2 + 3CO_2 \rightarrow 2CaCO_3 + 5C$$

CO_2 is absorbed in KOH and residual gas is dried over Conc H_2SO_4 and P_2O_5

SEPARATION OF RARE GASES BY DEWAR'S METHOD:

It is as follows

[He, Ne, Ar, Kr, and Xe] + Coconut charcoal at 171K



From liquid air - The difference in the boiling points of various constituents of liquid air make possible their separation by fractional distillation.

Element **He**	**Ne**	**N_2**	**Ar**	**O_2**	**Kr**	**Xe**
B.pt (K) **4**	**27**	**77**	**87**	**90**	**121**	**124**

HELIUM FROM OTHER SOURCES:

He is also obtained by heating mineral clavite to 1273K . The gas evolved is collected over potash solution to free from any CO_2. It may also be obtained from mineral by heating with dil.H_2SO_4 or $KHSO_4$.

Properties- The noble gases are inert in nature because of their completely filled s and p subshells. In 1962 the first compound of noble gases was prepared. It is hexa fluoroplatinate prepared by *Bartlett*.

$$Xe + PtF_6 \rightarrow Xe[PtF_6]$$

Now many compounds of Xe and Kr are known with fluorine and oxygen.

No compounds of He, Ne or Ar exist, except under very special conditions (very unstable, not neutral compounds)

Rn is known to react with fluorine but its radio activity makes the study of its compounds difficult and dangerous. Kr forms one stable neutral molecule, KrF_2. A, Kr- N bond has also been reported, stable only below –50° C.

Xe forms several compounds with fluorine and oxygen and Xe-N and Xe-C bonds have been reported.

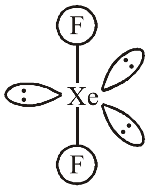
$$Xe + F_2 \xrightarrow{673K} XeF_2$$
2 : 1

$$Xe + 2F_2 \xrightarrow[5-6Atm]{673K} XeF_4$$
1 : 5

$$Xe + 3F_2 \xrightarrow[50-60\ Atm]{573K} XeF_6$$
1 : 20

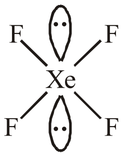
STRUCTURES OF XENON FLUORIDES :

XeF_2 hybridization sp^3d



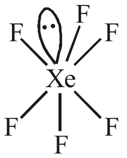
Linear

XeF_4 hybridization sp^3d^2



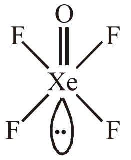
square planar

XeF_6 Hybribisation sp^3d^3

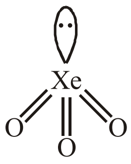


Pentagonal pyramidal or distorted octahedral

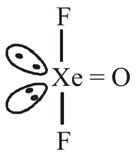
XeO_3 is the anhydride of Xenic acid H_2XeO_4 - The structures of oxyfluorides and oxides of Xenon are as follows.



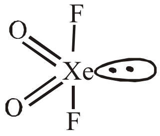
$XeOF_4$
Square pyramidal
(sp^3d^2)



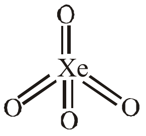
XeO_3
trigonal pyramidal
(sp^3)



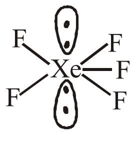
$XeOF_2$
T – shaped
(sp^3d)



XeO_2F_2
See-Saw
(sp^3d)



XeO_4
Tetrahedral
(sp^3)



XeF_5^-
Pentagonal planar
(sp^3d^3)

Uses

(1) ***Helium*** - It is non-inflamable. It has low density and its lifting power is 92% that of hydrogen and used to lift weather balloons and airships. It is used as breathing mixture (or oxygen dilutant) for divers. Mixture of O_2 and He is used in the treatment of asthma. It is also used for inflating the tyres of aeroplanes.

(2) ***Neon*** - When an electric current is passed through a sample of the gas, it has a characteristic orange - red glow. Neon lighting is used for advertising. The noble gases argon (purple), Xenon (blue green) and Krypton (pale violet) are also used in "neon" lighting.

(3) ***Argon*** - It is used primarily to create an inert atmosphere in light bulbs, welding and fluorescent bulbs. It is also used in geiger counters, as it becomes ionised in the presence of radiation. The ratio of ^{40}K to ^{40}Ar can be used to date the age of rocks since argon is obtained by radioactive decay of an isotope of potassium.

(4) ***Krypton*** - The light emitted by Krypton in an electric discharge tube is used for runway and approach lights in airports.

(5) ***Xenon*** - It is used in electrical flash bulbs for high speed photography.

(6) ***Radon*** - In radiotherapy of cancer.

CLATHRATES :

A number of organic and inorganic compounds having noble gases trapped into the cavities of crystal lattices are called ***enclosure*** or ***clathrate*** compounds. They are known as ***cage compounds*** also.

The substance having cavities in crystal lattices is called the host and atom of noble gases entraped in it is called the guest which are held by Van der waals forces of attraction. The clathrates are non stoichiometric compounds. When clathrates are heated or dissolved the guest atom escapes from the host.

He and Ne do not form clathrates due to their small size.

Types of Clathrates - They are of two types.

(i) ***Gas hydrates*** - Solid water having entraped Ar, Kr, or Xe

(ii) ***Quinol Clathrates*** - Quinol having entraped Ar, Kr, and Xe

Uses of Clathrates

(i) ***Separation of noble gases*** - Since Ne does not form a clathrate with Quinol it is separated from Ar, Kr and Xe. The latter form a clathrate with quinol.

(ii) Xe- 133 clathrate is a source of γ- radiations

(iii) Kr - 85 clathrate is a source of β – radiations

(iv) As an anaesthetic - Xe clathrate is used for this

(v) For transporting isotopes of noble gases.

Exercise-1 | NCERT BASED QUESTIONS

Very Short/Short Answer Questions

1. Why do noble gases form compounds with fluorine and oxygen only?
2. Which compound led to the discovery of noble gas compounds.
3. Among the noble gases, Xe forms maximum noble gas compounds with fluorine. Why is it so?
4. Why do boiling points of noble gases increases from helium to radon?
5. Neon is generally used for warning signals. Why?
6. Give equations for the following :

   (*i*) $XeF_2 + H_2O \longrightarrow$

   (*ii*) $XeF_6 + H_2O \longrightarrow$

   (*iii*) $XeF_6 + PF_5 \longrightarrow$

   (*iv*) $XeF_6 + NaF \longrightarrow$
7. How is XeO_3 prepared? Write chemical equation.
8. Solubility of noble gases in water increases as we more down the group. Explain.
9. Why noble gases have low boiling point?
10. Xenon does not form fluorides, such as XeF_3 and XeF_5. Why?

Multiple Choice Questions

11. Which of the following fluorides of xenon is impossible?
(a) XeF_2 (b) XeF_3 (c) XeF_4 (d) XeF_6

12. The structure of XeF_6 is
(a) distorted octahedral (b) pyramidal
(c) tetrahedral (d) None of these

13. Which of the following statements is false ?
(a) Radon is obtained from the decay of radium
(b) Helium is inert gas
(c) Xenon is the most reactive among the rare gases
(d) The most abundant rare gas found in the atmosphere is helium

14. In XeF_2, XeF_4, XeF_6 the number of lone pairs on Xe are respectively
(a) 2, 3, 1 (b) 1, 2, 3 (c) 4, 1, 2 (d) 3, 2, 1.

15. Total number of lone pair of electrons in $XeOF_4$ is
(a) 0 (b) 1 (c) 2 (d) 3

16. Which of the following is least polarisable ?
(a) Ne (b) He (c) Xe (d) Kr

17. End-product of the hydrolysis of XeF_6 is
(a) XeF_4O (b) XeF_2O_2 (c) XeO_3 (d) XeO_3^-

18. For advertisement, the coloured discharge tubes contain :
(a) He (b) Ne (c) Ar (d) Kr

19. Which one of the following noble gases is not found in the atmosphere?
(a) Rn (b) Kr (c) Ne (d) Ar

20. Noble gases are group of elements which exhibit
(a) high chemical activity
(b) low chemical activity
(c) minimum electronegativity
(d) paramagnetic properties

21. Which one of the following statements regarding helium is incorrect ?
(a) It is used to produce and sustain powerful superconducting magnets.
(b) It is used as a cryogenic agent for carrying out experiments at low temperatures.
(c) It is used to fill gas balloons instead of hydrogen because it is lighter and non-inflammable.
(d) It is used in gas-cooled nuclear reactors.

22. Which inert gas show abnormal behaviour on liquefaction
(a) Xe (b) He (c) Ar (d) Kr

23. The ease of liquefaction of noble gases increases in the order
(a) $He < Ne < Ar < Kr < Xe$ (b) $Xe < Kr < Ne < Ar < He$
(c) $Kr < Xe < He < Ne < Ar$ (d) $Ar < Kr < Xe < Ne < He$

Exercise-2 | CONCEPTUAL MCQs

1. The last member of the family of inert gases is
(a) argon (b) radon
(c) xenon (d) neon

2. Which of the following is the correct sequence of the noble gases in their group in the periodic table?
(a) Ar, He, Kr, Ne, Rn, Xe (b) He, Ar, Ne, Kr, Xe, Rn
(c) He, Ne, Kr, Ar, Xe, Rn (d) He, Ne, Ar, Kr, Xe, Rn

3. Which of the following noble gases *do not* have an octet of electrons in its outermost shell?
(a) Neon (b) Radon
(c) Argon (d) Helium

4. Number of unpaired electrons in inert gas is
(a) zero (b) 8
(c) 4 (d) 18

5. In the following four elements, the ionisation potential of which one is the highest ?
(a) Oxygen (b) Argon
(c) Barium (d) Cesium

6. The elements which occupy the peaks of ionisation energy curve are
(a) Na, K, Rb, Cs (b) Na, Mg, Cl, I
(c) Cl, Br, I, F (d) He, Ne, Ar, Kr

7. Gradual addition of electronic shells in the noble gases causes a decrease in their
(a) ionisation energy (b) atomic radius
(c) boiling point (d) density

8. Which of the following noble gas is least polarisable?
(a) He (b) Xe
(c) Ar (d) Ne

9. In which of the following groups, when He is placed, its all the properties are satisfied
(a) with alkali metals (b) with halogens
(c) with inert gases (d) None of these

10. The most abundant inert gas in the atmosphere is
(a) He (b) Ne
(c) Ar (d) Kr

11. The lowest boiling point of helium is due to its
(a) inertness
(b) gaseous nature
(c) high polarisability
(d) weak van der Waals forces between atoms

12. Which one of the following elements is most reactive ?
(a) He (b) Ne
(c) Ar (d) Xe

13. Which of the noble gas has highest polarisability?
(a) He (b) Ar
(c) Kr (d) Xe

14. What is the atomic number (Z) of the noble gas that reacts with fluorine ?
(a) 54 (b) 10
(c) 18 (d) 2

15. Noble gases are group of elements which exhibit very
(a) high chemical activity
(b) low chemical activity
(c) minimum electronegativity
(d) much paramagnetic properties

16. The correct order of solubility in water for He, Ne, Ar, Kr, Xe is
(a) He > Ne > Ar > Kr > Xe (b) Ne > Ar > Kr > He > Xe
(c) Xe > Kr > Ar > Ne > He (d) Ar > Ne > He > Kr > Xe

17. The noble gas which was discovered first in the sun and then on the earth
(a) argon (b) xenon
(c) neon (d) helium

18. XeF_4 on partial hydrolysis produces
(a) XeF_4 (b) $XeOF_2$
(c) $XeOF_4$ (d) XeO_3

19. Which element out of He, Ar, Kr and Xe forms least number of compounds ?
(a) He (b) Ar
(c) Kr (d) Xe

20. The element which has not yet been reacted with F_2 is
(a) Ar (b) Xe
(c) Kr (d) Rn

21. What are the products formed in the reaction of xenon hexafluoride with silicon dioxide ?
(a) $XeSiO_4 + HF$ (b) $XeF_2 + SiF_4$
(c) $XeOF_4 + SiF_4$ (d) $XeO_3 + SiF_2$

22. XeF_6 on complete hydrolysis gives
(a) Xe (b) XeO_2
(c) XeO_3 (d) XeO_4

23. XeF_4 involves which hybridization
(a) sp (b) sp^2
(c) sp^2d (d) sp^3d^2

24. Shape of $XeOF_4$ is
(a) octahedral (b) square pyramidal
(c) pyramidal (d) T-shaped

25. The hybridization of Xe in XeF_2 is
(a) sp^3 (b) sp^2
(c) sp^3 d (d) sp^2d

26. Which is a planar molecule ?
(a) XeO_4 (b) XeF_4
(c) $XeOF_4$ (d) XeO_2F_2

27. Which of the following has sp^3 hybridization ?
(a) XeO_3 (b) BCl_3
(c) XeF_4 (d) BBr_3

28. Which of the following two are isostructural ?
(a) XeF_2, IF_2^- (b) NH_3, BF_3
(c) CO_3^{2-}, SO_3^{2-} (d) PCl_5, ICl_5

29. The number of lone pair of electrons present on Xe in XeF_2 is
(a) 3 (b) 4
(c) 2 (d) 1

30. Match List I with List II and select the answer using the codes given below :

Code	*List I*	*Code*	*List II*
A	XeF_4	1	Distorted octahedral
B	XeF_6	2	Tetrahedral
C	XeO_3	3	Square planar
D	XeO_4	4	Trigonal pyramidal

(a) A-4, B-1, C-3, D-2 (b) A-2, B-3, C-1, D-4
(c) A-1, B-4, C-2, D-3 (d) A-3, B-1, C-4, D-2

31. Hybridization and structure of XeF_4 is
(a) sp^3d, trigonal bipyramidal(b) sp^3, tetrahedral
(c) sp^3d^2, square planar (d) sp^3d^2, hexagonal

32. Number of lone pairs of electrons on Xe atoms XeF_2, XeF_4 and XeF_6 molecules are respectively
(a) 3, 2 and 1 (b) 4, 3 and 2
(c) 2, 3 and 1 (d) 3, 2 and 0

33. Which one of the following is correct pair with respect to molecular formula of Xenon compound and hybridization state of Xenon in it?
(a) XeF_4, sp^3 (b) XeF_2, sp
(c) XeF_2, sp^3d (d) XeF_4, sp^2

34. The coloured discharge tubes for advertisement mainly contain
(a) xenon (b) helium
(c) neon (d) argon

35. Sea divers go deep in the sea water with a mixture of which of the following gases
(a) O_2 and He (b) O_2 and Ar
(c) O_2 and CO_2 (d) CO_2 and Ar

36. Which of the following is the life saving mixture for an asthmas patient ?
(a) Mixture of helium and oxygen
(b) Mixture of neon and oxygen
(c) Mixture of xenon and nitrogen
(d) Mixture of argon and oxygen

37. In the clathrates of xenon with water, the nature of bonding between xenon and water molecule is
(a) covalent
(b) hydrogen bonding
(c) co-ordinate
(d) dipole-induced dipole interaction

38. Which of the following cannot be formed ?
(a) He^{2+} (b) He^{+}
(c) He (d) He_2

Exercise-3 | PAST COMPETITION MCQs

1. Noble gases do not react with other elements because
(a) they are mono atomic **[CBSE PMT 1994]**
(b) they are found in abundance
(c) the size of their atoms is very small
(d) they are completely paired up and stable electron shells

2. Which of the following statements is false ? **[CBSE PMT 1994]**
(a) Radon is obtained from the decay of radium
(b) Helium is inert gas
(c) Xenon is the most reactive among the rare gases
(d) The most abundant rare gas found in the atmosphere is helium

3. XeF_2 is isostructural with : **[NEET 2013]**
(a) ICl_2^- (b) $SbCl_3$
(c) $BaCl_2$ (d) TeF_2

4. Which one of the following statement regarding helium is **incorrect** ? **[AIEEE 2004]**
(a) It is used to produce and sustain powerful superconducting magnets
(b) It is used as a cryogenic agent for carrying out experiments at low temperatures
(c) It is used to fill gas balloons instead of hydrogen because it is lighter and non-inflammable
(d) It is used in gas-cooled nuclear reactors

5. Which one of the following reactions of xenon compounds is not feasible? **[AIEEE 2009]**
(a) $3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12HF + 1.5O_2$
(b) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$
(c) $XeF_6 + RbF \longrightarrow Rb[XeF_7]$
(d) $XeO_3 + 6HF \longrightarrow XeF_6 + 3H_2O$

6. Which of the following has maximum number of lone pairs associated with Xe ? **[AIEEE 2011 RS]**
(a) XeF_4 (b) XeF_6
(c) XeF_2 (d) XeO_3

7. Total number of lone pair of electrons in $XeOF_4$ is
(a) 0 (b) 1 **[IIT-JEE 2004]**
(c) 2 (d) 3

8. The shape of XeO_2F_2 molecule is **[IIT-JEE 2012]**
(a) trigonal bipyramidal (b) square planar
(c) tetrahedral (d) see-saw

Exercise-4 | Applied MCQs

1. Density of nitrogen gas prepared from air is slightly greater than that of nitrogen prepared by chemical reaction from a compound of nitrogen due to the presence of
(a) argon
(b) carbon dioxide
(c) some N_3 molecules analogous to O_3
(d) greater amount of N_2 molecules derived from N-15 isotope

2. A radioactive element X decays to give two inert gases X is
(a) ${}^{238}_{92}U$ (b) ${}^{226}_{88}Ra$
(c) Both (a) and (b) (d) Neither (a) nor (b)

3. Coconut charcoal at 100°C adsorbs a mixture of
(a) He and Kr (b) Ar, Kr and Xe
(c) Kr and Xe (d) He and Ne

4. If two liters of air is passed repeatedly over heated copper and heated Mg till no further reduction in volume takes place the volume finally obtained will be approximately
(a) 200 mL (b) 20 mL
(c) zero (d) 10 mL

5. The atomic weight of noble gases is obtained by using the relationship
(a) Atomic weight = equivalent weight × valency
(b) Atomic weight = equivalent weight/ valency
(c) At. weight = valency/ equivalent weight
(d) 2 × V.D. = molecular weight = atomic weight

6. Compounds formed when the noble gases get entrapped in the cavities of crystal lattices of certain organic and inorganic compounds are known as
(a) Interstitial compounds (b) Clathrates
(c) Hydrates (d) Picrates

7. The noble gas which behaves abnormally in liquid state is
(a) Xe
(b) Ne
(c) He
(d) Ar

8. Which is called stranger gas
(a) Kr
(b) Xe
(c) He
(d) Ne

9. In order to prevent the hot metal filament from getting burnt, when the electric current is switched on, the bulb is filled with
(a) CH_4
(b) An inert gas
(c) CO_2
(d) Cl_2

10. In Kroll and IMI process of the production of titanium, the inert gas used is
(a) Ne
(b) Ar
(c) Kr
(d) Xe

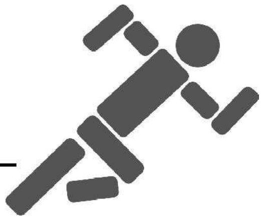
11. Which is called lazy gas?
(a) Kr
(b) Ar
(c) He
(d) Ne

12. Which statement about noble gases is not correct?
(a) Xe forms XeF_6
(b) Ar is used in electric bulbs
(c) Kr is obtained during radioactive disintegration
(d) He has the lowest b.pt among all the noble gases

13. Which has the same electronic configuration as of inert gas?
(a) Ag^{3+}
(b) Cu^{2+}
(c) Pb^{4+}
(d) Ti^{4+}

14. Which noble gas does not form clathrates?
(a) Xe
(b) Kr
(c) He
(d) Ar

Hints & Solutions



EXERCISE 1

2. Formation of $O_2^+[PtF_6]^-$ led to the discovery of first noble gas compound $Xe[PtF_6]$.

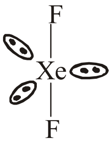
5. Neon lights are visible from distance even in fog and mist and hence neon is generally used for warning signals.

6.
$(i)\ 2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$
$(ii)\ XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$
$(iii)\ XeF_6 + PF_5 \longrightarrow [XeF_5]^+[PF_6]^-$
$(iv)\ XeF_6 + NaF \longrightarrow Na^+[XeF_7]^-$

7. XeO_3 is prepared by hydrolysis of XeF_6 or XeF_4.
$XeF_6 + 3H_2O \xrightarrow{\text{Hydrolysis}} XeO_3 + 6HF$
$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

11. **(b)** **12.** **(a)** **13.** **(d)** **14.** **(d)** **15.** **(b)** **16.** **(b)**
17. **(c)** **18.** **(b)** **19.** **(a)** **20.** **(b)** **21.** **(c)** **22.** **(b)**
23. **(a)**

EXERCISE 2

1. **(b)** Radon is the last member of family
2. **(d)** He, Ne, Ar, Kr, Xe, Rn
3. **(d)** Electronic configuration of He is $1s^2$
4. **(a)** Inert gases do not contain unpaired electrons
5. **(b)** Ionization potential of inert gases is highest in periodic table due to stable electronic configuration.
6. **(d)**
7. **(a)** Ionisation energy decreases as we move away from nucleus due to less electrostatic attraction between electrons and nucleus
8. **(a)** The smaller the size the least is the polarisability
9. **(c)** The differentiating electron enter in s subshell in case of He, hence it is s- block element. Its electronic configuration $1s^2$ makes it inert in nature hence it is placed with inert gases.
10. **(c)** Ar is the most abundant in atmosphere
11. **(d)** Due to weak van der Waal's forces, He has lowest boiling point
12. **(d)** Xe forms maximum compounds hence it is most reactive
13. **(d)** The larger the size the more is the polarisiability
14. **(a)** Atomic number Xe is 54. Xe reacts with F_2 and forms many compounds
15. **(b)** Noble gases exhibit low chemical activity
16. **(c)** Solubility increases from He to Rn
17. **(d)** He was observed in the spectrum of the sun
18. **(b)** $XeF_4 + H_2O \rightarrow 2HF + XeOF_2$
19. **(a)** No compound of He as yet been reported
20. **(a)** No compound of Ar as yet been reported with F_2
21. **(c)** $2XeF_6 + SiO_2 \rightarrow SiF_4 + 2XeOF_4$
22. **(c)** $XeF_6 + 3H_2O \rightarrow 6HF + XeO_3$
23. **(d)** Hybridisation in $XeF_4 = \frac{1}{2}(8+4+0-0) = 6\ sp^3d^2$
24. **(b)** $XeOF_4$ square pyramidal
25. **(c)** Hybridisation of XeF_2 is sp^3d
26. **(b)** XeF_4 is planar (see text)
27 **(a)** In XeO_3 the hybridisation is sp^3
28. **(a)** XeF_2 and IF_2^- both are linear and have hybridisation sp^3d
29. **(a)** XeF_2 has  structure hence number of lone pair of electrons 3

30. **(d)** XeF_4 is square planar (A-3) ; XeF_6 is distorted octahedral (B-1); XeO_3 trigonal pyramidal (C-4) and XeO_4 is tetrahedral (D-2).

31. (c) Hybridisation of XeF_4 is sp^3d^2 and structure is square planar

32. (a)

	XeF_2	XeF_4	XeF_6
Valence electrons of Xe	8	8	8
Electrons involved in bond formation	2	4	6
Lone pairs left	3	2	1

33. (c) Hybridisation in each case is $XeF_4 sp^3d^2$, $XeF_2 sp^3d$,

34. (c) Coloured discharge tubes mainly contain Neon

35. (a) Breathing mixture is $(O_2 + He)$

36. (a) Mixture of $(He + O_2)$ is used for asthma patient

37. (d) In clathrates the forces are dipole - induced dipole interaction

38. (d) He_2 Bond order $= \frac{1}{2}(2-2) = 0$ Hence cannot be formed.

EXERCISE 3

1. (d) On account of highly stable ns^2np^6 configuration in the valence shell. These elements have no tendency either to lose gain or share electrons with atoms of other elements i.e., their combining capacity or valency is zero. Further all the orbitals in the atoms of these elements are doubly occupied i.e electrons are not available for sharing.

2. (d) The most abundant rare gas found in the atmosphere is argon and not helium.

3. (a) $\mathrm{F}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Xe}}}\!:-\mathrm{F}$ *sp*^{3}*d* and Linear

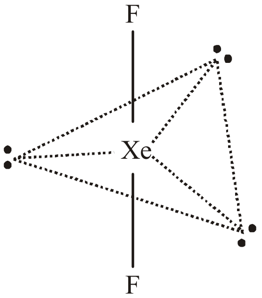
$^{-}\mathrm{Cl}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{I}}}\!:-\mathrm{Cl}$ *sp*^{3}*d* and Linear

4. (c) Helium is heavier than hydrogen although it is non-inflammable

5. (d) The products of the concerned reaction react each other forming back the reactants.

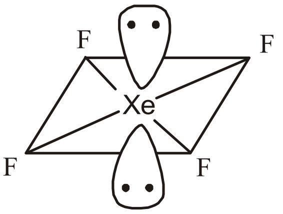
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF \cdot$$

6. (c) XeF_2 :



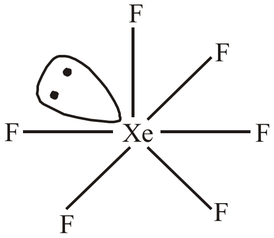
3ℓp

XeF_4 :

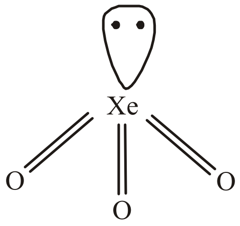


2ℓp

XeF_6 :



XeO_3 :

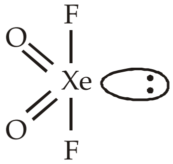


1ℓp

Hence XeF_2 has maximum no. of lone pairs of electrons.

7. (b) In $XeOF_4$, Xenon is *sp*^{3}*d*^{2} hybridised and has one lone pair.

8. (d) XeO_2F_2 has trigonal bipyramidal geometry, but due to presence of lone pair of electrons on equitorial position, its actual shape is *see-saw.*



EXERCISE 4

1. (a) Air contains about 1% inert gases, mainly Ar. (At.wt 40) The atomic wt of N_2 is 28

2. (b) $_{88}Ra^{226} \rightarrow {}_{86}Rn^{222} + {}_2He^4$. Both are inert gases

3. (b) Coconut charcoal at 100°C absorbs Ar, Kr and Xe

4. (b) Cu and Mg $\xrightarrow[\text{mainly } N_2 \text{ and } O_2]{\text{air}}$ CuO, MgO and Mg_3N_2

Air contains 1% inert gases which are left unreacted 1% of two liters is 20 ml

5. (d) $2 \times VD = M.wt =$ Atomic wt of inert gas since inert gases are monoatomic in nature

6. (b) The statement stands for the definition of Clathrates

7. (c) He behaves abnormally in liquid state

8. (b) Xe is also known as stranger gas

9. (b) Inert gases do not support combustion

10. (b) Argon is used in Kroll and IMI process for titanium to provide an inert atmosphere

11. (b) Ar is called lazy gas

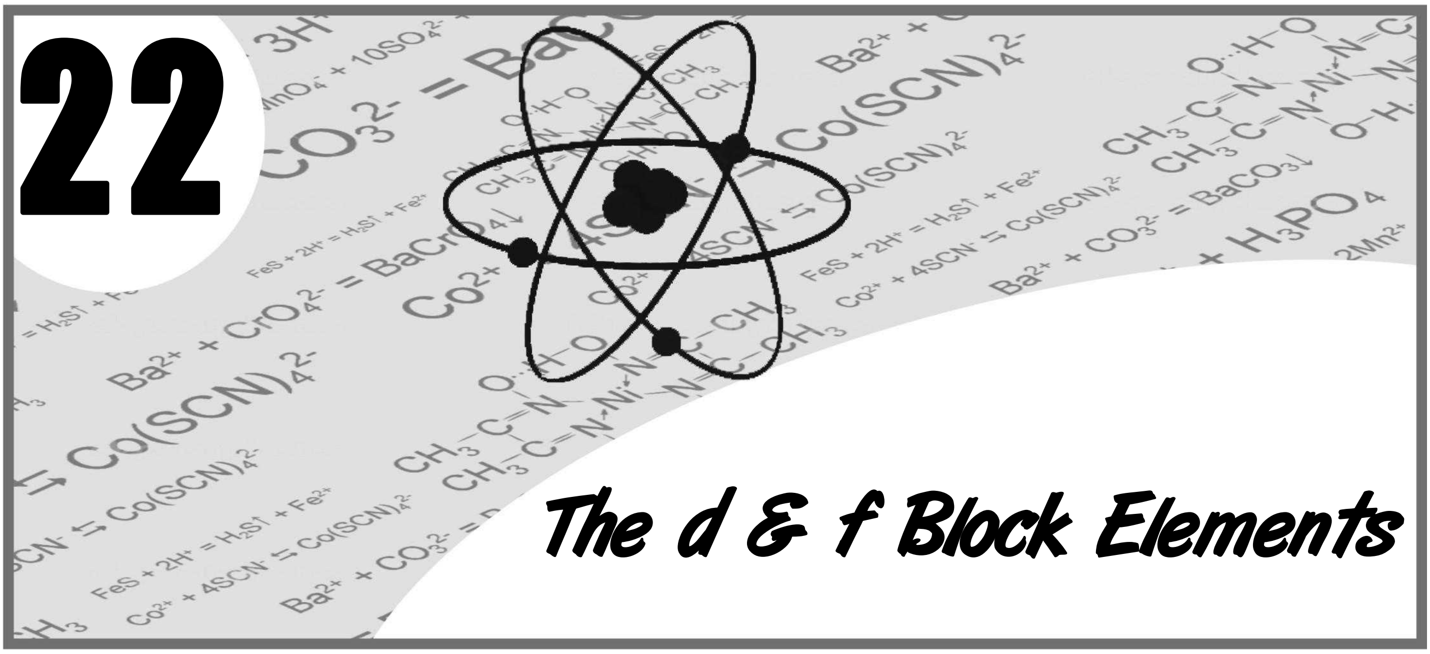
12. (c) He is obtained during radioactive decay

13. (d) $_{22}Ti = 1s^2, 2s^2p^6, 3s^2p^6d^2, 4s^2$; $Ti^{4+} = 1s^2, 2s^2p^6, 3s^2p^6$

14. (c) He does not form clathrates due to small size and low molecular weight. Ne also does not form clathrates for the same reason

22

The d & f Block Elements



GENERAL CHARACTERISTICS :

1. **Transition elements :-** Elements where the last orbitals filled are the d orbitals known as transition elements. They have been placed in the middle of the periodic table between electropositive s-block and electronegative p-block elements.
2. **General Electronic Configuration :-** Transition metals have the electronic configuration $(n-1)d^{1-10}ns^{0-2}$. When electrons fill orbitals, ns-orbital is filled first than $(n-1)$ d-orbital.When losing during oxidation ,ns electrons are lost first than (n-1)d electrons.

   Zn ,Cd, Hg ,the end members of first three series have their general electronic configuration $(n-1)d^{10}ns^2$. These do not show properties of transition elements to any appreciable extent and are called **non-typical** transition elements.
3. **Classification -** Transition elements consist of the following four series

3d series	$_{21}$Sc to $_{30}$Zn	$3d^{1-10}4s^{1-2}$
4d series	$_{39}$Y to $_{48}$Cd	$4d^{1-10}5s^{0-2}$
5d series	$_{57}$La $_{72}$ Hf to $_{80}$Hg	$5d^{1-10}6s^{1-2}$
6d series	$_{89}$ Ac $_{104}$Rf to $_{111}$Rg	

4. Electronic configurtion of transition elements-

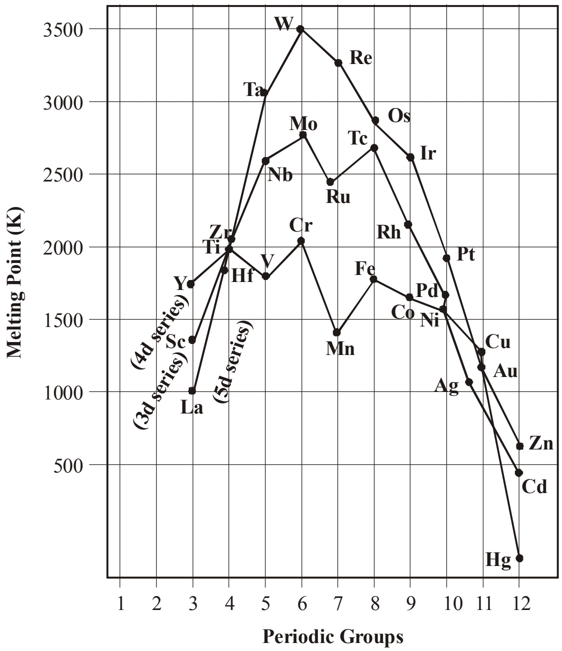
3d-Series			*4d-Series*			*5d-Series*		
Atomic number	*Element*	*Electronic configuration*	*Atomic number*	*Element*	*Electronic configuration*	*Atomic number*	*Element*	*Electronic configuration*
21	Sc	$[Ar]3d^1 4s^2$	39	Y	$[Kr]4d^1 5s^2$	57	La	$[Xe]5d^1 6s^2$
22	Ti	$[Ar]3d^2 4s^2$	40	Zr	$[Kr]4d^2 5s^2$	72	Hf	$[Xe]4f^{14} 5d^2 6s^2$
23	V	$[Ar]3d^3 4s^2$	41	Nb	$[Kr]4d^4 5s^1$	73	Ta	$[Xe]4f^{14} 5d^3 6s^2$
24	Cr	$[Ar]3d^5 4s^1$	42	Mo	$[Kr]4d^5 5s^1$	74	W	$[Xe]4f^{14} 5d^4 6s^2$
25	Mn	$[Ar]3d^5 4s^2$	43	Tc	$[Kr]4d^5 5s^2$	75	Re	$[Xe]4f^{14} 5d^5 6s^2$
26	Fe	$[Ar]3d^6 4s^2$	44	Ru	$[Kr]4d^7 5s^1$	76	Os	$[Xe]4f^{14} 5d^6 6s^2$
27	Co	$[Ar]3d^7 4s^2$	45	Rh	$[Kr]4d^8 5s^1$	77	Ir	$[Xe]4f^{14} 5d^7 6s^2$
28	Ni	$[Ar]3d^8 4s^2$	46	Pd	$[Kr]4d^{10} 5s^0$	78	Pt	$[Xe]4f^{14} 5d^9 6s^1$
29	Cu	$[Ar]3d^{10} 4s^1$	47	Ag	$[Kr]4d^{10} 5s^1$	79	Au	$[Xe]4f^{14} 5d^{10} 6s^1$
30	Zn	$[Ar]3d^{10} 4s^2$	48	Cd	$[Kr]4d^{10} 5s^2$	80	Hg	$[Xe]4f^{14} 5d^{10} 6s^2$

5. **Physical properties of transition elements-**

(i) ***Metallic character-*** Transition metals can lose valence electrons and form cations $M \rightarrow M^{+n} + ne^-$ They have simple hcp, ccp and bcc lattices characteristic of true metals. Except Hg they are solids at room temperature and are dense ($d = 5g/cm^3$ in general, in case of osmium 22.6g/ cm^3), lustrous, malleable, ductile thermal and electrical conductors.

There is gradual decrease in electropositive character from left to right

(ii) ***Melting and boiling point -*** Due to strong metallic bond , they have high mpts and bpts. The mpts of these elements rise to a maximum and then fall with the increase in atomic number the manganese and technitium show abnormal values as shown by graph)

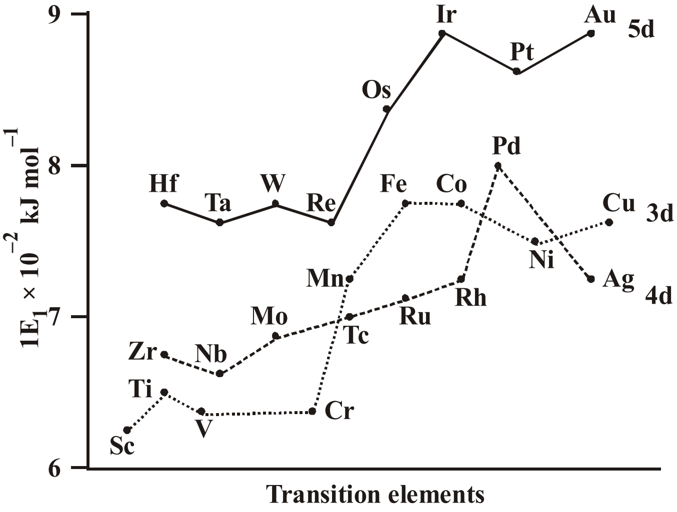


Melting point of Transition metals

(iii) ***Ionisation energy-*** The ionisation energy increases with the increase in the atomic number but not in regular manner. The ionisation energies of 5d elements are higher than those of 4 d and 3d elements due to greater effective nuclear charge which in turn is due to poor shielding of nucleus by 4f electrons.

Formation of Ni^{++} requries 2.49 kJ mol^{-1} and formation Pt^{++} requries 2.66 kJ mol^{-1} . Hence Ni (II) compounds are thermodynamically more stable than Pt (II) Compounds.

Formation of Ni^{4+} requires 11.29 kJ mol^{-1} and formation of Pt^{4+} requires 9.36 kJ mol^{-1} . Hence Pt (IV) compounds are relatively more stable than nickel (IV) compounds. Thus K_2PtCl_6 is well known where as the corresponding nickel compound is not known. (Ionisation energy graph is sketched here for ready reference)



First ionization energies of 3d-4d- and 5d- transition series

(iv) ***Electrode potential*** (E^0) ($E^0\ M^{n+}/M$) is governed by three factors

(a) Heat of sublimation

(b) Heat of ionisation

(c) Heat of hydration

For the 3d transition metals the $E^0 M^{2+}/M$ values are

V	Cr	Mn	Fe	Co	Ni	Cu
-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	0.35
						(Volts)

The irregular trend is due to variation in ionization energies and sublimation energies. Except copper 3d elements are good reducing agents but weaker than s-block elements.

(v) ***Oxidation states*** -In different types of compounds , transition metals exhibit different oxidation states. The highest oxidation state is exhibited in fluorides and oxides. In lower oxidation state the compounds formed are ionic and in higher oxidation state they are covalent in nature. Osmium exhibit +8 O.S. (highest)often but Ru exhibit +8 oxidation state rarely. Transition metals also show oxidation states +1 and zero.

Fe^{3+} is more stable than Fe^{2+}. Hence Fe^{2+} act as reducing agent Cr^{3+} is more stabe than Cr^{2+}. Hence Cr^{2+} act as reducing. Mn^{2+} is more stable than Mn^{3+} Hence Mn^{3+} act as oxidising agent

(vi) ***Atomic and Ionic radii -*** The values for atomic radii and ionic radii are in between the values for s and p-block elements. In 3d transition series the ionic radii for M^{2+} ion decreases upto the middle of the period then becomes almost constant (see table)

Due to lanthanide contraction the second and third member of each group have atomic redii close to each other (Zr.160 pm,Hf 159pm)

TABLE

Element	*Sc*	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Co*	*Ni*	*Cu*	*Zn*
Atomic radii (pm)	144	132	122	117	117	117	116	115	117	125
I. E. kJ mol^{-1}	631	656	650	652	717	762	758	736	745	906
Oxidation State	+3	(+2)	+2	+2	+2	+2	+2	+2	+1	+2
	+3	+3	+3	(+3)	+3	+3	(+3)	+2		
	+4	+4	(+4)	+4	(+4)	(+6)	(+4)			
	+5	(+5)	(+6)							
		+6	+7							

Element	*Y*	*Zr*	*Nb*	*Mo*	*Tc*	*Ru*	*Ph*	*Pd*	*Ag*	*Cd*
Atomic radii	180	160	160	146	136	134	134	137	144	154
(pm)										
I.E. (kJ mol^{-1})	616	674	664	685	703	711	720	804	731	876
Oxidation State	+3	(+3)	(+2)	(+2)	+4	+2	+3	+2	+1	+2
	+4	(+3)	+3	(+5)	+3	+4	(+3)	(+2)		
	(+4)	+4	+7	+4	(+6)	+4	(+3)			
	+5	+5		(+5)						
		+6		(+6)						
				(+7)						
				(+8)						

Element	*La*	*Hf*	*Ta*	*W*	*Re*	*Os*	*Ir*	*Pt*	*Au*	*Hg*
Atomic radii (pm)	187	159	146	139	137	135	136	138	144	157
I.E. (kJ mol^{-1})	541	760	760	770	759	840	900	870	889	1007
Oxidation State	+3	(+3)	(+2)	+2	+3	(+2)	(+2)	+2	+1	+1
	+4	(+3)	(+3)	+4	(+3)	+3	(+3)	+3	+2	
	(+4)	+4	+5	+4	+4	+4				
	+5	+5	+6	+6	(+6)	(+5)				
		+6	+7	+8		(+6)				

(vii)Density **-** d-block elements have high density because of their small atomic sizes and strong metallic bonding.

Density	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
g/ml	3.0	4.54	6.10	7.19	7.40	7.87	8.70	8.90	8.92	7.13

(viii)Atomic volume **-** Atomic volume decreases along the period due to decrease in size.

(ix) Reactivily **-**d-block elements are less reactive due to high ionisation energies. Some are almost inert and known as noble metals, e.g. Au, Pt, Ru, Rh, Os, Ir etc.

(x) Complex formation **-** They are well known to form a large number of complex compounds mainly due to

(i) Small atomic size and higher nuclear charge.

(ii) Presence of partly filled or vacant orbitals eg. $K_4[Fe(CN)_6]$

(xi) Coloured ions **-** The colour exhibited by transition metal ions is due to the presence of unpaired electrons in d-orbitals which permits the d-d excitation of electrons.

Colour of a complex depends on the ***metal,*** its ***oxidation*** state and its ***ligands***. e.g.

$$\left[\mathrm{Cu}\left(\mathrm{H_2O}\right)_4\right]^{2+} \text{ is Pale blue}$$

$$\left[\mathrm{Cu}\left(\mathrm{NH_3}\right)_4\right]^{2+} \text{ is Dark blue}$$

$CuSO_4.5H_2O$ is blue in colour and anhydrous $CuSO_4$ is colourless. In absence of ligands all d orbitals are degenerate (same energy) and the possbility of d-d excitation is no more. In presence of ligand $d_{x^2-y^2}$ and d_{z^2} have higher energy, d-d transition take place by absorption of light, hence the colour.

(xii) **Magnetic properties** -They are

(i) **Paramagnetic-** This is due to the presence of unpaired electrons in d-orbitals. Paramagnetic character increases with the number of unpaired electrons.

(ii) **Diamagnetic -** Diamagnetic substances are repelled by an applied magnetic field.

(iii) **Ferromagnetism -** In this case permanent magnetic moment is acquired by substance e.g. Fe. Magnetic moment is given by

$\mu = \sqrt{n(n+2)}$ **B.M.** where n = number of unpaired electrons and B.M. = Bohr magneton (unit of magnetic moment)

(xiii) **Catalytic properties** - The transition metals and their compounds behave as catalyst due to

(a) The presenc of partly filled d-orbitals and exhibiting various oxidation states.

(b) Their formation of intermediate complex with reactants and thus lowering the energy of activation

(c) Their rough surface area provides active sites for adsorption of reactant molecules. eg.

Iron in the preparation of NH_3 ***(Habers process)***

Finely divided nickel for hydrogenation

Pt or V_2O_5 in the preparation of H_2SO_4 ***(Contact process)***

Pt in the preparation of nitric acid ***(Ostwald's process)***

(xiv) **Formation of alloys** -d block elements have a strong tendency to form alloys since their atomic sizes are very similar and in the crystal lattice one metal can be readily replaced by another. Alloys so formed are hard, have high m.pts. The metals Mo, W, Cr, Ni, and V are used for the production of stainless steel and alloy steel.

Amalgam is an alloy formed by mercury with other metals. ***Iron*** and ***platinum*** do not form any alloy with mercury.

(xv) Interstitial compounds - The empty space persent in a crystal lattice is known as interstitial place. The non metal atoms due to their small size (eg H, B, N, C etc.) when occupy such place the resulting compound is known interstitial compound. Such compounds are hard and rigid e.g. cast iron and steel.

(xvi) Non stoichiometric compounds -The compounds not having the elements in the exact ratio as shown by the moleculer formula are known as non stoichiometric compouds e.g., FeO, CuO etc. In FeO the Fe : O is approx. 0.94 : 1 and not exactly 1:1.

IRON [Fe, At.No.26, $[Ar]3d^6 4s^1$]

Being reactive in nature it does not occur in free state.

1. Ores of Iron-

Haematite	Fe_2O_3
Magnetite	Fe_3O_4
Limonite or hydrated ferric oxide	$Fe_2O_3.3H_2O$
Iron pyrites	FeS_2
Siderite	$FeCO_3$
copper pyrites	$CuFeS_2$

2. Extraction - It is extracted from haematite Fe_2O_3 in a blast furnace by reduction with carbon and carbon monoxide. The steps inolved are-

(a) Concentration - The crushed ore is agitated with water and then concentrated by electromagnetic method.

(b) Roasting or Calcination- To remove volatile substances and organic matter. FeO changes to Fe_2O_3

$$S + O_2 \rightarrow SO_2$$
$$4As + 3O_2 \rightarrow 2As_2O_3$$

$$FeCO_3 \rightarrow FeO + CO_2$$
$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$
$$4FeO + O_2 \rightarrow 2Fe_2O_3$$

(c) Smelting - Roasted or calcinated ore is mixed with lime stone and coke and fed into blast furnace. Reactions taking place in the blast furnace.

(i) Lower region $C + O_2 \rightarrow CO_2 + 97,000$ cal.

(ii) Middle region

$$CO_2 + C \rightarrow 2CO - 39000 \text{ cal.}$$
$$CaCO_3 \rightarrow CaO + CO_2 - \text{heat}$$
$$CaO + SiO_2 \rightarrow CaSiO_3 \text{ (Slag)}$$

(iii) Upper region

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2 \uparrow$$
$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$$
$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$
$$FeO + C \rightarrow Fe + CO$$

The gases leaving the furnace contain CO and used to heat incoming air blast.The two layers in the blast furnace are-

Upper layer - Molten Iron - It is poured out in moulds and known as *PIG IRON* or *CAST IRON*.It contains 3-5% carbon and varying amounts of Mn, Si, P and S which make the iron hard and brittle.

Lower layer - Molten $CaSiO_3$ (slag)

3. Wrought -Iron -It is obtained by heating cast iron with haematite. The impurities are oxidised.

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \uparrow$$
$$2Fe_2O_3 + 3Si \rightarrow 4Fe + 3SiO_2 \uparrow$$
$$Fe_2O_3 + 3Mn \rightarrow 2FeO + 3MnO$$
$$MnO + SiO_2 \rightarrow MnSiO_3 \text{ (slag)}$$

It containes carbon 0.2-0.5% and traces of P and Si. It is pure form of Iron and soft , malleable, ductile. It is used to make magnets in electric cranes and dynamos, railway carriage couplings being corrosion resistant.

4. Steel - It contains carbon 0.1-1.5%and manufactured by following methods.

(a) Bessemer process - Molten pig iron is heated in large pear shaped furnace lined with silica bricks at 1873K when impurities such as Mn, Si, C burn off. When all carbon is completely burn off the requisite amount of carbon is added. Bessemer converter is lined with lime (CaO) or magnesia (MgO) when pig iron contains high percentage of phosphorous.

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

$$P_4O_{10} + 6CaO \rightarrow \underset{\text{Thomas slag}}{2Ca_3(PO_4)_2}$$

(b) ***Open hearth process-*** The cast iron, scrap iron , haematite ore and lime are mixed together and melted in open hearth furnace lined with SiO_2 or calcined dolomite (MgO. CaO) depending upon the nature of impurities.

$$2Fe_2O_3 + 3Si \rightarrow 4Fe + 3SiO_2$$
$$Fe_2O_3 + 3Mn \rightarrow 2Fe + 3MnO$$
$$MnO + SiO_2 \rightarrow MnSiO_3 (slag)$$
$$P_4 + 5O_2 \rightarrow P_4O_{10}$$
$$P_4O_{10} + 6CaO \rightarrow 2Ca_3(PO_4)_2 (slag)$$

(c) ***Electric furnace process -*** It is combination of Bessemer and open hearth process.

(5) Types of steel -

- *(i)* ***Soft steel-*** contains carbon 0.25%
- *(ii)* ***Mild steel -*** contains carbon 0.25-0.5%
- *(iii)* ***Hard steel-*** contains carbon 0.5-1.5 %
- *(iv)* ***Alloy steel-*** contains varying percentage of Ni, Cr, Mn, Co,W, V e.g. stainless steel is an alloy of Fe, Cr and Ni.

(6) Heat treatment of steel - The hardness of steel depends on its carbon content and heat treatment.

- *(i)* ***Quenching-*** It involves the heating of steel to red hot (1123K) and cooling it by plunging into cold water or oil. It makes the steel hard and brittle.
- *(ii)* ***Annealing-*** The steel is heated well below red heat and then cooled slowly. The steel becomes soft.
- *(iii)* ***Tempering*** - In this process the quenched steel is reheated to 504 to 574K and allowed to cool slowly. The brittleness disappears and hardness is retained.
- *(iv)* ***Nitriding-*** It involves the heating of steel in an atmosphere of ammonia when surface is coated with iron nitride. The steel becomes hard.
- *(v)* ***Case hardening-***The steel is heated in charcoal and then quenched.The steel becomes hard.

(7) Alloys of steel-The important alloy steels are

Name	*Composition*	*Uses and Properties*
(i) Tungsten steel	Fe 94%, W 5%, C 1%	It is very hard, resistant to water and used for making Rock drills and Safetys
(ii) Stainless steel	Fe 73% Cr 18%, Ni 8%, C 1%	It is resistant to corrosion. Used for making cutlery
(iii) Manganese steel	Fe 86%, Mn 13%, C 1%	It is hard, used for manufacturing high speed cutting tools
(iv) Invar	Fe 64%, Ni 36%	It has small coefficent of expansion, used in watches, meter scales and pendulum rods
(v) Permalloy	Fe 21%, Ni 78%, C 1%	It is strongly magnetised by electric current and lose magnetism when current is let off, used for manufacturing electromagnets and ocean cable.
(vi) Nickel steel	Fe 96-98%, Ni 2-4%	Resistant to corrosion, hard and elastic wire, used for making cables, gears and drive shafts.

(8) Some chemical properties of Iron-

(i) Red hot iron burns in O_2 giving sparks

$$3Fe + 2O_2 \rightarrow Fe_3O_4$$

(ii) When steam is passed over red hot iron, hydrogen is liberated and megnetic oxide of iron (ferroso ferric oxide) is formed-

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

(iii) Action of dil. H_2SO_4 -

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

(iv) Hot and conc. H_2SO_4 -

$$Fe + 2H_2SO_4 \rightarrow FeSO_4 + SO_2 + H_2O$$

(v) Action of dil. HNO_3 -

$$4Fe + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

(9) Passivity - The inertness exhibited by metals under conditions when chemical activity is to be expected is called passivity.Iron becomes passive with conc. HNO_3, Chromic acid , conc. H_2SO_4 and $KMnO_4$ etc. It is due to the formation of a thin layer of oxide at the surface of iron.

(10) Compounds of Iron :

(1) Ferric chloride -

(i) It is $FeCl_3.6H_2O$

(ii) ***Preparation*** - (i) By passing dry chlorine over heated iron, anhydrous ferric chloride is obtained

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3 \rightarrow Fe_2Cl_6$$

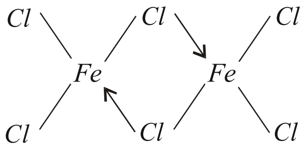
(iii) By the action of hydrochloric acid on ferric hydroxide or ferric oxide

$$Fe(OH)_3 + 3HCl \rightarrow 2FeCl_3 + 3H_2O$$
$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$$

It is soluble in water, alcohol and ether. $FeCl_3.6H_2O$ is yellow. Its aqueous solution is acidic. Sublimes at 300ºC, covalent and dissociates above 973K first into $FeCl_3$ then $FeCl_2$ and Cl_2 e.g.

$$Fe_2Cl_6 \overset{973K}{\rightleftharpoons} 2FeCl_3 \underset{above}{\overset{973K}{\rightleftharpoons}} 2FeCl_2 + Cl_2$$

Structure



- Oxidising nature of $FeCl_3$ is shown by following reactions

$$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$$

$$2FeCl_3 + SO_2 + 2H_2O \longrightarrow 2FeCl_2 + H_2SO_4 + 2HCl$$

- $FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3 \downarrow + 3NH_4Cl$ (brown ppt)
- $FeCl_3 + 3NH_4CNS \longrightarrow$

$$Fe(SCN)_3 + 3NH_4Cl \text{ (blood red colour)}$$

- $4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow$

$$\underset{\text{Ferric cyanide}}{Fe_4[Fe(CN)_6]_3} + 12KCl \text{ (prussion blue)}$$

- Action of heat -

$$2FeCl_3.6H_2O \longrightarrow Fe_2O_3 + 6HCl + H_2O$$

Uses - Used in medicine as *ASTRINGENT* and *ANTISEPTIC*. Its concentrated solution is used for etching copper and silver.

$$2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+}$$
$$Fe^{3+} + Ag \rightarrow Fe^{2+} + Ag^{+}$$

2. ***Ferrous Sulphate*** $FeSO_4.7H_2O$ ***(Green vitriol) :***

Prepartion

(i) $Fe + \text{dil } H_2SO_4 \rightarrow FeSO_4 + H_2$

(ii) ***Manufacture*** - From iron pyrites by oxidation by air

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4$$

Properties - Hydrated $FeSO_4.7H_2O$ is green and anhydrous $FeSO_4$ is colourless.

- ***Action of heat*** -

$$FeSO_4.7H_2O \xrightarrow{300^0C} FeSO_4 + 7H_2O \xrightarrow{strong} Fe_2O_3 + SO_2 + SO_3$$

- Its aqueous solution is acidic due to cationic hydrolysis

$$Fe^{++} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^+$$

- ***Reducing nature*** - It is strong reducing is nature.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
$$2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O$$

- Addition compound with NO which is dark brown

$$FeSO_4 + NO \rightarrow FeSO_4.NO \xrightarrow{\Delta} FeSO_4 + NO$$

- $FeSO_4 + 6KCN \rightarrow K_4[Fe(CN)_6] + K_2SO_4$

Uses - As mordant in dyeing, insecticide and in the preparation of Mohr's salt.

3. ***Ferrous ammonium sulphate (Mohr's salt)*** -

$FeSO_4(NH_4)_2SO_4.6H_2O$

Preparation - By mixing saturated solutions of $FeSO_4$ and $(NH_4)_2SO_4$ at about 50^0C and cooling.

Properties - It is light green crystalline compound and does not effloresce.

4. ***Ferric oxide*** Fe_2O_3 - In nature it occurs as haematite.

Used in Bosch process as calalyst and polishing powder by jewellers and as red pigment.

5. ***Iron sulphide FeS*** - By heating iron fillings with dil. H_2SO_4,

$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$

The reaction is carried out in Kipp's apparatus. $FeSO_4$ is obtained as by product. H_2S finds an extensive application in analytical chemistry. It has smell of rotten eggs.

COPPER - ${}_{29}Cu$ $[Ar]3d^{10}4s^1$

It occurs in nature in large quantities in Michegan (USA).

Important ores are

(i) Copper glance Cu_2S

(ii) Copper pyrites $CuFeS_2$

(iii) Malachite $Cu(OH)_2CuCO_3$

(iv) Cuprite Cu_2O (Ruby copper) (v) Azurite $Cu(OH)_2.2CuCO_3$

Extraction - It is mainly extracted from copper pyrites.

Concentration - The ore is concentrated by froth floatation process.

Roasting - The concentrated ore is strongly heated by hot blast of air on the hearth of reverberatory furnace. The following changes take place

$$S + O_2 \rightarrow SO_2 \uparrow$$
$$4As + 3O_2 \rightarrow 2As_2O_3 \uparrow$$
$$4Sb + 3O_2 \rightarrow 2Sb_2O_3 \uparrow$$
$$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$$
$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

Smelting- The roasted ore is mixed with sand and heated in blast furnace.

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$
$$FeO + SiO_2 \rightarrow FeSiO_3 \left(slag\right)$$
$$Cu_2O + FeS \rightarrow FeO + Cu_2S$$

The mixture of copper and iron sulphides melt together to form "***matte***".

Bessemerisation - The molten matte mixed with little sand is poured into Bessemer converter. The following changes take place

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$
$$FeO + SiO_2 \rightarrow FeSiO_3 \left(slag\right)$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

The copper thus produced is called ***'blister copper'*** and contains 2.0% impurities of Ag, Au, Ni, Zn, Pb, Sn, As, S etc.

Refining - It is carried out by either of the following methods

(i) **By polling -** The melt is stirred vigrously with green poles of wood and oxides are reduced by hydrocarbons emanating from wood.

(ii) **Electrolytic refining of copper-** Slabs of impure copper are made anode and thin sheets of pure copper as the cathode. Acidic copper sulphate is used as electrolyte.

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

$$\text{At Cathode } Cu^{2+} + 2e^- \rightarrow Cu$$

$$\text{At anode } Cu \rightarrow Cu^{2+} + 2e^-$$

The impurities like Zn, Fe, Ni,Co remain in solution being more electropositive in nature and Ag, Au, Pt, (less electropositive) collect below the anode in the form of ***anode mud*** or ***slime*** 99.99% pure copper is obtained. Anode mud provides about 25% of U.S. Silver production and 13% of U.S. gold production.

Properties of copper - In aqueous solution it has two oxidation states +1 (cuprous) and +2 (cupric). Cu (I) salts tend to be white and insoluble in water while many salts of Cu (II) are water solubale however Cu(OH)$_2$ is insoluble. CuS is one of the least soluble compounds.

- Cu (I) disproportionates easily in aqueous solution.

$$2Cu^+ \rightarrow Cu^{2+} + Cu$$

- ***Action of*** O_2 **-** It is attacked by O_2 first forming copper (I) oxide Cu_2O **(Red)** and then copper (II) oxide CuO **(Black).**
- It forms a green layer of basic carbonate in presence of CO_2 and moisture.

$$2Cu + H_2O + CO_2 + O_2 \rightarrow Cu\left(OH\right)_2.CuCO_3$$

- Not attacked by dilute acids e.g. HCl and H_2SO_4 but dissolves in these acids in presence of air.

$$2Cu + 2H_2SO_4 \ (dil.) + O_2 \rightarrow 2CuSO_4 + 2H_2O$$
$$Cu + 2H_2SO_4\left(Conc.\right) \rightarrow CuSO_4 + SO_2 + 2H_2O$$
$$3Cu + 8HNO_3\left(dil.\right) \rightarrow 3Cu\left(NO_3\right)_2 + 2NO + 4H_2O$$
$$Cu + 4HNO_3\left(Conc.\right) \rightarrow Cu\left(NO_3\right)_2 + 2NO_2 + 2H_2O$$

Alloys of Copper :

	Name	*Composition*	*Properties*	*Uses*
1	Bronze	Cu-75-90% Sn 10-25%	Brittle, hard resistant to corrosion	Coins, statues Blades
2	Bell metal	Cu 80% Sn 20%	Hard brittle	Bells
3	Gun metal	Cu 88% Sn 10% Zn 2%	Very hard resistant to Corrosion	For making guns, canons machine parts
4	Brass	Cu 60-80% Zn 20-40%	Malleable and ductile, hard	Utensils, casting, cartriges
5	Aluminum bronze	Cu-90% Al-10%	light, strong resistant to corrosion	Jewellary, coins, frames
6	Monel metal	Cu-30% Ni-67% Fe+Mn-3%	very resistant to chemical action high tensile strength	Automobile, engine parts
7	German silver or nickel silver	Cu-50% Zn-30% Ni-20%	White shining malleable, ductile resistant to corrosion	Utensils Ornaments
8	Silica bronze	Cu-97% Sn-2% Si-1%	very hard non corrosive good conductor	Telephone and telegraph wires
9	Phosphorous bronze	Cu-85% Sn-13% P-2%	very hard tough non corrosive	Suspension wire instrument, gears ships, propellors

Compounds of copper :

Copper Sulphate $CuSO_4.5H_2O$ **(Blue vitriol or nila thotha) -**

Preparation **-** (i). By dissolving Cu (II) oxide or carbonate in dilute H_2SO_4.

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$
$$CuCO_3 + H_2SO_4 \rightarrow CuSO_4 + CO_2 + H_2O$$

Manufacture -Form scrap copper

$$2Cu + 2H_2SO_4\left(dil, hot\right) + O_2\left(air\right) \rightarrow 2CuSO_4 + 2H_2O$$

Properties **-** Blue crystalline compound.

(i) ***Action of heat*** -

$$\underset{\text{Blue}}{CuSO_4.5H_2O} \xrightarrow{373\text{ K}} \underset{\text{Bluish white}}{CuSO_4.H_2O} \xrightarrow{423\text{ K}}$$

$$\underset{\text{White}}{CuSO_4} \xrightarrow{\text{strong}} CuO + SO_3$$

(ii) ***Action of*** NH_4OH **-**

$$CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2 + (NH_4)_2SO_4$$
$$Cu(OH)_2 + 2NH_4OH + (NH_4)_2SO_4$$
$$\rightarrow \left[Cu\left(NH_3\right)_4\right]SO_4 + 4H_2O$$

Tetrammine copper sulphate is known as ***SCHWITZER'S REAGENT***. It is used to dissolve cellulose in the manufacture of artificial silk.

(iii) **Action of KI -**

$$2CuSO_4 + 4KI \rightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

(It does not react with KCl, KBr or KF)

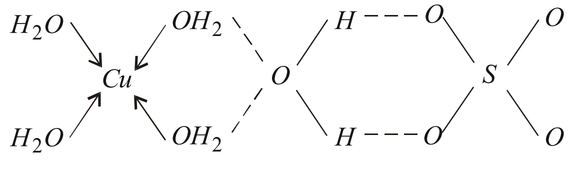
(iv) **Action of potassium ferrocyanide -**

$$2CuSO_4 + K_4\left[Fe(CN)_6\right] \rightarrow \underset{\text{Chocolate coloured pricipitate}}{Cu_2\left[Fe(CN)_6\right]} + 2K_2SO_4$$

(v) **Action of KCN -**

$$2CuSO_4 + 10KCN \rightarrow 2K_3\left[Cu(CN)_4\right] + 2K_2SO_4 + (CN)_2$$

(vi) **Structure of** $CuSO_4.5H_2O$ -



Four H_2O with cation and fifth with anion.

Uses **-** In electroplating, as mordant in dyeing.

- **Bordeaux mixture -**(Mixture of $CuSO_4.5H_2O$ + Lime) is known as Bordeaux mixture. It is used as fungicide. In the preparation of ***Fehling solution*** and electric battries.

Cuprous chloride - Copper (I) chloride $\left(CuCl \text{ or } Cu_2Cl_2\right)$

Preparation -

(i) It can be prepared from Cu alone or in combination with $CuO, CuCl_2, CuSO_4$ by action of concentrated hydrochloric acid.

$$2Cu + 2HCl + O \rightarrow Cu_2Cl_2 + H_2O$$
$$CuO + Cu + 2HCl \rightarrow Cu_2Cl_2 + H_2O$$
$$CuCl_2 + Cu \rightarrow Cu_2Cl_2$$
$$CuSO_4 + Cu + 2HCl \rightarrow Cu_2Cl_2 + H_2SO_4$$

(ii) By passing SO_2 in a solution of $CuSO_4$ and $NaCl$

$$2CuSO_4 + 2NaCl + SO_2 + 2H_2O \rightarrow$$
$$Cu_2Cl_2 + Na_2SO_4 + 2H_2SO_4$$

Properties **-** It is a white solid, almost insoluble in water.

- **Action of conc. HCl -** It dissolves forming soluble complex.

  $$Cu_2Cl_2 + 2HCl \rightarrow 2H\left[CuCl_2\right]$$

  or $Cu_2Cl_2 + 6HCl \rightarrow 2H_3CuCl_4$

  On dilution white precipitate again appears.
- **Action of ammonia -** It dissolves forming soluble complex

  $$Cu_2Cl_2 + 4NH_3 \rightarrow 2Cu\left(NH_3\right)_2 Cl$$
- **Action of acetyline -** Red precipitate of cuprous acetylide is obtained.

  $$Cu_2Cl_2 + C_2H_2 + 2NH_4OH \rightarrow$$
  $$CuC \equiv CCu + NH_4Cl + 2H_2O$$
- With **carbon monoxide** it forms addition product.

  $$Cu_2Cl_2 + 2CO \rightarrow 2CuCl.CO$$
- **With air -** In air it is slowly oxidised to green basic cupric chloride.

  $3CuO.CuCl_2.3H_2O$
- **With** $NaOH$ **-**

  $$Cu_2Cl_2 + 2NaOH \rightarrow \underset{\text{Yellow ppt. changing to red}}{Cu_2O} + 2NaCl + H_2O$$
- With H_2S - $2CuCl + H_2S \rightarrow \underset{\text{black ppt.}}{Cu_2S} + 2HCl$

Uses **-** In gas analysis for absorbing C_2H_2 and CO. In combination with NH_4Cl as catalyst for synthetic rubber.

Cupric Chloride Copper (II) Chloride $CuCl_2.2H_2O$ -

Preparation -

(i) Form copper , cupric oxide or copper carbonate by the action of conc. HCl.

$$2Cu + 4HCl + O_2 \rightarrow 2CuCl + 2H_2O$$
$$CuO + 2HCl \rightarrow CuCl_2 + H_2O$$
$$CuCO_3 + 2HCl \rightarrow CuCl_2 + CO_2 + H_2O$$

(ii) Anhydrous cupric chloride is prepared by burning copper in current of chlorine

$$Cu + Cl_2 \rightarrow CuCl_2$$

Properties - Hydrated $CuCl_2.2H_2O \rightarrow$ greenish

Anhydrous $CuCl_2 \rightarrow$ Brown powder

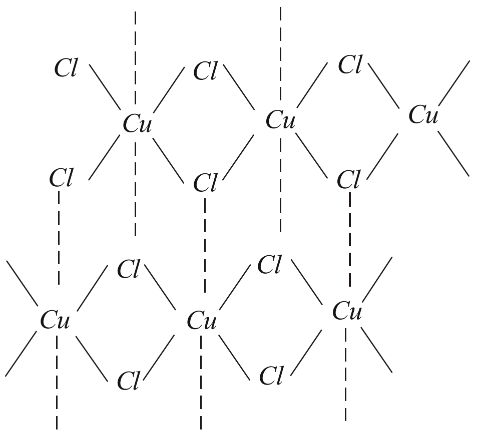
- Aqueous dilute solution is blue due to complex $[Cu.(H_2O)_4]^{2+}$
- Concentrated solution is green due to complex $[CuCl_4]^{2-}$
- ***With Ammonia*** - First a precipitate which dissolves in excess of NH_4OH.

$$CuCl_2 + NH_4OH \rightarrow Cu(OH)_2 \downarrow +$$

$$+NH_4Cl \rightarrow \left[Cu(NH_3)_4\right]^{2+} \text{ blue}$$

- ***Action of heat*** - $\underset{\text{anhydrous}}{2CuCl_2} \rightarrow Cu_2Cl_2 + Cl_2$
- Hydrated salt on heating gives
  $3CuCl_2.2H_2O \rightarrow CuO + Cu_2Cl_2 + 2HCl + Cl_2 + 5H_2O$

Structure -



Cuprous oxide - Cu_2O **(Red oxide of copper)**

Preparation - When ***Fehling solution*** is reduced by glucose or aldehyde.

$$CuSO_4 + 2NaOH \rightarrow Na_2SO_4 + Cu(OH)_2 \rightarrow CuO + H_2O$$
$$2CuO + HCHO \rightarrow Cu_2O + HCOOH$$

Properties - Red colour ,insoluble in water.It forms stable complexes.

Uses- In making ruby red glass and enamel.In manufacturing anti rust paints.

Cupric oxide (black oxide of copper) -

Preparation - By heating malachite which is native copper carbonate. $CuCO_3.Cu(OH)_2 \rightarrow 2CuO + H_2O + CO_2$

Properties - Black powder reduced to metallic copper by H_2 or CO.

Uses - In the manufacture of glass.It gives green colour to glazes and glass.

SILVER (Ag)

It is found in nature and in combined state.

Principal ores are -

(i) Argentite (silver glance) Ag_2S
(ii) Horn silver AgCl,
(iii) Pyrargyrite (ruby silver) $Ag_2S.Sb_2S_3$.

In small quantities in lead ,copper and zinc ores.

1. **Extraction-** Mac Arther Forest's cyanide process -

(i) Concentraction- Ore is concentrated by froth floatation process.

(ii) Treatment with NaCN - The powdered ore is treated with NaCN solution (0.7%) and air is bubbled through the mixture.

(a) $8NaCN + 4Ag + 2H_2O + O_2$
$$\rightarrow 4Na\left[Ag(CN)_2\right] + 4NaOH$$

(b) $AgCl + NaCN \rightarrow AgCN + NaCl$
$AgCN + NaCN \rightarrow Na\left[Ag(CN)_2\right]$

(c) $Ag_2S + 2NaCN \rightleftharpoons Na_2S + 2AgCN$
$AgCN + NaCN \rightarrow Na[Ag(CN)_2]$

Reversible reaction is prevented by oxidation of Na_2S by air.

$$4Na_2S + 2H_2O + 5O_2 \rightarrow 2Na_2SO_4 + 2S + 4NaOH$$

(iii) Precipitation of silver - It is done with zinc.

$$Zn + 2Na\left[Ag(CN)_2\right] + 4NaOH \rightarrow$$
$$Na_2ZnO_2 + 4NaCN + 2Ag + 2H_2O$$

(iv) Refining - Electrolytic method

Anode - impure silver $(Ag \rightarrow Ag^+ + e^-)$

Cathode - pure silver $(Ag^+ + e^- \rightarrow Ag)$

Electrolyte - $AgNO_3$ solution $+ 10\%$ HNO_3

2. **Silver** from argentiferous lead (Desilverisation of lead). Lead, extracted form galena (PbS) contains small amount of silver and is called argentiferous lead. Silver is recovered from it by

(i) Parke's process - Molten argentiferous lead is shaken with zinc when whole of silver passes into zinc. On cooling Ag-Zn alloy solidifies and being lighter floats over molten lead.It is separated, melted and distilled.Zinc distills over and silver is left behind. Success of the method depends upon the fact that

(a) Silver is more soluble in molten zinc and
(b) Molten Zn and lead are immiscible

(ii) Pattison's process - (When silver is less than 1.0%).The lead-silver mixture containing 2.6%. Silver melts at lower temperature than pure lead. When molten argentiferous lead is allowed to cool pure lead solidifies first and removed. The silver content of the mixture is allowed to raise to 2.6%.The silver is then recovered by cupellation.

Properties - It is a noble metal not attacked by atmospheric oxygen. The surface is tarnished due to fromation of Ag_2S due to H_2S present in air.

$$4Ag + 2H_2S + O_2 \rightarrow 2Ag_2S + 2H_2O$$

- Dissolves in dilute and concentrated nitric acid

$$3Ag + 4HNO_3\,(dil.) \rightarrow 3AgNO_3 + 2H_2O + NO\uparrow$$
$$Ag + 2HNO_3\,(conc.) \rightarrow AgNO_3 + H_2O + NO_2\uparrow$$

- Dissolves in alkalicyanide

$$4Ag + 8KCN + 2H_2O + O_2 \rightarrow 4K\left[Ag(CN)_2\right] + 4KOH$$

- Dissolves in conc. sulphuric acid (not in dil. sulphuric acid)

$$2Ag + 2H_2SO_4 \rightarrow Ag_2SO_4 + 2H_2O + SO_2\uparrow$$

Uses- For making ornaments (80%Ag+20%Cu), electroplating, preparation of mirrors.

Fineness- It is the amount of silver present in 1000 parts of silver alloy. 925 fine silver means an alloy of 92.5% silver and 7.5%copper.

Compounds of silver -

Silver nitrate or Lunar caustic $AgNO_3$:

Preparation - By the action of dilute nitric acid on silver.

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O$$

Properties - It is colourless crystalline solid, soluble in water. It leaves black deposit when rubbed on the skin due to formation of finely divided silver.

- **Action of heat -**

$$2AgNO_3 \rightarrow 2AgNO_2 + O_2\uparrow$$
$$2AgNO_3 \xrightarrow[\text{Strong}]{\Delta} 2Ag + 2NO_2 + O_2\uparrow$$

- **Tollen's reagent** - The ammonical silver nitrate solution is known as Tollen's reagent.

$$2AgNO_3 + 2NH_4OH \rightarrow Ag_2O\downarrow + 2NH_4NO_3 + H_2O$$
$$Ag_2O + 4NH_4OH \rightarrow 2\left[Ag(NH_3)_2\right]OH + 3H_2O$$

- Reaction with aqueous solution of certain compounds.

$$AgNO_3 \xrightarrow{NaCl} AgCl\text{(white precipitate)}$$
$$AgNO_3 \xrightarrow{NaBr} AgBr\text{(pale yellow)}$$
$$AgNO_3 \xrightarrow{NaI} AgI\text{ (yellow)}$$
$$AgNO_3 \xrightarrow{K_2CrO_4} Ag_2CrO_4\text{ (red)}$$
$$AgNO_3 \xrightarrow{NaCNS} AgCNS\text{ (white)}$$
$$AgNO_3 \xrightarrow{Na_3PO_4} Ag_3PO_4\text{ (yellow)}$$
$$AgNO_3 \xrightarrow{Na_2S_2O_3} Ag_2S_2O_3 \xrightarrow{H_2O} Ag_2S\text{ (black)}$$
$$AgNO_3 \xrightarrow{KCN} AgCN \xrightarrow{KCN} K\left[Ag(CN)_2\right]$$
$$AgNO_3 \xrightarrow{Na_2S} Ag_2S$$
$$AgNO_3 \xrightarrow{Cu} \text{Ag deposited}$$
$$AgNO_3 \xrightarrow{I_2\text{(excess)}} AgI + HIO_3 + HNO_3$$

Uses - For silvering mirror ,electroplating, in medicines, for the preparation of silver halides used in photography. Particularly AgBr which is most sensitive to light.

$$2AgBr \rightarrow 2Ag + Br_2$$

GOLD

Occurrence - It occurs free as Reef gold, Vein gold or auriferous quartz. Some improtant **ores** are

(i) Claverite AuI_2,

(ii) Sylvanite $(Ag.Cu)Te_2$

(iii) Auriferous pyrites. These are sulphide ores of Cu, Ag, lead which contain gold.

Extraction - By cyanide or Mac Arther Forest cyanide process -

(i) Concentration - Sulphides and tellurides are concentrated by froth floatation process.

(ii) Roasting - The concentrated ore is roasted to remove oxidisable impurities of Te, As and S.

(iii) Formation of complex- NaCN solution is sprayed over the crushed ore and the gold with air, forming complex ion in solution.

$$4Au + 8NaCN + 2H_2O + O_2 \rightarrow \underset{\text{solution}}{4Na\left[Au(CN)_2\right]} + 4NaOH$$

The gold is then recovered as a solid by reduction.

$$2Na\left[Au(CN)_2\right] + Zn \rightarrow Na_2\left[Zn(CN)_4\right] + 2Au$$

(iv) **Parting -** Removal of impurities of Ag and Cu from gold is known as parting.Impure gold is boiled with conc. H_2SO_4 when Ag and Cu dissolve and Au remains unaffected.

(v) **Purification -** By electrolytic method using gold chloride 2.5-6.0% and conc. HCl.

- **Plattner chlorine extraction process -** From auriferous pyrites. The moistened auriferous pyrites is saturated with chlorine, leached with water then treated with $FeSO_4$ or H_2S which precipitates gold. Auriferous pyrites (moistened) $+Cl_2 \rightarrow AuCl_3$

$$AuCl_3 + 3FeSO_4 \rightarrow Au + FeCl_3 + Fe_2(SO_4)_3$$
$$2AuCl_3 + 3H_2S \rightarrow 2Au + 6HCl + 3S$$

Impurities of Ag and Cu are removed by ***parting*** (as above).

Properties - Pure gold is soft, hardened by Ag or Cu.

Fineness of gold - It is expressed in terms of carats. Pure gold is 24 carats. 22 carats mean it contains 22 parts by weight of gold and 2 parts by weight of other metals generally copper.

It is very inert and not attacked by oxygen ,water and acids.

- It is attacked by aqua regia $(3\,\text{conc.}\,HCl + 1\,\text{conc.}\,HNO_3)$

$$3HCl + HNO_3 \rightarrow NOCl + 2H_2O + 2Cl$$
$$Au + 3Cl \rightarrow AuCl_3$$

- It is attacked by chlorine also.

$$2Au + 3Cl_2 \rightarrow 2AuCl_3$$

- $AuCl_3$ auric chloride forms red crystals. Soluble in water and decomposed on heating.

$$AuCl_3 \rightarrow \underset{\text{light yellow powder}}{AuCl} + Cl_2$$

ZINC (Zn) :

Zinc - It is not found free in nature.The principal ores are -

(i)	Zinc blende (sphalerite)	ZnS
(ii)	Zincite or Red zinc oxide	ZnO
(iii)	Franklinite	$ZnO.Fe_2O_3$
(iv)	Calamine or Zinc spar	$ZnCO_3$
(v)	Willemite	$2ZnO.SiO_2$

Extraction - It is extracted by reduction process from ZnS (Zinc blende).

Concentration - The ore is concentrated by froth flotation process.

Roasting - The concentrated Zinc blende is roasted in a current of air.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

(SO_2 is utilised for the manufacturing of H_2SO_4)

If calamine ore is used, it is calcined.

$$ZnCO_3 \rightarrow ZnO + CO_2$$

Reduction - The ZnO is reduced by mixing with carbon and heating in fire clay retort.

$$ZnO + C \rightarrow Zn + CO$$

Purification - Zinc so obtained contains the impurities of Fe, Pb, Cd, As or Sb. It is purified by

(a) Distillation or

(b) Electrolytic method

Anode impure (Zn) $\quad Zn - 2e^- \rightarrow Zn^{++}$

Cathode pure (Zn) $\quad Zn^{++} + 2e \rightarrow Zn$

Electrolyte - Acidic solution of $ZnSO_4$.

(c) **Liquation -** Molten Zn is allowed to flow down on sloping hearth when non fusible impurities are left behind.

Electrolytic method - Pure $ZnSO_4$ is electrolysed when Zn is deposited on aluminium cathode. It is scrapped off and melted to obtain 99.95% pure metal.

- **Zinc dust -**It is prepared by atomising molten zinc with blast of air.
- **Granulated Zinc -** It is prepared by pouring molten Zinc into cold water.

Properities- It is bulish white metal, stable in air.

- In moist air a protective covering of basic zinc carbonate is formed at its surface $2ZnCO_3.3Zn(OH)_2.H_2O$
- **Action of heat -**When heated to 500°C it catches fire with bluish white flames forming ZnO which is very light and called **philospher's wool.**

- **Chemical properties -**

(i) Action with acids

$$Zn + H_2SO_4(\text{dilute}) \rightarrow ZnSO_4 + H_2 \uparrow$$

$$4Zn + 5H_2SO_4(20\%H_2SO_4) \rightarrow 4ZnSO_4 + H_2S + 4H_2O$$

$$3Zn + 4H_2SO_4(20\%H_2SO_4) \rightarrow 3ZnSO_4 + S + 4H_2O$$

$$Zn + 2H_2SO_4(\text{hot and conc.}) \rightarrow ZnSO_4 + SO_2 + 2H_2O$$

$$4Zn + 10HNO_3(\text{cold and dilute}) \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$3Zn + 8HNO_3(\text{mode. conc.}) \longrightarrow 3Zn(NO)_3 + 2NO + 4H_2O$$

$$Zn + 4HNO_3(\text{conc. hot}) \longrightarrow ZnNO_3 + 2NO_2 + 2H_2O$$

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$

- **Displacement reactions**

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu \downarrow$$

$$Zn + Pb(NO_3)_2 \rightarrow Zn(NO_3)_2 + Pb$$

$$Zn + 2Na[Ag(CN)_2] \rightarrow Na_2[Zn(CN)_4] + 2Ag$$

$$Zn + 2Na[Au(CN)_2] \rightarrow Na_2[Zn(CN)_4] + 2Au$$

- With non metals

$$Zn + Cl_2 \rightarrow ZnCl_2$$

$$Zn + S \rightarrow ZnS$$

- It is powerful reducing in nature.

$$Fe_2(SO_4)_3 + Zn \rightarrow 2FeSO_4 + ZnSO_4$$

Uses- Galvanising, sherardizing, in Parke's process for desilverisation of lead , for extraction of Ag and Au (Cyanide proces). Zinc compounds are used in paints, filling rubber etc.

Compounds of Zn

ZnO - Zinc oxide, Philospher's wool, zinc white or chinese white.

Preparation - (i) $Zn + air \xrightarrow{\text{buring}} ZnO$

(ii) $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

(iii) $Zn(NO_3)_2 \xrightarrow{\Delta} ZnO + NO_2 + O_2$

Properties - It is white powder becomes yellow on heating but again white on cooling. It sublimes at 673K.

- **With alkali -** It forms zincate.

$$ZnO + 2NaOH + H_2O \rightarrow \underset{\text{Sodium Zincate}}{Na_2[Zn(OH)_4]}$$

- **Reduction** $ZnO + H_2 \rightarrow Zn + H_2O$

$$ZnO + C \rightarrow Zn + CO$$

- Dissolves in acids to form corresponding salts.

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$

Uses - As a white paint , in medicines, glaze in ceramics and filler in rubber industry.

$ZnSO_4.7H_2O$ (White vitriol) -

Preparation - By the action of dil. H_2SO_4 on Zinc metal, ZnO or $ZnCO_3$

$$(Zn, ZnO \text{ or } ZnCO_3) + \text{dil. } H_2SO_4 \rightarrow ZnSO_4.7H_2O$$

Properties - Colourless, crystalline compound, highly soluble in water.

Action of heat -

$$ZnSO_4.7H_2O \xrightarrow{373K} ZnSO_4.H_2O + 6H_2O \xrightarrow{723K} Zn$$

$$SO_4(\text{anhydrous}) \xrightarrow[\Delta]{\text{Strong}} ZnO + SO_2 + O_2$$

Uses - It is used to prepare ***lithophone*** $(\mathbf{BaSO_4 + ZnS})$ white pigment, galvanising iron and steel, as mordant in calico printing, in medicine as eye lotion.

Zn (II) Chloride $ZnCl_2.2H_2O$

Preparation - It is prepared by the action of dilute HCl on Zn, ZnO or $ZnCO_3$

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2 \uparrow$$
$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$$
$$ZnCO_3 + 2HCl \rightarrow ZnCl_2 + CO_2 + H_2O$$

Properties - It is very deliquescent, soluble in water and organic solvents.

Anhydrous zinc chloride

$$ZnCl_2.2H_2O \xrightarrow{\Delta} ZnCl_2 + 2H_2O$$

Uses - As timber preservative, flux in soldering, preparation of vulcanised paper and fibre.

MERCURY (Hg)

Occurrence - It occurs in free state as small quantities. Its chief ore is -

(i) Cinnabar HgS

(ii) Tiemannite

(iii) Calomel Hg_2Cl_2.

Extraction -

(i) **Concentration -** Cinnabar ore is concentrated by froth floatation process.

(ii) **Roasting-** Roasting is carried out in a shaft furnace when mercury is obatined by auto reduction.

$$2HgS + 3O_2 \rightarrow 2HgO + 2SO_2$$
$$2HgO \rightarrow 2Hg + O_2$$

Roasting may be carried out with iron scrap or quicklime.

$$HgS + Fe \rightarrow FeS + Hg$$
$$4HgS + 4CaO \rightarrow 4Hg + 3CaS + CaSO_4$$

(iii) **Purification-** It contains the impurities of Zn, Pb, Sn or Bi. Some of these impurities get oxidised in air and form a black scum on the surface. Finally it is purified by distillation in vacuum.

Properties - It is silvery white liquid also known as ***Quick silver*** *or* ***live silver***. It is the heaviest liquid known. Sp. gr. 13.59 at $0^o C$.

- **Action of air -** It is not attacked by air either dry or moist at ordinary temperature.
- It forms mercuric oxide at $300^o C$.

$$2Hg + O_2 \rightarrow 2HgO$$

- Dilute acids have no action on mercury except dil. HNO_3.

$$6Hg + 8HNO_3 \rightarrow 3Hg_2(NO_3)_2 + 2NO + 4H_2O$$

- **With concentrated acids**

$$Hg + 4HNO_3 \rightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O$$
$$Hg + 2H_2SO_4 \rightarrow HgSO_4 + 2SO_2 + 2H_2O$$

- **Deadening of Hg -** On Shaking vigrously alone or with fats or sugar it changes to grey powder. This is called deadening of mercury.
- **Tailing of mercury-** In presence of ozone it loses its meniscus which is known as tailing of mercury.
- **Amalgams-** The alloys of mercury with metals excepts (Fe and Pt) are commonly known as amalgams.
- **Ammonium amalgam -** Sodium amalgam when placed in conc. solution of NH_4Cl, there is swelling and butter like mass is formed which is ammonium amalgam.
- **Mercury tree -** When small amount of Hg is poured into $AgNO_3$ solution. (Ag-Hg) is formed which grows like a tree and called mercury tree.

Uses- In thermometers, barometers, electric cells etc.

Compounds of mercury -

1. **Mercuric oxides** HgO

Preparation - (i) By heating mercury in air or O_2

$$Hg + \text{excess air} \xrightarrow[623K]{\Delta} HgO(\text{Red})$$

(ii) By heating mercuric ***nitrate***

$$2Hg(NO_3)_2 \rightarrow 2HgO + 4NO_2 + O_2$$

(iii) From mercuric chloride by the action of NaOH

$$HgCl_2 + 2NaOH \rightarrow \underset{\text{yellow}}{HgO} + 2NaCl + H_2O$$

Red HgO and yellow HgO differ in their particle size. On heating yellow form changes to red.

Uses - It is used as pigment in oil paints and as mild antiseptic in ointments.

2. **Mercurous chloride or calomel** Hg_2Cl_2

Preparation - (i) From mercurous nitrate

$$Hg_2(NO_3)_2 + 2NaCl \rightarrow Hg_2Cl_2 + 2NaNO_3$$

(ii) From **mercuric chloride** by action of mercury

$$HgCl_2 + Hg \rightarrow Hg_2Cl_2$$

Properties - It is insoluble in water purified by sublimation.

- **Action of** NH_3 - It becomes black with ammonia.

$$Hg_2Cl_2 + 2NH_3 \rightarrow \underset{\text{Black}}{[Hg + Hg(NH_2)Cl]} + NH_4Cl$$

- **Action of heat -** It is dicomposed.

$$Hg_2Cl_2 \rightarrow HgCl_2 + Hg$$

Uses - In ceramics for golden colour and as calomel electrode.

3. **Mercuric chloride or corrosive sublimate** $HgCl_2$ -

Preparation -

(i) By heating mercury in a current of chlorine.

$$Hg + Cl_2 \rightarrow HgCl_2$$

(ii) **Manufacture -** By heating mercuric sulphate with equal quantity of sodium chloride.

$$HgSO_4 + 2NaCl \rightarrow HgCl_2 + Na_2SO_4$$

Properties - Colourless, crystalline substance, covalent in nature and gives 5-8% solution in water.

(i) With $SnCl_2$ it is reduced to mercury

$$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4$$

(ii) **With KI** -It gives scarlet precipitate soluble in excess of KI.

$$\underset{\text{Scarlet ppt.}}{HgCl_2 + 2KI \rightarrow HgI_2} + 2KCl$$

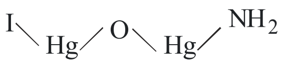
$$HgI_2 + 2KI \rightarrow \underset{\substack{\text{Clear solution}\\ \text{(Nessler's solution)}}}{K_2HgI_4}$$

(iii) **With NaOH -** It gives HgO.

$$HgCl_2 + 2NaOH \rightleftharpoons 2NaCl + HgO + H_2O$$

Nessler's reagent - An ***alkaline*** solution of $K_2\,Hg\,I_4$ is known as Nessler's reagent. It is used for the identification of ammonia and ammonia salts.

$$2K_2HgI_4 + 3KOH + NH_3 \rightarrow$$



$$I{-}Hg{-}O{-}Hg{-}NH_2 + 3KI + 2H_2O$$

Brown (iodide of Millon's base)

Mercuric iodide (HgI_2) -

Preparation - (i) By adding KI solution to any mercuric salt solution.

$$HgCl_2 + 2KI \rightarrow \underset{\text{scarlet}}{HgI_2} + 2KCl$$

$$\text{Scarlet } HgI_2 \underset{\text{below}}{\overset{\text{Above 400K}}{\rightleftharpoons}} HgI_2 \text{ Yellow}$$

It is soluble in excess of KI forming complex ion $[HgI_4]^{2-}$ .Its alkaline solution is Nessler's reagent as shown above.

Mercuric sulphate $HgSO_4$ -

Preparation - (i) By treating Hg with conc. H_2SO_4

$$Hg + 2H_2SO_4 \rightarrow HgSO_4 + SO_2 + 2H_2O$$

Properties - It is white opaque mass, decomposes on heating to gives Hg (I) Sulphate.

$$3HgSO_4 \rightarrow Hg_2SO_4 + Hg + 2SO_2 + O_2$$

Potassium permanganate $KMnO_4$;

Preparation - On large scale it is prepared from pyrolusite (MnO_2). The steps involved are as follows

(i) **Preparation** of potassium manganate K_2MnO_4 - By fusing manganese dioxides with KOH or K_2CO_3.

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\text{Fusion}} 2K_2MnO_4 + 2H_2O$$

$$2MnO_2 + 2K_2CO_3 + O_2 \xrightarrow{\text{Fusion}} \underset{\text{green mass}}{2K_2MnO_4} + 2CO_2$$

(ii) **Oxidation** of K_2MnO_4 to MnO_4

To K_2MnO_4 solution is either added

(i) H_2SO_4 or

(ii) passed CO_2 or

(iii) passed O_3 or

(iv) passed Cl_2

$$3K_2MnO_4 + 2H_2SO_4 \longrightarrow$$
$$2K_2SO_4 + 2KMnO_4 + MnO_2\downarrow + 2H_2O$$

$$3K_2MnO_4 + 4CO_2 + 2H_2O \longrightarrow$$
$$2KMnO_4 + MnO_2\downarrow + 4KHCO_3$$

$$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$$

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

(The last oxidation is known as STADELER 's process)

(iii) **Electrolytic oxidation** - Now a days elecrtrolytic oxidation is prefered. The manganate solution is electrolysed between iron electrodes separated by diaphragm.

$$\text{At anode} \quad \underset{\text{green}}{MnO_4^{2-}} \rightarrow \underset{\text{purple}}{MnO_4^-} + e^-$$

$$\text{At cathode} \quad 2H^+ + 2e^- \rightarrow H_2$$

Properties - It is dark purple solid, soluble in water giving purple solution. Its melting point is 523 K.

Chemical properties -

(i) **Action of heat -** $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

(ii) **Oxidising nature** - It is strong oxidising agent , both in alkali as well as in acidic medium and also in neurtral. In acidic medium -

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
$$\text{or} \quad MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$S^{2-} \longrightarrow S + 2e^-$$
$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$$
$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$
$$NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$
$$C_2O_4{}^{2-} \longrightarrow 2CO_2 + 2e^-$$
$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$

In alkaline medium -

$$2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + O$$
$$\text{or } MnO_4^- + e^- \rightarrow MnO_4^{2-}$$

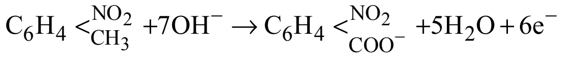
In neutral medium -

$$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3O$$

$$\text{or } MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

In alkaline medium it oxides potassium iodide to potassium iodate and nitro toluene to **nitro benzoic acid.**

$$I^- + 6OH^- \rightarrow IO_3^- + 3H_2O + 6e^-$$



$$C_6H_4 <^{NO_2}_{CH_3} + 7OH^- \rightarrow C_6H_4 <^{NO_2}_{COO^-} + 5H_2O + 6e^-$$

(iii) **Action of hydrogen -** It burns on heating in a current of H_2 .

$$2KMnO_4 + 5H_2 \rightarrow 2KOH + 2MnO + 4H_2O$$

(iv) Equivalent weight of $KMnO_4$ in different medium -

(a) Equivalent weight in acid medium $= \dfrac{\text{Molecular weight}}{5}$

(b) Equivalent weight in alkaline medium

$$= \frac{\text{Molecular weight}}{1}$$

(c) Equivalent weight in neutral medium

$$= \frac{\text{Molecular weight}}{3}$$

(See ionic equations above)

Uses - As oxidising agent , disinfectant, 1% alkaline solution of $KMnO_4$ is used to test unsaturation in organic compounds under the name of ***Baeyer's reagent***. It is used for the volumetric estimation of Fe^{++} salts,oxalic acid etc.

Potassium dichromate ($K_2Cr_2O_7$)

It is manufactured from chromite ore $(FeCr_2O_4)$. The steps involved are -

(i) **Preparation of sodium dichromate -** Finely powdered chromite is mixed with soda ash and quick lime and roasted in reverberatory furnace or rotatory furnace in exess of air.

$$4Fe(CrO_2)_2 + 8Na_2CO_3 + 7O_2 \rightarrow$$
$$8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

Chromite can be fused with molten alkali in presence of air.

$$4Fe(CrO_2)_2 + 16NaOH + 7O_2 \rightarrow$$
$$8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$$

The solution is filtered and acidified with dil. H_2SO_4 when sodium dichromate is obtained.

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

(ii) Conversion of sodium dichromate to potassium dichromate.

$$Na_2CrO_7 + 2KCl \rightarrow 2NaCl + K_2Cr_2O_7$$

Hot concentrated solution of $(Na_2Cr_2O_7)$ Potassium dichromate is less soluble and seperates out on crystallisation.

Properties - It is garnet red prismatic (orange) crystalline compound having melting point 398°C. Soluble in water.

Chemical properties -

(i) **Action of heat -**

$$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + \underset{\text{Chromic oxide}}{2Cr_2O_3} + 3O_2$$

(ii) **Action of cold** H_2SO_4 -

$$K_2CrO_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + 2CrO_3 + H_2O$$

(Red crystals of chromic anhydride)

(iii) **Action of alkali -**

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O$$

(iv) **Oxidising nature -** It is powerful oxidising in nature.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow$$
$$\cdot K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$$\text{or } Cr_2O_7{}^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

thus $SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

$$C_2O_4{}^{2-} \longrightarrow 2CO_2 + 2e^-$$

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$

(v) **Formation of chromyl chloride -** When a chloride is heated with potassium dichromate and conc. H_2SO_4 orange red vapour of chromyl chloride are formed.

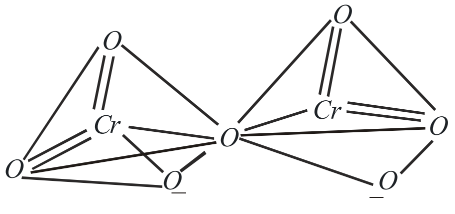
$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow$$
$$2CrO_2Cl_2 + 2KHSO_4 + 4NaHSO_4 + 3H_2O$$

(vi) With **lead salts** it gives insoluble chromate salt.

$$2Pb(NO_3)_2 + K_2Cr_2O_7 + H_2O \rightarrow$$
$$2PbCrO_4 + 2KNO_3 + 2HNO_3$$

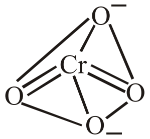
Uses - (i) In chrome tanning, (ii) In dyeing-calico printing, (iii) In photography (iv) chromic acid $(\text{mixture of } K_2Cr_2O_7 + H_2SO_4)$ used as cleaning agent, (v) In preparation of compounds such as $K_2SO_4.Cr_2(SO_4)_2.24H_2O, CrO_2Cl_2$ etc.

Structure - It consists of two tetrahedra with common oxygen atom



Dichromate ion $Cr_2O_7^{2-}$

Structure of chromate ion : It has tetrahedral structure



Chromate ion CrO_4^{2-}

At pH about 4 dichromate ion ($Cr_2O_7^{2-}$) and chromate ion (CrO_4^{2-}) exist in equilibrium. These are interconvertible.

$$\underset{\text{(yellow)}}{2CrO_4^{2-}} + 2H \underset{\text{Alkali}}{\overset{\text{Acid}}{\rightleftharpoons}} 2HCrO_4^{-} \underset{\text{Alkali}}{\overset{\text{Acid}}{\rightleftharpoons}} \underset{\text{(orange)}}{Cr_2O_7^{2-}} + H_2O$$

INNER TRANSITION ELEMENTS

The elements in which the filling of atomic orbitals by electrons take place in f subshells, two levels inside the outer subshell, are known as inner transition elements. Thus these elements form a series within the transition series. They are also known as f- block elements since the differentiating electron enters the f -subshell.

Classification of f-block elements - They have been classified into two series.

(i) **4 f-series (first inner transition series) -** The differentiating electron enters in 4 f orbitals. The elements belonging to this series are also known as ***Lanthanides or Lanthanones.***

(ii) **5 f -series (second inner transition series) -**The differentiating electron enters in 5 f orbitals. The elements belonging to this series are also known as ***Actinides or actinones.***

For the sake of symmetry of the periodic table they have been placed outside the periodic table.

Lanthanides - The fifteen elements from lanthanum (At. no. 57) to lutetium (At. no. 71) are known as ***lanthanides*** or ***rare earths*** (because they were obtained as earths (oxides) from relatively rare minerals).

The properties of inner transition elements are : following

(i) **Electronic Configuration -** The general electronic configuration of these elements is

$[Xe]4f^{0-14}5d^{0-1}6s^2$

The lanthanum electronic configuration $[Xe]4f^0 5d^1 6s^2$ and lutetium electronic configuration $[Xe]4f^{14}5d^1 6s^2$, have no partially filled 4 f orbital in their ground state, are considered as lanthanides due to their properties close to these elements.

(ii) **Oxidation state -** The common oxidation state of lanthanides is +3 but some elements also exhibit +2 and +4 oxidation states in which they leave behind stable ions eg.

Eu^{2+} $[Xe]4f^7$, Yb^{2+} $[Xe]4f^{14}$

Ce^{4+} $[Xe]4f^0$, Tb $[Xe]4f^7$

An aqueous solution of Ce^{4+} is a good oxidising agent. The Eu^{2+} and Yb^{2+} can exist in aqueous solution and are good reducting agents. But there are exceptions also e.g.

Sm^{2+} $[Xe]4f^6$ Tm^{2+} $[Xe]4f^{13}$

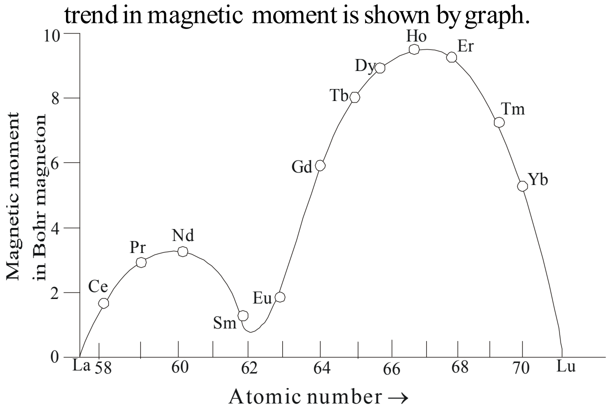
Pr^{4+} $[Xe]4f^1$ Nb $[Xe]4f^2$

(iii) **Magnetic properties -** Magnetic properties have ***spin and orbit*** contributions (Contrast "spin only"of transition metals). Hence magnetic momentums are given by the formula.

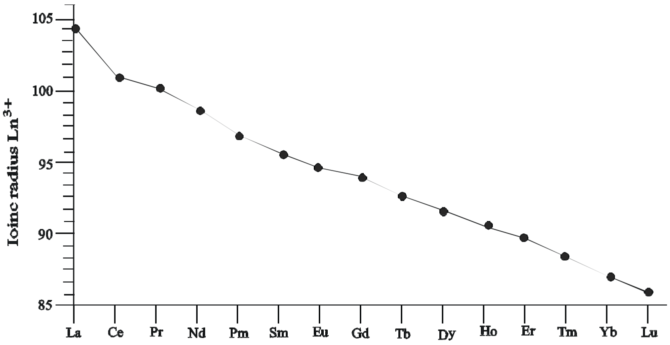
$$\mu = \sqrt{4S(S+1) + L(L+1)}$$

where L = Orbital quantum number, S = Spin quantum number

All lanthanide ions with the exception of La^{3+}, Lu^{3+} and Ce^{4+} are paramagnetic in nature. The trend in magnetic moment is shown by graph.



(iv) **Lanthanide contraction -** There is a steady decrease in the radii as the atomic number of the lanthanide elements increases. For every additional proton added in nucleus the corresponding electron goes to $4f$ subshell. The shape of f -orbitals is very much diffused and they have poor shielding effect. The effective nuclear charge increases which causes the contraction in the size of electron charge cloud. This contraction in size is **quite *regular*** and known as ***Lanthanide contraction.***



(v) **Consequences of lanthanide contraction -**

(a) Covalent character of cations increase.

(b) ***Electronegatively*** - The electronegativity of trivalent ions increase slightly.

(c) ***Basicity*** - There is decrease in basic strength of oxides and hydroxides.

(d) ***E°value*** - There is small increase in standard electrode potential values.

(v) **Colour** - The species containing unpaired electrons are coloured and so is the case with lanthanide ions. The f-f transitions are possible due to absorption of light from the visible region.

(vii) **Melting and boiling point** - Lanthanides have high melting and boiling points but there is no regular trend.

(viii) **Density -** Lanthanides have densities varying from 6.77 to $9.74\, g\, cm^{-3}$. But there is no definite trend for these values.

(ix) **TheElement electronegatively** values of lanthanides are almost same as that of s-block elements. Lanthanides form ionic compounds.

(x) **Ionisation energies** - The ionisation energy values of lanthanides are not very high due to their large size and are comparable with those of alkaline earth metals.

(xi) **Complex compound** - Due to having large ionic size they have little tendency to form complexes.

(xii) **Reactivity** - Due to their low values of ionisation energies the lanthanides are very reactive.

(xiii) **Alloys -** They form alloy especially with iron e.g. *MISCH METAL* rare earths $94-95\%$ iron 5% and S, C, Ca and Al in traces.

Atomic number	*Name*	*Symbol*	*Electronic configuration*	*Oxidation states*	*Density (g/ml)*	*Melting point (K)*	*Boiling point (K)*	*M^{3+} radii (pm)*
57	Lanthanum	La	$[Xe]4f^0 5d^1 6s^2$	+3	6.17	1193	3742	106
58	Cerium	Ce	$[Xe]4f^1 5d^1 6s^2$	+3,+4	6.77	1068	3741	103
59	Praseodymium	Pr	$[Xe]4f^3\ 6s^2$	+3,+4	6.78	908	3400	101
60	Neodymium	Nd	$[Xe]4f^4\ 6s^2$	+2,+3	7.00	1297	3300	100
61	Promethium	Pm	$[Xe]4f^5\ 6s^2$	+3	7.20	------	-----	98
62	Samarium	Sm	$[Xe]4f^6\ 6s^2$	+2,+3	6.93	1345	2173	96
63	Europium	Eu	$[Xe]4f^7\ 6s^2$	+2,+3	5.24	1099	1712	95
64	Gadolinium	Gd	$[Xe]4f^7 5d^1 6s^2$	+3	7.95	1585	3273	94
65	Terbium	Tb	$[Xe]4f^9\ 6s^2$	+3,+4	8.33	1629	3073	92
66	Dysprosium	Dy	$[Xe]4f^{10}\ 6s^2$	+3,+4	8.56	1680	2873	91
67	Holmium	Ho	$[Xe]4f^{11}\ 6s^2$	+3	8.76	1734	2873	89
68	Erbium	Er	$[Xe]4f^{12}\ 6s^2$	+3	9.16	1770	3173	88
69	Thulium	Tm	$[Xe]4f^{13}\ 6s^2$	+2,+3	9.35	1818	2000	87
70	Ytterbium	Yb	$[Xe]4f^{14}\ 6s^2$	+2,+3	7.01	1097	1700	86
71	Lutetium	Lu	$[Xe]4f^{14} 5d^1 6s^2$	+3	9.74	1925	3600	85

ACTINIDES

Actinides - The fifteen elements from actinium (At. no. 89) to lawrencium (At. no. 103) are known as actinides and constitute the 5f. Series. From neptunium to onwards the elements are man made (artificially prepared) and also known as ***trans uranium*** elements.

(i) **Electronic configuration -** The differentiating electron enters the 5 f atomic orbital. Their general electronic configuration is

$[Rn]5f^{0-14}6d^{0-2}7s^2$

Since there is not much difference between 5 f and 6d, it is difficult to predict whether the electron has entered 5 f or 6d.

(ii) **Oxidation state -** The common oxidation state is +3 but other oxidation states are also exhibited by actinides the maximum being +7.

(iii) **Magnetic properties -** The magnetic moments of actinide ions are smaller than theoretical values. It is hard to interpret due to large spin orbit coupling.

(iv) **Actinide contraction -** It is similar to lanthanide contraction due to poor shielding of $5f$ electrons.

(v) **Melting and boiling points -** They have high values for melting and boiling points but there is no regular trend.

(vi) **Density -** The value of density vary from 7.0 gcm^{-3} to 19.84 gcm^{-3}. Again there is no regular trend.

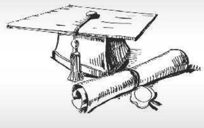
(vii) **Reducing character** -They are strong reducing agents as they have high E^0 values approximately 2.0 volts.

(viii) **Reactivity -** Actinides are very reactive in nature and combine with oxygen and halogens like lanthanides.

(ix) **Coloured ions -** Actinide ions are coloured due to the presence of unpaired electrons and $f-f$ transitions.

(x) **Complex formation -** They have higher tendency to form complex compounds.

Exercise-1 | NCERT BASED QUESTIONS



Very Short/Short Answer Questions

1. Why is HCl not used to acidify a permanganate solution in volumetric estimations of ferrous ion (Fe^{2+}) or oxalate ion ($C_2O_4^{2-}$)?
2. Why does V_2O_5 act as catalyst?
3. What is the oxidation state of chromium in (*a*) potassium dichromate (*b*) potassium chromate?
4. The *d*-electronic configuration of Co^{2+} and Cu^{2+} is d^7 and d^9 respectively. Which one of these ions will be more paramagnetic?
5. Lanthanum (Z = 57), gadolinium (Z = 64) and lutetium (Z = 71) are extra-ordinarily stable in + 3 oxidation state. Explain.
6. Why $KMnO_4$ is used in clearing surgical instruments in hospitals?
7. Write chemical equation for the conversion of:
   (a) Chromite ore to sodium chromate
   (b) Pyrolusite to potassium manganate
   (c) Potassium permanganate to manganese dioxide
8. There is only a very small increase in IE of an element in a transition series (or *d*-block elements) when we move along the period as compared to *s* and *p*-block elements. Explain, why.
9. Among lanthanides, why are ions like Sm^{2+}, Eu^{2+} and Yb^{2+} in aqueous solutions good reducing agents but an aqueous solution of Ce^{4+} is a good oxidising agent? Explain.
10. (a) Which oxidation state of Mn is most stable and why?
    (b) Which transition element show highest oxidation state and in which compound?
    (c) Which is the densest transition element?
11. Which of the following oxides is basic, amphoteric and acidic oxide: Sc_2O_3, MnO, FeO, Cu_2O, MnO_2, CuO, TiO_2, Mn_2O_7, CrO_3. Cr_2O_3
12. A substance is found to have a magnetic moment of 4·89 BM. How many unpaired electrons does it contain?
13. Write the IUPAC name of $\left[Co\left(NH_3\right)_5 Cl\right]Cl_2$. [Atomic no. of Co = 27]
14. Compare the chemistry of the actinoids with that of lanthanoids with reference to
    (i) electronic configuration
    (ii) oxidation states
    (iii) chemical reactivity
15. Write the structures and names of all the stereoisomers of the following compounds:
    (i) $\left[Co(en)_3\right]Cl_3$
    (ii) $\left[Pt\left(NH_3\right)_2 Cl_2\right]$
    (iii) $\left[Fe\left(NH_3\right)_4 Cl_2\right]Cl$
16. Complete the following chemical equations:
    (i) $MnO_4^-(aq) + S_2O_3^{2-}(aq) + H_2O(l) \rightarrow$
    (ii) $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \rightarrow$
17. State reason for the following :
    (i) Cu (I) ion is not stable in an aqueous solution.
    (ii) Unlike Cr^{3+}, Mn^{2+}, Fe^{3+} and the subsequent other M^{2+} ions of the 3d series of elements, the 4d and the 5d series metals generally do not form stable cationic species.
18. How would you account for the following:
    (i) Among lanthanoids, Ln (III) compounds are predominant, However, occasionally in solutions or in solid compounds, + 2 and + 4 ions are also obtained.
    (ii) The $E^\circ_{M^{2+}/M}$ for copper is positive (0.34 V). Copper is the only metal in the first series of transition elements showing this behaviour.
    (iii) The metallic radii of the third (5d) series of transition metals are nearly the same as those of the corresponding members of the second series.
19. (a) Which metal in the first transition series (3d series) exhibits + 1 oxidation state most frequently and why?
    (b) Which of the following cations are coloured in aqueous solutions and why?
    Sc^{3+}, V^{3+}, Ti^{4+}, Mn^{2+}
    (At. nos. Sc = 21, V = 23, Ti = 22, Mn = 25)

Long Answer Questions

20. The sums of first and second ionisation energies and those of third and fourth ionisation energies of nickel and platinum are given below:

Element	$IE_1 + IE_2$ (kJ mol^{-1})	$IE_3 + IE_4$ (kJ mol^{-1})
Ni	2·49	8·80
Pt	2·66	6·70

Taking these values in account, write
    (a) the most common oxidation states of Ni and Pt and its reason.
    (b) the name of the metal (Ni or Pt) which can form compounds is + 4 oxidation state more easily and why?
21. Explain the following:
    (a) Transition elements show similarity in properties along the period as well as down the group (*i.e.*, horizontal as well as vertical similarities).
    (b) In transition series, it is observed that melting point first increases and then starts decreasing.
    (c) Copper is a transition element but not sodium.
    (d) Zinc atom is bigger than copper atom.
    (e) Transition metals have low reactivity.

22. (a) Describe with the help of chemical equations the preparation of potassium dichromate from chromite ore.
(b) Give balanced chemical equations for what happens when acidified potassium dichromate solution reacts with
  (i) ferrous sulphate solution.
  (ii) hydrogen sulphide gas.
(c) Draw the structure of $Cr_2O_7^{2-}$.

Multiple Choice Questions

23. Which element belongs to d-block ?
(a) Na (b) Ca
(c) Cu (d) Ar

24. $(n-1)d^{10}ns^2$ is the general electronic configuration of
(a) Fe, Co, Ni (b) Cu, Ag, Au
(c) Zn, Cd, Hg (d) Se, Y, La

25. Which of the following is not property of the transition elements?
(a) Colour (b) Paramagnetism
(c) Fixed valency (d) None of these

26. Cuprous compounds such as CuCl, CuCN and CuSCN are the only salts stable in water due to
(a) high hydration energy of Cu^+ ions
(b) their inherent tendency not do disproportionate
(c) diamagnetic nature
(d) insolubility in water

27. The addition of excess of aqueous HNO_3 to a solution containing $[Cu(NH_3)_4]^{2+}$ produces
(a) Cu^+
(b) $[Cu(H_2O)_4]^{2+}$
(c) $Cu(OH)_2$
(d) $Cu(NO_3)_2$

28. An extremely hot copper wire reacts with steam to give
(a) CuO (b) Cu_2O
(c) Cu_2O_2 (d) CuO_2.

29. Which is not amphoteric ?
(a) Al^{3+} (b) Cr^{3+}
(c) Fe^{3+} (d) Zn^{2+}

Exercise-2 | CONCEPTUAL MCQs

1. How many 'd' electrons are present in Cr^{2+} ion?
(a) 4 (b) 5
(c) 6 (d) 3

2. Which of the following ions having following electronic structure would have maximum magnetic moment?
(a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$ (b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
(c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ (d) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

3. Which of the following element does not belong to first transition series?
(a) Fe (b) V
(c) Ag (d) Cu

4. The transition metals have a less tendency to form ions due to
(a) high ionisation energy
(b) low heat of hydration of ions
(c) high heat of sublimation
(d) All of these

5. Which of the following oxides of manganese is amphoteric?
(a) MnO_2 (b) Mn_2O_3
(c) Mn_2O_7 (d) MnO

6. Of the ions Zn^{2+}, Ni^{2+} and Cr^{3+}
$(\text{At.Nos Zn} = 30, \text{Ni} = 28, \text{Cr} = 24)$
(a) Only Zn^{2+} is colourless and Ni^{2+} and Cr^{3+} are coloured
(b) All three are colourless
(c) All three are coloured
(d) Only Ni^{2+} is coloured and Zn^{2+} and Cr^{3+} are colourless

7. $(n-1)d^{10}ns^2$ is the general electronic configuration of
(a) Fe, Co, Ni (b) Cu, Ag, Au
(c) Zn, Cd, Hg (d) Se, Y, La

8. Common oxidation state of scandium, a transition element is/are $[\text{Ar.No.of Sc} = 21]$
(a) +4 (b) +1
(c) +2 and +3 (d) +4 and +1

9. Which of the following is not correct about transition metals?
(a) Their melting and boiling points are high
(b) Their compounds are generally coloured
(c) They can form ionic or covalent compounds
(d) They do not exhibit varialbe valency

10. Which of the following has maximum unpaired electrons?
(a) Scandium (b) Chromium
(c) Manganese (d) Iron

11. The last electron in d-block elements goes to
(a) (n-1) d (b) nd
(c) np (d) (n-1) s

12. Which of the following ions is coloured?
(a) Cu^+ (b) Cu^{2+}
(c) Ti^{4+} (d) V^{5+}

13. What is wrong about transition metals?
(a) Diamagnetic
(b) Paramagnetic
(c) Form complexes
(d) Shows variable oxidation state

14. In 3d-series atomic number (Z) varies from
(a) $Z = 21 - 30$ (b) $Z = 22 - 30$
(c) $Z = 20 - 30$ (d) $Z = 31 - 40$

15. The first element in the 3d-transition series is
(a) Sc (b) Ti
(c) V (d) Ca

16. Which one of the following ionic species will impart colour to an aqueous solution?
(a) Ti^{4+} (b) Cu^{+}
(c) Zn^{2+} (d) Cr^{3+}

17. Formation of interstitial compound makes the transition metal
(a) more soft (b) more ductile
(c) more metallic (d) more hard

18. The elements which exhibit both vertical and horizontal similarites are
(a) inert gas elements (b) representative elements
(c) rare elements (d) transition elements

19. Oxidation state of osmium (Os) in OsO_4 is
(a) +4 (b) +6
(c) +7 (d) +8

20. Which of the following transition element shows the highest oxidation state ?
(a) Mn (b) Fe
(c) V (d) Cr

21. Which of the following has more unpaired d-electrons?
(a) Zn^{+} (b) Fe^{2+}
(c) Ni^{+} (d) Cu^{+}

22. An atom has electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$ in which group would it be placed?
(a) Fifth (b) Fifteenth
(c) Second (d) Third

23. Iron loses its magnetic property at
(a) Curie point (b) Boiling point
(c) Melting point (d) 1000 K

24. The number of unpaired electrons in a nickel atom in ground state are $(\text{At. No. of Ni} = 28)$
(a) 2 (b) 5
(c) 3 (d) 7

25. Zinc and mercury do not show variable valency like d-block element because
(a) they are soft
(b) their d-shells are complete
(c) they have only two electrons in the outermost shell
(d) their d-shells are incomplete

26. Elements which generally exhibit multiple oxidation states and whose ions are usally coloured are
(a) metalloids (b) non-metals
(c) transition elements (d) gases

27. Transition metals mostly are
(a) diamagnetic
(b) paramagnetic
(c) neither diamagnetic nor paramagnetic
(d) both diamagnetic and paramagnetic

28. Transition metals usually exhibit highest oxidation states in their
(a) chlorides (b) fluorides
(c) bromides (d) iodides

29. Which one of the following ions exhibit highest magnetic moment?
(a) Cu^{2+} (b) Ti^{3+}
(c) Ni^{2+} (d) Mn^{2+}

30. Which of the following is colourless in water?
(a) Ti^{3+} (b) V^{3+}
(c) Cu^{3+} (d) Sc^{3+}

31. The valence shell of transition elements consists of
(a) nd orbitals (b) (n-1) d orbitals
(c) ns np nd orbitals (d) (n-1) d ns orbitals

32. Which one of the following is diamagnetic ion?
(a) Co^{2+} (b) Cu^{2+}
(c) Mn^{2+} (d) Sc^{3+}

33. Which group contains coloured ions out of
1. Cu^{2+} 2. Ti^{4+}
3. Co^{2+} 4. Fe^{2+}
(a) 1, 2, 3, 4 (b) 1, 3, 4
(c) 2, 3 (d) 1, 2

34. If a non metal is added to the interstital sites of a metal, then the metal becomes
(a) softer (b) less tensile
(c) less malleable (d) more ductile

35. Transition metal with low oxidation number will act as
(a) a base (b) an acid
(c) an oxidising agent (d) None of these

36. Which of the following elements does not show variable oxidation states?
(a) Copper (b) Iron
(c) Zinc (d) Titanium

37. Which one of the following is an example of non-typical transition elements ?
(a) Li, K, Na (b) Be, Al, Pb
(c) Zn, Cd, Hg (d) Ba, Ga, Sr.

38. Super conductors are derived from compounds of
(a) p-Block elements (b) lanthanides
(c) actinides (d) transition elements

39. Corrosion of iron can be prevented by coating the surface with
(a) Zn (b) Sn
(c) Ni (d) Any of these

40. Which of the following compound is called Turnbull's blue?
(a) Ferricyanide (b) Ferrous ferricyanide
(c) Ferrous cyanide (d) Ferri-ferrocyanide

41. In an octahedral crystal field splitting the number of orbitals pushed down in energy is
(a) 3 (b) 2
(c) 5 (d) zero

42. Which one of the following pairs of ions have the same electronic configuration?
(a) Cr^{3+}, Fe^{3+} (b) Fe^{3+}, Mn^{2+}
(c) Fe^{3+}, Co^{3+} (d) Sc^{3+}, Cr^{3+}

43. Bonding in ferric chloride is
(a) covalent (b) ionic
(c) co-ordinate (d) None of these

44. Which one of the following elements constitutes a major impurity of pig iron?
(a) Silicon (b) Oxygen
(c) Sulphur (d) Graphite

45. A compound of a metal ion $M^{x+} (Z = 24)$ has a spin only magnetic moment of $\sqrt{15}$ Bohr Magnetons. The number of unpaired electrons in the compound are
(a) 2 (b) 4
(c) 5 (d) 3

46. Which of the following configuration is correct for iron?
(a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
(b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
(c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
(d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

47. Stainless steel contains
(a) $Fe + Cr + Cu$ (b) $Fe + C + Ni$
(c) $Fe + Cr + Ni + C$ (d) $Fe + Ni + Cu$

48. Which of the following is not an element?
(a) Graphite (b) Diamond
(c) 22-Carat gold (d) Rhombic sulphur

49. Which of the following elements does not exist in the native form?
(a) Au (b) Pt
(c) Fe (d) S

50. In the extraction of iron, slag is produced which is
(a) CO (b) $FeSiO_3$
(c) $MgSiO_3$ (d) $CaSiO_3$

51. The nature of an aqueous solutionof $FeCl_3$ is
(a) acidic (b) basic
(c) amphoteric (d) neutral

52. The oxidation number of Fe in Fe_3O_4 is
(a) +2 (b) +3
(c) 8/3 (d) 2/3

53. The iron obtained from blast funace is
(a) pig iron (b) silver
(c) soft iron (d) steel

54. Which of the following gives blood red colour with KCNS?
(a) Cu^{2+} (b) Fe^{3+}
(c) Al^{3+} (d) Zn^{2+}

55. The protection of steel by chrome plating is due to
(a) cathodic protection
(b) anodic protection
(c) covering of steel surface
(d) formation of alloy with iron

56. The nature of an aqueous solution of $FeCl_2$ is
(a) acidic (b) basic
(c) amphoteric (d) neutral

57. Which one of the following is the correct configuration of $Fe^{3+} (Z = 26)$?
(a) $[Ar]4s^2 3d^6$ (b) $[Ar]4s^2 3d^3$
(c) $[Ar]3d^5$ (d) $[Ar]4s^2 3d^4$

58. The number of ions formed on dissolving one molecule of $FeSO_4 (NH_4)_2 SO_4.6H_2O$ (Mohr's salt) is/are
(a) 6 (b) 3
(c) 5 (d) 4

59. If steel is heated to a temperature well below red heat and is then cooled slowly the process is called
(a) tempering (b) hardening
(c) softening (d) annealing

60. Which of the following is obtained when Fe reacts with dil. HNO_3?
(a) N_2O (b) NO
(c) NO_2 (d) None of these

61. Wrought iron, pig iron and steel differ in properties due to
(a) carbon content (b) malleability
(c) conductivity (d) softness

62. Green vitriol is
(a) $FeSO_4.7H_2O$ (b) $ZnSO_4.7H_2O$
(c) $CaSO_4.2H_2O$ (d) $CuSO_4.5H_2O$

63. Which of the following is not an ore of iron?
(a) Limonite (b) Magnetite
(c) Casiterite (d) All of these

64. Corrosion is basically a
(a) altered reaction in presence of H_2O
(b) electrochemical phenomenon
(c) interaction
(d) union between light metal and heavy metal

65. Which of the following are the constituents of gun metal?
(a) Cu, Sn
(b) Cu, Sn, Zn
(c) Zn, Sb, Pb
(d) Cu, Ca, Pb

66. When Cu reacts with $AgNO_3$ solution, the reaction takes place is
(a) oxidation of Cu
(b) reduction of Cu
(c) oxidation of Ag^+
(d) reduction of NO_3^-

67. Bordeaux used as fungicide is a mixture of
(a) $CuSO_4 + Ca(OH)_2$
(b) $CaSO_4 + Cu(OH)_2$
(c) $CuCO_3 + Cu(OH)_2$
(d) $CuO + CaO$

68. Which of the following ions will liberate iodine when treated with KI?
(a) Cu^{2+}
(b) Fe^{2+}
(c) Pb^{2+}
(d) Sn^{2+}

69. Which one of the following pairs of substances on reaction will not evolve H_2 gas?
(a) Iron and $H_2SO_4(aq.)$
(b) Iron and steam
(c) Copper and $HCl(g)$
(d) Sodium and ethyl alchohol

70. Which of the following metals is sometimes found in native state in nature?
(a) Al
(b) Cu
(c) Fe
(d) Mg

71. Which of the following is ionic in nature?
(a) CuF_2
(b) $CuCl_2$
(c) $CuBr_2$
(d) None of these

72. $CuSO_4$ reacts with KCN solution and forms
(a) $Cu(CN)$
(b) $Cu(CN)_2$
(c) $K_3[Cu(CN)_4]$
(d) $K_4[Cu(CN)_6$

73. When KI and $CuSO_4$ solutions are mixed, it gives
(a) $K_2SO_4 + I_2$
(b) $Cu_2I_2 + K_2SO_4$
(c) $CuI_2 + K_2SO_4$
(d) $Na_2SO_4 + I_2$

74. The final step in the metallurgical extraction of Cu metal from Cu pyrites takes place in a Bessemer converter. The reaction taking place is
(a) $Cu_2S + O_2 \rightarrow 2Cu + SO_2$
(b) $4Cu_2O + FeS \rightarrow 8Cu + FeSO_4$
(c) $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$
(d) $Cu_2S + 2FeO \rightarrow 2CuO + 2Fe + SO_2$

75. Matte contains mainly
(a) Cu_2S and FeS
(b) CuS and Fe_2S_3
(c) Fe
(d) Cu_2S

76. A metal which does not liberate $H_2(g)$ from acids is
(a) Cu
(b) Fe
(c) Mn
(d) Zn

77. Cuprous ion is colourless while cupric ion is coloured because
(a) both have half filled p-and d-orbitals
(b) cuprous ion has incomplete d-orbital and cupric ion has a complete d-orbital
(c) both have unpaired electrons in the d-orbitals
(d) cuprous ion has complete d-orbital and cupric ion has an imcomplete d-orbital.

78. In $Cu(Z = 29)$
(a) 13 electrons have spin in one direction and 16 electrons in other direction
(b) 14 electrons have spin in one direction and 15 electrons in other direction
(c) All the electrons have spin in one direction
(d) None of these

79. Cuprous ore among the following is
(a) chalcopyrites
(b) azurite
(c) cuprite
(d) malachite

80. The white anhydrous copper sulphate decomposes to give
(a) $CuSO_4.5H_2O$
(b) $CuSO_4.H_2O$
(c) $CuO + SO_3$
(d) Cu

81. An important ore of copper is
(a) bauxite
(b) galena
(c) siderite
(d) chalcopyrites

82. When the sample of copper with zinc impurity is to be purified by electolysis, the appropriate electordes are

	Cathode	**Anode**
(a)	Pure zinc	Pure copper
(b)	Impure sample	Pure copper
(c)	Impure zinc	Impure sample
(d)	Pure copper	Impure sample

83. Which of the following compounds gives red precipitate with $AgNO_3$?
(a) KI
(b) K_2CrO_4
(c) NaBr
(d) $NaNO_3$

84. When silver nitrate is heated to red hot, what is formed?
(a) Ag
(b) Ag_2O
(c) Ag_2O_3
(d) AgO_2

85. When horn silver ore is dissolved in excess of sodium cyanide solution compound formed is
(a) AgCN
(b) $Na[AgCN)_2]$
(c) $Na_2[Ag(CN)_3]$
(d) $Na_4[Ag(CN)_5]$

86. In the chemical reaction

$$Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^-$$

(a) water is oxidised
(b) water is reduced
(c) silver is oxidised
(d) silver is reduced

87. AgCl is soluble in NH_4OH solution. The solubility is due to the formation of

(a) AgOH (b) Ag_2O

(c) $\left[Ag(NH_3)_2\right]^+$ (d) NH_4Cl

88. The compound that is soluble in water is

(a) AgF (b) AgCl

(c) AgBr (d) AgI

89. In the metallurgy of which of the following cupellation process is used?

(a) Copper (b) Silver

(c) Iron (d) Aluminium

90. When potassium ferrocyanide crystals are heated with conc. H_2SO_4 the gas evolved is

(a) SO_2 (b) NH_3

(c) CO_2 (d) CO

91. In the extraction of silver, Ag_2S is dissolved in

(a) HCl (b) HNO_3

(c) KCN (d) H_2SO_4

92. Parke's process is used

(a) to extract Ag using NaCN

(b) to extract Cu using $CuFeS_2$

(c) to extract Ag from argentiferrous lead

(d) to extract Ag by forming amalgam

93. In the equation

$$4M + 8CN^- + 2H_2O + O_2 \rightarrow 4\left[M(CN)_2\right]^- + 4OH^-$$

Identify the metal M. It is

(a) copper (b) iron

(c) gold (c) zinc

94. A metal which is not affected by conc. H_2SO_4, HNO_3 or alkalies forms an compound X This compound X can be used to give a complex which finds its application for tonning in photography. The metal is

(a) Au (b) Ag

(c) Hg (d) Cu

95. Which of the following is not the characteristic of zinc?

(a) It is a volatile metal

(b) It dissolves in alkali forming sodium zincate

(c) It is brittle at very high temperatures

(d) Zinc dust is used as reducing agent

96. Galvanization of iron denotes coating with

(a) Al (b) Sn

(c) Cd (d) Zn

97. When Zn is treated with excess of NaOH, the product obtained is

(a) $Zn(OH)_2$ (b) ZnOH

(c) Na_2ZnO_2 (d) None of these

98. Acidified solution of chromic acid on treatment with H_2O_2 gives blue colour which is due to

(a) $CrO_3 + H_2O + O_2$ (b) $CrO_5 + H_2O$

(c) $H_2Cr_2O_7 + H_2O + O_2$ (d) None of these

99. In the extraction of zinc, the formation of blue flame is due the burning of

(a) ZnO (b) C

(c) Zn (d) CO

100. Which of the following compounds turns black on addition of NH_4OH ?

(a) $PbCl_2$ (b) Hg_2Cl_2

(c) $HgCl_2$ (d) AgCl

101. Mercury is the only metal which is liquid at 0°C. This is due to its

(a) very high ionisation energy and weak metallic bond

(b) low ionisation potential

(c) high atomic weight

(d) high vapour pressure

102. Which one of the following is false for Hg?

(a) It can evolve hydrogen from H_2S

(b) It is metal

(c) It has high specific heat

(d) It is less reactive than hydrogen.

103. Mercury sticks to the surface of the glass when it comes in contact with

(a) Hg_2O (b) HNO_3

(c) O_3 (d) grease

104. Which compound is volatile on heating?

(a) $MgCl_2$ (b) $HgCl_2$

(c) $ZnCl_2$ (d) None of these

105. Which ion is detected by Nessler's reagent?

(a) NH_4^+ (b) MnO_4^-

(c) PO_4^{3-} (d) CrO_4^{2-}

106. Mercurous ion is represented as

(a) Hg_2^{2+} (b) Hg^{2+}

(c) $Hg + Hg^{2+}$ (d) $3Hg^{3+}$

107. Nessler's reagent is

(a) potassium iodide in mercuric iodide

(b) $TiCl_4$

(c) anhydrous $AlCl_3$

(d) Al_2O_3 / Cr_2O_3

108. The equivalent weight of $KMnO_4$ (formula weight $= M$) when it is used as an oxidant in neutral medium is

(a) M (b) $\frac{M}{2}$

(c) $\frac{M}{3}$ (d) $\frac{M}{5}$

109. The starting material for the manufacture of $KMnO_4$ is
(a) pyrolusite (b) manganite
(c) magnatite (d) haematite

110. An explosion take place when conc. H_2SO_4 is added to $KMnO_4$. Which of the following is formed?
(a) Mn_2O_7 (b) MnO_2
(c) $MnSO_4$ (d) M_2O_3

111. If $KMnO_4$ is reduced by oxalic acid in an acidic medium then oxidation number of Mn changes from
(a) 4 to 2 (b) 6 to 4
(c) +7 to +2 (d) 7 to 4

112. The correct formula of permanganic acid is
(a) $HMnO_4$ (b) $HMnO_5$
(c) H_2MnO_4 (d) H_2MnO_3

113. In the preparation of $KMnO_4$ pyrolusite (MnO_2) is first converted to potassium manganate (K_2MnO_4). In this conversion, the oxidation state of manganese changes from
(a) +1 to +3 (b) +2 to +4
(c) +3 to +5 (d) +4 to +6

114. Which of the following oxides of Cr is amphoteric
(a) CrO_2 (b) Cr_2O_3
(c) CrO_5 (d) CrO_3

115. In potassium manganate the oxidation state of manganese is
(a) +5 (b) +6
(c) +7 (d) +8

116. Number of electrons transfered in each case when $KMnO_4$ acts as an oxidising agent to give MnO_2, Mn^{2+}, $Mn(OH)_3$ and MnO_4^{2-} are respectively
(a) 3,5,4 and 1 (b) 4,3,1 and 5
(c) 1,3,4 and 5 (d) 5,4,3 and 1

117. In an alkaline condition $KMnO_4$ reacts as follows:

$$2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + O$$

Its equivalent weight is
(a) 31.6 (b) 52.7
(c) 49 (d) 158

118. In which of the following compounds manganese has oxidation number equal to that of iodine in KIO_4 ?
(a) Potassium manganate
(b) Potassium permanganate
(c) Manganous chloride
(d) Manganese chloride

119. Which of the following compounds has colour but no unpaired electrons?
(a) $KMnO_4$ (b) K_2MnO_4
(c) $MnSO_4$ (d) $MnCl_2$

120. The colour of $CuCr_2O_7$ solution in water is green because?
(a) $Cr_2O_7^{2-}$ ions are green
(b) Cu^{2+} ions are green
(c) Both $Cr_2O_7^{2-}$ and Cu^{2+} ions are green
(d) Cu^{2+} ions are blue and $Cr_2O_7^{2-}$ ions are yellow

121. The most common lanthanide is
(a) lanthanum (b) cerium
(c) samarium (d) plutonium

122. Total number of inner transition elements in the periodic table is
(a) 10 (b) 14
(c) 28 (d) 30

123. The electronic configuration of gadolinium (At. No. 64) is
(a) $[Xe]4f^8 5d^1 6s^2$ (b) $[Xe]4f^7 5d^1 6s^2$
(c) $[Xe]4f^3 5d^5 6s^2$ (d) $[Xe]4f^6 5d^2 6s^2$

124. Which of the following element is responsible for oxidation of water to O_2 in biological process?
(a) Fe (b) Mn
(c) Cu (d) Mo

125. Which of the following compounds is not coloured?
(a) Na_2CuCl_4 (b) Na_2CdCl_4
(c) $K_4Fe(CN)_6$ (d) $K_3Fe(CN)_6$

126. The +3 ion of which one of the following has half filled 4f subshell?
(a) La (b) Lu
(c) Gd (d) Ac

127. Which of the following metal is found in gun metal, monel metal and constant alloys?
(a) Zn (b) Hg
(c) Fe (d) Cu

128. Non-lanthanide atom is
(a) La (b) Lu
(c) Pr (d) Pm

129. In which of the following lanthanides oxidation state +2 is most stable?
(a) Ce (b) Eu
(c) Tb (d) Dy

130. Which of the following elements shows maximum number of different oxidation states in its compounds?
(a) Eu (b) Ld
(c) Gd (d) Am

131. The alloy best suited for making meter scales is
(a) stainless steel (b) invar
(c) alnico (d) tungsten steel

132. Which metal is present in brass, bronze and German silver?
(a) Zn (b) Mg
(c) Cu (d) Al

133. Brass is an alloy of
(a) Al and Zn (b) Cu and Al
(c) Ni and Zn (d) Cu and Zn

Exercise-3 | PAST COMPETITION MCQs

1. Which one of the following ions is the most stable in aqueous solution? **[CBSE-PMT 2007]**
(a) V^{3+} (b) Ti^{3+} (c) Mn^{3+} (d) Cr^{3+}
(At.No. Ti = 22, V = 23, Cr = 24, Mn = 25)

2. Identify the incorrect statement among the following : **[CBSE-PMT 2007]**
(a) Lanthanoid contraction is the accumulation of successive shrinkages.
(b) As a result of lanthanoid contraction, the properties of 4*d* series of the transition elements have no similarities with the 5*d* series of elements.
(c) Shielding power of 4*f* electrons is quite weak.
(d) There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.

3. The correct order of decreasing second ionisation enthalpy of Ti (22), V(23), Cr(24) and Mn (25) is : **[CBSE-PMT 2008]**
(a) Cr > Mn > V > Ti (b) V > Mn > Cr > Ti
(c) Mn > Cr > Ti > V (d) Ti > V > Cr > Mn

4. Which one of the elements with the following outer orbital configurations may exhibit the largest number of oxidation states? **[CBSE-PMT 2009]**
(a) $3d^54s^1$ (b) $3d^54s^2$ (c) $3d^24s^2$ (d) $3d^34s^2$

5. Out of TiF_6^{2-}, CoF_6^{3-}, Cu_2Cl_2 and $NiCl_4^{2-}$ (*Z* of Ti = 22, Co = 27, Cu = 29, Ni = 28), the colourless species are: **[CBSE-PMT 2009]**
(a) Cu_2Cl_2 and $NiCl_4^{2-}$ (b) TiF_6^{2-} and Cu_2Cl_2
(c) CoF_6^{3-} and $NiCl_4^{2-}$ (d) TiF_6^{2-} and CoF_6^{3-}

6. Which of the following ions will exhibit colour in aqueous solutions? **[CBSE-PMT 2010]**
(a) La^{3+} (Z = 57) (b) Ti^{3+} (Z = 22)
(c) Lu^{3+} (Z = 71) (d) Sc^{3+} (Z = 21)

7. Which one of the following ions has electronic configuration [Ar] $3d^6$? **[CBSE-PMT 2010]**
(a) Ni^{3+} (b) Mn^{3+} (c) Fe^{3+} (d) Co^{3+}
(At. Nos. Mn = 25, Fe = 26, Co = 27, Ni = 28)

8. Which of the following pairs has the same size? **[CBSE-PMT 2010]**
(a) Fe^{2+}, Ni^{2+} (b) Zr^{4+}, Ti^{4+}
(c) Zr^{4+}, Hf^{4+} (d) Zn^{2+}, Hf^{4+}

9. Which of the following oxidation states is the most common among the lanthanoids? **[CBSE-PMT 2010]**
(a) 3 (b) 4 (c) 2 (d) 5

10. For the four successive transition elements (Cr, Mn, Fe and Co), the stability of +2 oxidation state will be there in which of the following order? **[CBSE-PMT 2011]**
(a) Mn > Fe > Cr > Co (b) Fe > Mn > Co > Cr
(c) Co > Mn > Fe > Cr (d) Cr > Mn > Co > Fe

11. Acidified $K_2Cr_2O_7$ solution turns green when Na_2SO_3 is added to it. This is due to the formation of : **[CBSE-PMT 2011]**
(a) $Cr_2(SO_4)_3$ (b) CrO_4^{2-} (c) $Cr_2(SO_3)_3$ (d) $CrSO_4$

12. Which of the statements is not true? **[CBSE-PMT 2012]**
(a) On passing H_2S through acidified $K_2Cr_2O_7$ solution, a milky colour is observed.
(b) $Na_2Cr_2O_7$ is preferred over $K_2Cr_2O_7$ in volumetric analysis.
(c) $K_2Cr_2O_7$ solution in acidic medium is orange.
(d) $K_2Cr_2O_7$ solution becomes yellow on increasing the pH beyond 7.

13. Which one of the following does not correctly represent the correct order of the property indicated against it? **[CBSE-PMT 2012]**
(a) Ti < V < Cr < Mn : increasing number of oxidation states
(b) $Ti^{3+} < V^{3+} < Cr^{3+} < Mn^{3+}$: increasing magnetic moment
(c) Ti < V < Cr < Mn : increasing melting points
(d) Ti < V < Mn < Cr : increasing 2nd ionization enthalpy

14. Four successive members of the first series of the transition metals are listed below. For which one of them the standard potential $\left(E^{\circ}_{M^{2+}/M}\right)$ value has a positive sign? **[CBSE-PMT 2012]**
(a) Co (Z = 27) (b) Ni (Z = 28)
(c) Cu (Z = 29) (d) Fe (Z = 26)

15. The catalytic activity of transition metals and their compounds is mainly due to : **[CBSE-PMT 2012]**
(a) their magnetic behaviour
(b) their unfilled *d*-orbitals
(c) their ability to adopt variable oxidation state
(d) their chemical reactivity

16. Which of the following exhibit only + 3 oxidation state ? **[CBSE-PMT 2012]**
(a) U (b) Th (c) Ac (d) Pa

17. A magnetic moment of 1.73 BM will be shown by one among the following : **[NEET 2013]**
(a) $[Ni(CN)_4]^{2-}$ (b) $TiCl_4$
(c) $[CoCl_6]^{4-}$ (d) $[Cu(NH_3)_4]^{2+}$

18. Which of the following lanthanoid ions is diamagnetic ? (At nos. Ce = 58, Sm = 62, Eu = 63, Yb = 70) **[NEET 2013]**
(a) Sm^{2+} (b) Eu^{2+} (c) Yb^{2+} (d) Ce^{2+}

19. $KMnO_4$ can be prepared from K_2MnO_4 as per the reaction:

$$3MnO_4^{2-} + 2H_2O \rightleftharpoons 2MnO_4^{2-} + MnO_2 + 4OH^-$$

The reaction can go to completion by removing OH^- ions by adding. **[NEET 2013]**
(a) KOH (b) CO_2 (c) SO_2 (d) HCl

20. Most common oxidation states of Ce (cerium) are **[AIEEE 2002]**
(a) +2, +3 (b) +2, +4 (c) +3, +4 (d) +3, +5.

21. Arrange Ce^{+3}, La^{+3}, Pm^{+3} and Yb^{+3} in increasing order of their ionic radii. **[AIEEE 2002]**
(a) $Yb^{+3} < Pm^{+3} < Ce^{+3} < La^{+3}$ (b) $Ce^{+3} < Yb^{+3} < Pm^{+3} < La^{+3}$
(c) $Yb^{+3} < Pm^{+3} < La^{+3} < Ce^{+3}$ (d) $Pm^{+3} < La^{+3} < Ce^{+3} < Yb^{+3}$.

22. Which of the following ions has the maximum magnetic moment? **[AIEEE 2002]**
(a) Mn^{+2} (b) Fe^{+2} (c) Ti^{+2} (d) Cr^{+2}.

23. Which is the correct order of ionic sizes? **[AIEEE 2002]**
(a) Ce > Sn > Yb > Lu (b) Sn > Ce > Lu > Yb
(c) Lu > Yb > Sn > Ce (d) Sn > Yb > Ce > Lu.
(At.Nos. : Ce = 58, Sn = 50, Yb = 70 & Lu = 71)

24. When $KMnO_4$ acts as an oxidising agent and ultimately forms $[MnO_4]^{-1}$, MnO_2, Mn_2O_3, Mn^{+2} then the number of electrons transferred in each case respectively is **[AIEEE 2002]**
(a) 4, 3, 1, 5 (b) 1, 5, 3, 7 (c) 1, 3, 4, 5 (d) 3, 5, 7, 1.

25. The radius of La^{3+} (Atomic number of La = 57) is 1.06Å. Which one of the following given values will be closest to the radius of Lu^{3+} (Atomic number of Lu = 71) ? **[AIEEE 2003]**
(a) 1.40 Å (b) 1.06 Å (c) 0.85 Å (d) 1.60 Å

26. What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid? **[AIEEE 2003]**
(a) $Cr_2O_7^{2-}$ and H_2O are formed
(b) CrO_4^{2-} is reduced to +3 state of Cr
(c) CrO_4^{2-} is oxidized to +7 state of Cr
(d) Cr^{3+} and $Cr_2O_7^{2-}$ are formed

27. Which one of the following nitrates will leave behind a metal on strong heating ? **[AIEEE 2003]**
(a) Copper nitrate (b) Manganese nitrate
(c) Silver nitrate (d) Ferric nitrate

28. The atomic numbers of vanadium (V), Chromium (Cr), manganese (Mn) and iron (Fe) are respectively 23, 24, 25, and 26. Which one of these may be expected to have the highest second ionization enthalpy ? **[AIEEE 2003]**
(a) Cr (b) Mn (c) Fe (d) V

29. Cerium (Z = 58) is an important member of the lanthanoids. Which of the following statements about cerium is **incorrect**? **[AIEEE 2004]**
(a) The +4 oxidation state of cerium is not known in solutions
(b) The +3 oxidation state of cerium is more stable than the +4 oxidation state
(c) The common oxidation states of cerium are +3 and +4
(d) Cerium (IV) acts as an oxidizing agent

30. Calomel (Hg_2Cl_2) on reaction with ammonium hydroxide gives **[AIEEE 2005]**
(a) HgO (b) Hg_2O
(c) $NH_2-Hg-Hg-Cl$ (d) $HgNH_2Cl$

31. The lanthanide contraction is responsible for the fact that **[AIEEE 2005]**
(a) Zr and Zn have the same oxidation state
(b) Zr and Hf have about the same radius
(c) Zr and Nb have similar oxidation state
(d) Zr and Y have about the same radius

32. Which of the following factors may be regarded as the main cause of lanthanide contraction? **[AIEEE 2005]**
(a) Greater shielding of 5d electrons by 4f electrons
(b) Poorer shielding of 5d electrons by 4f electrons
(c) Effective shielding of one of the 4f electron by another in the subshell
(d) Poor shielding of one of the 4f electron by another in the subshell

33. Nickel (Z = 28) combines with a uninegative monodentate ligand X^- to form a paramagnetic complex $[NiX_4]^{2-}$. The number of unpaired electron(s) in the nickel and geometry of this complex ion are, respectively: **[AIEEE 2006]**
(a) one, square planar (b) two, square planar
(c) one, tetrahedral (d) two, tetrahedral

34. Lanthanoid contraction is caused due to **[AIEEE 2006]**
(a) the same effective nuclear charge from Ce to Lu
(b) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge
(c) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge
(d) the appreciable shielding on outer electrons by 5d electrons from the nuclear charge

35. The "spin-only" magnetic moment [in units of Bohr magneton, (μ_B)] of Ni^{2+} in aqueous solution would be (At. No. Ni = 28) **[AIEEE 2006]**
(a) 6 (b) 1.73 (c) 2.84 (d) 4.90

36. Identify the incorrect statement among the following: **[AIEEE 2007]**
(a) 4*f* and 5*f* orbitals are equally shielded.
(b) *d*-Block elements show irregular and erratic chemical properties among themselves.
(c) La and Lu have partially filled *d*-orbitals and no other partially filled orbitals.
(d) The chemistry of various lanthanoids is very similar.

37. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because **[AIEEE 2007]**
(a) the 5f orbitals extend further from the nucleus than the 4f orbitals
(b) the 5f orbitals are more buried than the 4f orbitals
(c) there is a similarity between 4f and 5f orbitals in their angular part of the wave function
(d) the actinoids are more reactive than the lanthanoids.

38. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being **[AIEEE 2008]**
(a) 4*f* orbitals more diffused than the 5*f* orbitals
(b) lesser energy difference between 5*f* and 6*d* than between 4*f* and 5*d* orbitals
(c) more energy difference between 5f and 6d than between 4f and 5d orbitals
(d) more reactive nature of the actionids than the lanthanoids

39. Amount of oxalic acid present in a solution can be determined by its titration with $KMnO_4$ solution in the presence of H_2SO_4. The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl **[AIEEE 2008]**
(a) gets oxidised by oxalic acid to chlorine
(b) furnishes H^+ ions in addition to those from oxalic acid
(c) reduces permanganate to Mn^{2+}
(d) oxidises oxalic acid to carbon doxide and water

40. Knowing that the chemistry of lanthanoids(Ln) is dominated by its + 3 oxidation state, which of the following statements is incorrect? **[AIEEE 2009]**
(a) The ionic size of Ln (III) decrease in general with increasing atomic number
(b) Ln (III) compounds are generally colourless.
(c) Ln (III) hydroxide are mainly basic in character.
(d) Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character.

41. In context of the lanthanoids, which of the following statements is not correct? **[AIEEE 2011]**
(a) There is a gradual decrease in the radii of the members with increasing atomic number in the series.
(b) All the members exhibit +3 oxidation state.
(c) Because of similar properties the separation of lanthanoids is not easy.
(d) Availability of 4*f* electrons results in the formation of compounds in +4 state for all the members of the series.

42. The outer electron configuration of Gd (Atomic No. : 64) is : **[AIEEE 2011]**
(a) $4f^3\,5d^5\,6s^2$ (b) $4f^8\,5d^0\,6s^2$
(c) $4f^4\,5d^4\,6s^2$ (d) $4f^7\,5d^1\,6s^2$

43. Iron exhibits +2 and + 3 oxidation states. Which of the following statements about iron is incorrect ? **[AIEEE 2012]**
(a) Ferrous oxide is more basic in nature than the ferric oxide.
(b) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.
(c) Ferrous compounds are less volatile than the corresponding ferric compounds.
(d) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.

44. Which of the following arrangements does not represent the correct order of the property stated against it ? **[JEE M 2013]**
(a) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour
(b) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size
(c) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution
(d) Sc < Ti < Cr < Mn : number of oxidation states

45. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^\circ_{M^{3+}/M^{2+}}$ value ? **[JEE M 2013]**
(a) Cr(Z = 24) (b) Mn(Z = 25)
(c) Fe(Z = 26) (d) Co(Z = 27)

46. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are **[IIT-JEE 2011]**
(a) II, III in haematite and III in magnetite
(b) II, III in haematite and II in magnetite
(c) II in haematite and II, III in magnetite
(d) III in haematite and II, III in magnetite

Exercise-4 | Applied MCQs

1. In nitroprusside ion the iron and NO exist as Fe^{II} and NO^+ rather than Fe^{III} and NO. These forms can be differentiated by
(a) estimating the concentration of iron
(b) measuring the concentration of CN
(c) measuring the solid state magnetic moment
(d) thermally decomposing the compound.

2. Anhydrous ferric chloride is prepared by
(a) heating hydrated ferric chloride at a high temperature in a stream of air
(b) heating metallic iron in a stream of dry chlorine gas
(c) reaction of metallic iron with hydrochloric acid
(d) reaction of metallic iron with NaCl solution

3. When MnO_2 is fused with KOH, a coloured compound is formed, the product and its colour is:
(a) K_2MnO_4, purple green (b) $KMnO_4$, purple
(c) Mn_2O_3, brown (d) Mn_3O_4, black

4. Titanium shows magnetic moment of 1.73 B.M. in its compound. What is the oxidation number of Ti in the compound?
(a) +1 (b) +4
(c) +3 (d) +2

5. Which of the following is paramagnetic?
(a) $\left[Fe(CN)_6\right]^{4-}$ (b) $\left[Ni(CO)_4\right]$
(c) $\left[Ni(CO)_4\right]^{2-}$ (d) $\left[CoF_6\right]^{3-}$

6. If an aqueous solution of KCN is added to a solution of ferrous salt then the complex formed is represented by
(a) $\left[Fe(CN)_6\right]^{4-}$ (b) $\left[Fe(CN)_6\right]^{3-}$
(c) $\left[Fe(H_2O)_6\right]^{3+}$ (d) $\left[Fe(H_2O)_6\right]^{2+}$

7. The temperature of blast furnace to produce iron from its ore Fe_2O_3 varies from $500^\circ C$ at the top of the furnace to about $1900^\circ C$ at the bottom of the furnace. The reaction between the ore Fe_2O_3 and CO at the lowest temperature $\left(\sim 500^\circ C\right)$ is

(a) $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$

(b) $Fe_2O_3 + CO \rightarrow 2FeO + CO_2$

(c) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

(d) $Fe_2O_3 + CO + CaCO_3 \rightarrow Fe_2O_3 + CO + CO_2 + CaO$

8. The blue complex formed on addition of conc. NH_4OH solution to a Cu^{2+} salt solution has the structure?

(a) $\left[Cu(NH_4)_4\right]^{2+}$ (b) $\left[Cu(NH_3)_2\right]^{2+}$

(c) $\left[Cu(NH_3)_4\right]^{2+}$ (d) $\left[Cu(NH_4)_2\right]^{2+}$

9. When $CuSO_4$ solution is added to $K_4\left[Fe(CN_6)\right]$ the formula of the product formed is?

(a) $Cu_2Fe(CN)_6$ (b) KCN

(c) $Cu(CN)_3$ (d) $Cu(CN)_2$

10. In order to refine "blister copper" it is melted in furnace and is strirred with green logs of wood. The purpose is

(a) to expel the dissolved gases in the blister copper

(b) to bring the impurities to surface and oxidise them

(c) to increase the carbon content of copper

(d) to reduce the metallic oxide impurities with hydrocarbon gases liberated from the wood.

11. Identify the incorrect statement

(a) $CuSO_4$ reacts with KCl in aqueous solution to give Cu_2Cl_2

(b) $CuSO_4$ reacts with KI in aqueous solution to give Cu_2I_2

(c) $CuSO_4$ react with $NaOH$ and glucose in aqueous medium to give Cu_2O

(d) $CuSO_4$ on strong heating gives CuO

12. In the extraction of copper, the reaction which takes place in Bessemer converter is

(a) $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$

(b) $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$

(c) $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

(d) $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$

13. Copper is extracted from copper pyrites ore by heating in a blast furnace. The method is based on the principle that

(a) copper has more affinity for oxygen than sulphur at high temperature

(b) iron has less affinity for oxygen than sulphur at high temperature

(c) sulphur has less affinity for oxygen at high temperature

(d) copper has less affinity for oxygen than sulphur at high temprature

14. Colourless solutions of the following four salts are placed separately in four different test tubes and a strip of copper is dipped in each one of these. Which solution will turn blue?

(a) KNO_3 (b) $AgNO_3$

(c) $Zn(NO_3)_2$ (d) $ZnSO_4$

15. Which of the following does not react with AgCl?

(a) $Na_2S_2O_3$ (b) NH_4OH

(c) $NaNO_3$ (d) Na_2CO_3

16. Which of the following reactions represents "developing" in photography

(a) $AgNO_3 + NaBr \rightarrow AgBr + NaNO_3$

(b) $AgBr + 2Na_2S_2O_3 \rightarrow Na_3\left[Ag(S_2O_3)_2\right] + NaBr$

(c) $AgBr + h\nu \rightarrow AgBr^*$

(d) $C_6H_4(OH)_2 + +2AgBr^* \rightarrow C_6H_4O_2 + 2HBr + 2Ag$

17. In the extraction of silver from argentite ore the ore is treated with dilute solution of NaCN in water in the presence of Y, whereby the following reaction takes place

$$Ag_2X + 4NaCN + 2Y \rightarrow 2Na\left[Ag(CN)_2\right] + Na_2XO_4$$

X and Y in this reaction are represented by

(a) Cl and S (b) S and O_2

(c) O and O_2 (d) O and S

18. The black compound formed during the reaction between sodium thiosulphate and silver nitrate is

(a) silver thiosulphate $(Ag_2S_2O_3)$

(b) silver sulphide (Ag_2S)

(c) silver sulphate (Ag_2SO_4)

(d) silver sulphite (Ag_2SO_3)

19. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because

(a) Zn acts as an oxidising agent when react with HNO_3

(b) HNO_3 is weaker acid than H_2SO_4 and HCl

(c) In electrochemical series Zn is above hydrogen

(d) NO_3^- ion is reduced in preference to hydronium ion

20. Which of the following is used in the preparation of chlorine?

(a) Only MnO_2

(b) Only $KMnO_4$

(c) Both MnO_2 and $KMnO_4$

(d) Either MnO_2 or $KMnO_4$

21. In acidic medium $KMnO_4$ oxidises $FeSO_4$ solution. Which of the following statements is correct?

(a) 10 ml of 1N $KMnO_4$ solution oxidises 10 ml of 5N $FeSO_4$ solution

(b) 10 ml of 1M $KMnO_4$ solution oxidises 10 ml of 5N $FeSO_4$ solution

(c) 10 ml of 1M $KMnO_4$ solution oxidises 10 ml of 1M $FeSO_4$ solution

(d) 10 ml of 1N $KMnO_4$ solution oxidises 10 ml of 0.1M $FeSO_4$ solution

22. Number of moles of $K_2Cr_2O_7$ reduced by one mole of Sn^{2+} ions is

(a) $\frac{1}{3}$ (b) 3

(c) $\frac{1}{6}$ (d) 6

23. CrO_3 dissolves in aqueous NaOH go give

(a) CrO_4^{2-} (b) $Cr(OH)_3$

(c) $Cr_2O_7^{2-}$ (d) $Cr(OH)_2$

Hints & Solutions

EXERCISE 1

3. In both $K_2Cr_2O_7$ and K_2CrO_4, Cr is in + 6 oxidation state.
4. Co^{2+} contains three unpaired electrons ∴ more paramagnetic
5. The extra-ordinary stability of La, Gd and Zu is due to the empty, half-filled and fulley filled 4*f*-orbitals respectively.
6. This is because $KMnO_4$ has a germicidal action.
10. (a) + 2 oxidation state (exactly half-filled *d*-orbitals)
  (b) Osmium, (Os) in osmium tetraoxide (OsO_4).
  (c) Osmium (Os) is the densest transition element.
11. Acidic: Mn_2O_7 CrO_3 (oxides in higher oxidation states).
Amphoteric: MnO_2, CuO, TiO_2 (oxides in moderate oxidation states).
Basic: MnO, Cr_2O_3 (oxides in higher oxidation states).
12. n = 4.
20. (*b*) Pt can form compounds of + 4 oxidation state more easily
21. (*e*) This is because of
  (*i*) high heat of atomisation, and
  (*ii*) high ionisation energies
23. (c) **24. (c)** **25. (c)** **26. (a)** **27. (b)**
28. (b) **29. (c)**

EXERCISE 2

1. (a) Cr^{2+} electronic configuration is $[Ar]3d^4$, hence number of d electrons is 4.
2. (b) The more the number of unpaired electrons, the more is magnetic moment.Therefore the answer is (b).
3. (c) Ag belongs to second transition series.
4. (d) All statements are correct.
5. (a) The more the oxidation state, the more is the acid character, MnO, Mn_2O_3 are basic, MnO_2 is amphoteric and Mn_2O_7 is acidic.
6. (a) Electronic configuration of
$Zn^{2+}[Ar]3d^{10}4s^0$; $Ni^{2+}[Ar]3d^8, 4s^0$;
$Cr^{3+}[Ar]3d^3, 4s^0 Zn^{2+}$ colourless (no unpaired electrons) Ni^{2+} and Cr^{3+} coloured due to unpaired electrons
7. (c)
8. (c)
9. (d) Transition metals exhibit variable valency
10. (b) Cr has maximum unparied electrons .The number is 6.
$\{_{24}Cr \ : \ [Ar]3d^5 4s^1\}$
11. (a)
12. (b) $Cu^+[Ar]3d^{10}, Cu^{2+}[Ar]3d^9$, $Ti^{4+}[Ar]3d^0, V^{5+}[Ar]3d^0$.
only Cu^{2+} contains unpaired electron hence it is coloured
13. (a) They may or may not be diamagnetic
14. (a) 3d series starts from $Sc(Z-21)$ and ends with Zn(Z–30).
15. (a)
16. (d) Only $Cr^{3+}[Ar]3d^3$ contains unpaired electrons hence will give coloured solution
17. (d) A covalent bond is formed between small interstial non-metal and transition metal which make it hard
18. (d) Transition element due to similar (almost) sizes exhibit both vertical and horizontal similarities.
19. (d) O.S. of Os in OsO_4 is $+8$
20. (a) Highest O.S. by Mn (+7)
21. (b) $Zn^+[Ar]3d^{10}4s^1, Fe^{2+}[Ar]3d^6 4s^0, Ni^+[Ar]3d^8 4s^1$,
$Cu^+[Ar]3d^{10}4s^0$;
Fe^{2+} contain maximum number of unpaired electrons.
22. (a) Group number is given by $[ns+(n-1)d]$ electrons.
$\therefore [2+3]=5$
23. (d) Iron loses magnetic properties at 1000K.
24. (a) $Ni(28)$ $Ni[Ar]3d^8 4s^2$ contain 2 unpaired electrons.
25. (b) Zn and Hg have d-shells completely filled hence they do not exhibit variable valency.
26. (c) The statement is true for transition elements.
27. (b) Transition metals are generally paramagnetic since they contain unpaired electrons.
28. (b) Since reduction potential of fluorine is highest transition metals exhibit highest oxidation state with fluorine.
29. (d) Since Mn^{2+} contains maximum number of unparied electrons hence it has maximum magnetic moment
30. (d) Since Sc^{3+} does not contain any unpaired electron it is colourless in water.
31. (d) Since transition metals can lose electrons from $(n-1)d$ *ns* orbitals hence they are valence orbitals.
32. (d) Sc^{3+} is diamagnetic as it does not contain any unpaired electron while others contain.
33. (b) $Cu^{2+}[Ar]3d^9$ $Ti^{4+}[Ar]3d^0$ $Co^{2+}[Ar]3d^7$ $Fe^{2+}[Ar]3d^6$
1,3,4 are coloured ions hence the answer is b.
34. (c) If non metal is added to the interstital site the metal becomes less malleable due to formation of covalent bond between metal and non metal
35. (b) Transition metal in lower oxidation state will exist as cation which are lewis acids.
36. (c) Zinc does not show variable oxidation state due to completely filled d-orbitals

37. (c) Zn, Cd, Hg do not show properties of transition elements hence they are known as non typical transition elements

38. (d) Super conductors are derived from compounds of transition metals

39. (d) Corrosion can be prevented by Zn (galvanizing or sherardizing) with Sn (known as tinning) and Ni by electroplating

40. (b) Ferrous ferricyanide is known as Turbull's blue

41. (a) In octahedral crystal field the d - orbitals split in to t_{2g} and e_g orbitals. eg (d_{xy}, d_{yz} and d_{zx}) occupy lower level and eg $\left(d_{x^2-y^2}, d_{z^2}\right)$ occupy higher energy level.

42. (b) $_{24}Cr$, $_{26}Fe$, $_{27}Co$, $_{25}Mn$, $_{21}Sc$

Electonic configuration

$Cr: [Ar]3d^5 4s^1, Fe: [Ar]3d^6 4s^2$, $Co: [Ar]3d^7 4s^2$,

$Mn: [Ar]3d^5 4s^2$, $Sc: [Ar]3d^1 4s^2$

Configuration of ions

$$\begin{array}{ccccc} Cr^{3+} & Fe^{3+} & Co^{3+} & Mn^{2+} & Sc^{3+} \\ [Ar]3d^3 & [Ar]3d^5 & [Ar]3d^6 & [Ar]3d^5 & [Ar]3d^0 \end{array}$$

Fe^{3+}, Mn^{2+} have same electronic configuration

43. (a) Due to small size of Fe^{3+} the bonding in $FeCl_3$ is covalent.

44. (d) The impurity in pig iron is due to carbon hence graphite

45. (d) Magetic moment $\mu = \sqrt{n(n+2)}$ where n = number of unpaired electrons $\sqrt{15} = \sqrt{n(n+2)}$ $\therefore$ n = 3

46. (d)

47. (c) Stainless steel contains Fe, Cr, Ni and C.

48. (c) 22 carat gold is an alloy (see text)

49. (c) Iron does not exist in native form

50. (d) Slag is $CaSiO_3$

51. (a) Acidic due to cationic hydrolysis

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

$$Fe^{+++} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$$

52. (c) Let the O.N. be x $\therefore 3x + 4(-2) = 0$ $\therefore x = 8/3$

53. (a) Iron obtained from blast furnace is known as pig Iron

54. (b) $Fe^{3+} + 3KCNS \rightarrow Fe(CNS)_3 + 3K^+$

Ferric sulphocyanide is blood red

55. (c) It is the covering of steel by more reactive metal

56. (a) Acidic due to cationic hydrolysis

$$Fe^{2+} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^+$$

57. (c) Ans(c) correct

58. (c) $FeSO_4.(NH_4)_2SO_4.6H_2O$ in solution will give $Fe^{2+}, 2\left(SO_4^{2-}\right), 2\left(NH_4^+\right)$ hence total number of ions is 5

59. (d) It is annealing

60. (d) With dil. HNO_3, Fe gives NH_4NO_3

61. (a) They contain different percentage of carbon

62. (a) Green vitrol is $FeSO_4.7H_2O$

63. (c) Cassiterite is not an ore of iron. Liomite and magnetite are the ores of iron. Cassiterite is an ore of Sn.

64. (b) Corrosion is electrochemical phenomenon (See chapter on electrochemistry)

65. (b) Gun metal is alloy of Cu, Zn, Sn.

66. (a) $Cu^0 + 2AgNO_3 \rightarrow \overset{2+}{Cu}(NO_3)_2 + 2Ag$.

It is oxidation of copper $\left(Cu^0 \rightarrow Cu^{2+}\right)$

67. (a) $CuSO_4 + Ca(OH)_2$ is Bordeaux mixture

68. (a) $2Cu^{2+} + 4KI \rightarrow Cu_2I_2 + I_2 + 4K^+$

69. (c) $Cu + HCl \rightarrow$ No reaction (others will give H_2) See applications of ECS (electrochemistry).

70. (b) Cu is found in native state

71. (a) CuF_2 is ionic in nature (Fajan's rule), for fixed cation the smaller the anion, the more is ionic character.

72. (c) $2CuSO_4 + 10KCN \rightarrow 2K_3\left[Cu(CN)_4\right] + 2K_2SO_4 + (CN)_2$

73. (b) Correct (see text)

74. (c)

75. (a) Matte contains Cu_2S and FeS

76. (a) Cu has more reduction potential than hydrogen. Cu does not evolve H_2 with acids (See application of ECS in chapter of elctrochemistry)

77. (d) In $Cu^+[Ar]3d^{10}$ there is no unpaired electron, $Cu^{2+}[Ar]3d^9$ contains one unpaired electron hence coloured

78. (b) Out of 29 electrons, 14 electrons have spin in one direction and 15 electrons in other direction.

79. (c) Cuprite Cu_2O

80. (c) $CuSO_4 \xrightarrow{\Delta} CuO + SO_3$

81. (d) Chalcopyrites $CuFeS_2$, Bauxite $\left(Al_2O_3.2H_2O\right)$, Galena (PbS), Siderite $(FeCO_3)$

82. (d) In electrolytic purification anode is always of impure sample and cathode of pure metal

83. (a) $2AgNO_3 + K_2CrO_4 \rightarrow \underset{\text{Red precpitate}}{Ag_2CrO_4} + 2KNO_3$

84. (a) $2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$

85. (b) $AgCl + 2NaCN \rightarrow Na\left[Ag(CN)_2\right] + NaCl$

86. (d) $Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^-$ silver is reduced $(Ag^+ \rightarrow Ag^0)$ gain of electron which is reduction

87. (c) $AgCl(s) + 2NH_4OH(aq) \rightarrow \left[Ag(NH_3)_2\right]Cl(aq) + 2H_2O(l)$

88. (a) AgF being ionic in nature is highly soluble in water others are insoluble.

89. (b) Cupellation process is used in the metallurgy of silver

90. (d) $K_4\left[Fe(CN)_6\right] + 6H_2SO_4 + 6H_2O \rightarrow$

$$2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

This is one of the methods for the preparation of carbon monoxide

91. (c) Ag_2S is dissolved in KCN to give $K\left[Ag(CN)_2\right]$

92. (c) Parke's process (See text) It is for extraction of silver

93. (c) This is cyanide process for gold $(M = Au)$

94. (a) Cu, Hg and Ag are attacked by conc acids but gold is not attacked. $AuCl_3$ forms $H[AuCl_4]$ a complex with HCl which is used for tonning in photography.

95. (c) At ordinary temperature Zn metal is brittle not at high temperature

96. (d) Galvanisation is coating with zinc

97. (c) $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$

98. (b) $H_2Cr_2O_7 + 4O \rightarrow \underset{\text{Blue peroxide of chromium}}{2CrO_5} + H_2O$

99. (d) CO burns with blue flame

100. (b) Hg_2Cl_2 with NH_4OH form black $\left[Hg + Hg(NH_2)Cl\right]$

101. (a) Metallic bonding in mercury is weak

102. (a) Mercury being less reactive cannot evolve H_2 from H_2S.

103. (c) It is tailing of mercury due to formation of $Hg_2O(2Hg + O_3 \rightarrow Hg_2O + O_2)$

104. (b) $HgCl_2$ sublimes on heating

105. (a) NH_4^+ ions are detected by Nessler's reagent (see text)

106. (a) Mercurous ion Hg_2^{2+} or $\overset{+1}{Hg} - \overset{+1}{Hg}$

107. (a) Nessler's reagent is $K_2[HgI_4]$ dissolved in KOH

108. (c) $MnO_4^- + 3e^- \rightarrow Mn^{4+}$. In neutral medium

$\therefore Eq.wt. = M/3$

109. (a) Pyrolusite (It is MnO_2)

110. (a) $2KMnO_4 + H_2SO_4(Conc) \rightarrow K_2SO_4 + \underset{\text{Explosive}}{Mn_2O_7} + H_2O$

111.(c) In acid medium $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

(O.S. of Mn changes form +7 to +2)

112. (a) Permanganic acid is $HMnO_4$

113. (d) In MnO_2 (O.S. of Mn is +4) in K_2MnO_4 (O.S.of Mn is +6). Hence O.S. changes by 2

114. (a) CrO_2 is amphoteric in nature

115. (b) K_2MnO_4 is potassium manganate O.S. of Mn is +6

116. (a)

	$KMnO_4$	MnO_2	Mn^{2+}	$Mn(OH)_3$	MnO_4^{2-}
O.S of Mn	+7	+4	+2	+3	+6
electrons needed	0	3	5	4	1

117. (d) Change in O.S. is by 1. Hence eq wt is $\frac{158}{1} = 158$

118. (b) In KIO_4 O.S of I is +7 and in $KMnO_4$ O.S. of Mn is +7

119. (a) Electronic configuration of Mn is $[Ar]3d^5 4s^2$. Being transition metal it has 7 valence electrons and all are involved in bond formation in MnO_4^-. Hence it has no unpaired electron

120. (d) Green colour of $CuCr_2O_7$ is due to blue colour of Cu^{2+} ions and yellow colour of $Cr_2O_7^{2-}$ ions

121. (b) Cerium is the most common lanthanide

122. (c) The number is 28(14 lanthanide +14 Actinides)

123. (b) Electronic configuration of gadolinium is

$[Xe]4f^7 5d^1 6s^2$

124. (b) Oxidation of water takes place in presence of Mn in biological process

125. (b) $Na_2CdCl_4.Cd^{2+}$ does not contain any unpaired electron hence colourless

126. (c)

127. (d) Copper (see alloys)

128. (a) La (lanthanum) is non lanthanide atom

129. (b) Eu^{2+} has electronic configuration $[Xe]4f^7$ hence stable due to half filled atomic orbitals.

130.(d)

	Eu	La	Gd	Am
O.S=	+2 ,+3	+3	+3,+4,+5,+6	

131. (b) Invar due to small coefficient of thermal expansion

132. (c) Copper is present in brass, bronze and german silver (see list - of alloys)

133. (d) Brass is an alloy of Cu and Zn

EXERCISE 3

1. (d) For chromium ion + 3 oxidation state is most stable.

2. (b) As a result of lanthanoid contraction change in ionic radii on going from elements of 4*d* to 5*d* transition series is very small. Thus chemical properties of 4*d* and 5*d* series of transition elements are similar.

3. (a) Ti ; Z (22) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$

V ; Z (23) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

Cr ; Z (24) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

Mn ; Z (25) is $1s^2 2s^2 2p^6 3s^2 3d^5 4s^2$

The second electron in all the cases (except Cr) has to be removed from 4*s*-orbital and for Cr it has to be removed from completely half filled 3*d*-orbital which have extra stability thus $I.E_2$ is highest for Cr. Now among rest elements more will be the nuclear charge more will be the value of $I.E_2$. As nuclear charge depends upon atomic number. Therefore correct order of $I.E_2$ is Mn > V > Ti.

i.e. Cr > Mn > V > Ti. So correct answer is (a).

4. **(b)** Mn - $3d^5\,4s^2$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ $\boxed{\uparrow\downarrow}$

The no. of various oxidation states possible are + 2, + 3, + 4, + 5, + 6 and + 7.

5. **(b)** The colour exhibited by transition metal ions is due to the presence of unpaired electrons in *d*-orbitals which permits the *d* - *d* excitation of electrons.

In TiF_6^{2-} – Ti is in + 4 O.S. ; $3d^0$ = colourless

In CoF_6^{3-} – Co is in + 3 O.S ; $3d^5$ = coloured

In Cu_2Cl_2 – Cu is in +1 O.S. ; $3d^{10}$ – colourless

In $NiCl_4^{2-}$ – Ni is in + 2 O.S ; $3d^8$ – coloured

6. **(b)** La^{3+} : 54 e^- = [Xe]

Ti^{3+} : 19 e^- = [Ar] 3 d^1 (Coloured)

Lu^{3+} : 68 e^- = [Xe] $4f^{14}$

Sc^{3+} : 18 e^- = [Ar]

7. **(d)** Ni^{3+} : [Ar] $3d^7$

Mn^{3+} : [Ar] $3d^4$

Fe^{3+} : [Ar] $3d^5$

Co^{3+} : [Ar] $3d^6$

8. **(c)** Due to lanthanide contraction, the size of Zr and Hf (atom and ions) become nearly similar

9. **(a)**

10. **(a)**

11. **(a)** The green colour appears due to the formation of Cr^{+++} ion

$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + 4H_2O$$

12. **(b)** $Na_2Cr_2O_7$ is hygroscopic.

13. **(c)** The melting points of the transition element first rise to a maximum and then fall as the atomic number increases manganese have abnormally low melting point.

14. **(c)** $E^o_{Cu^{+2}/Cu} = 0.34\,V$

other has – ve $E^o_{R.P.}$

$E^o_{Co^{++}/Co} = -0.28\,V$

$E^o_{Ni^{++}/Ni} = -0.25V$

$E^o_{Fe^{++}/Fe} = -0.44V$

15. **(c)** The transition metals and their compounds are used as catalysts. Because of the variable oxidation states they may form intermediate compound with one of the readtants. These intermediate provides a new path with lowe activation energy. $V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$
$2V_2O_4 + O_2 \rightarrow 2V_2O_5$

16. **(c)** Ac (89) = [Rn] [$6d^1$] [$7s^2$]

17. **(d)** $[Cu(NH_3)_4]^{2+}$ hybridisation dsp^2

$Cu^{+2} - 3d^9$ has one unpaired e^-

$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$

So magnetic moment

$$\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)}$$

$$= \sqrt{3} = 1.73$$

18. **(c)**

$Sm^{2+}(Z=62)$ $[Xe]4f^6\,6s^2$ – 6 unpaired e^-

$Eu^{2+}(Z=63)$ $[Xe]4f^7\,6s^2$ – 7 unpaired e^-

$Yb^{2+}(Z=70)$ $[Xe]4f^{14}\,6s^2$ – 0 unpaired e^-

$Ce^{2+}(Z=58)$ $[Xe]4f^1\,5d^1\,6s^2$ – 2 unpaired e^-

Only Yb^{2+} is diamagnetic.

19. **(b)** HCl and SO_2 are reducing agents and can reduce MnO_4^-. CO_2 which is neither oxidising and nor reducing will provide only acidic medium. It can shift reaction in forward direction and reaction can go to completion.

20. **(c)** Common oxidation states of Ce(Cerium) are + 3 and + 4

21. **(a)** According to their positions in the periods, these values are in the order:

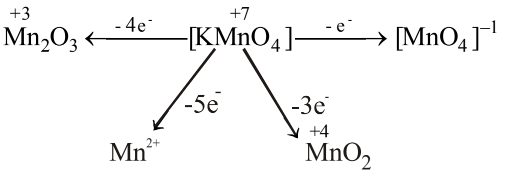
$Yb^{+3} < Pm^{+3} < Ce^{+3} < La^{+3}$

At. Nos. 70 61 58 57

This is due to lanthanide contraction.

22. **(a)** Mn^{2+} has the maximum number of unpaired electrons (5) and therefore has maximum magnetic moment.

23. **(a)**

24. **(a)** 

25. **(c)** $\Omega \propto \frac{1}{z}$

$$\frac{\Omega_1}{\Omega_2} = \frac{z_2}{z_1} \Rightarrow \frac{1.06}{\Omega_2} = \frac{71}{57} \Rightarrow \Omega_2 = 0.85\,Å$$

26. **(a)** $Cr_2O_7^{2-} + OH^- \longrightarrow 2CrO_4^{2-} + H^+$

The above equilibrium shifts to L.H.S. on addition of acid.

27. **(c)** $AgNO_3 \rightarrow Ag + NO_2 + \frac{1}{2}O_2$

28. **(a)** Electronic configuration of Cr is

$\overset{3d}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$ $\overset{4s}{\boxed{\uparrow}}$

So due to half filled orbital I.P. is high of Cr.

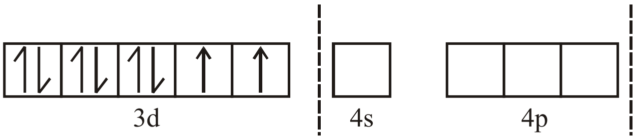
29. **(a)** The +4 oxidation state of cerium is also known in solution

30. **(d)** $Hg_2Cl_2 + 2NH_4OH \longrightarrow HgNH_2Cl + NH_4Cl + 2H_2O$

31. (b) In vertice columns of transition elements, there is an increase in size from first member to second member as expected but from second member to third member, there is very small change in size and some times sizes are same. This is due to lanthanide contraction. This is the reason for Zr and Hg to have same radius.

32. (d) In lanthanides, there is poorer shielding of 5d electrons by 4f electrons resulting in greater attraction of the nucleus over 5d electrons and contraction of the atomic radii.

33. (d) $[Ni\,X_4]^{2-}$, the electronic configuration of Ni^{2+} is



It contains two unpaired electrons and the hybridisation is sp^3 (tetrahedral).

34. (b) The configuration of Lanthanides show that the additional electron enters the 4f subshell. The shielding of one 4f electron by another is very little or imperfect. The imperfect shielding of f electrons is due to the shape of f orbitals which is very much diffused. Thus as the atomic number increases, the nuclear charge increases by unity at each step while no comparable increase in the mutual shielding effect of 4f occurs. This causes a contraction in the size of the 4f subshell. as a result atomic and ionic radii decreases gradually from La to Lu.

35. (c) The number of unpaired electrons in $Ni^{2+}(aq) = 2$
Water is weak ligand hence no pairing will take place spin magnetic moment

$$= \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8} = 2.82$$

36. (a) 4*f* orbital is nearer to nucleus as compared to 5*f* orbital therefore, shielding of 4*f* is more than 5*f*.

37. (a) More the distance between nucleus and outer orbitals, lesser will be force of attraction on them. Distance between nucleus and 5f orbitals is more as compared to distance between 4f orbital and nucleus. So actinoids exhibit more number of oxidation states in general than the lanthanoids.

38. (b) The main reason for exhibiting larger number of oxidation states by actinoids as compared to lanthanoids is lesser energy difference between 5*f* and 6*d* orbitals as compared to that between 4*f* and 5*d* orbitals.

In case of actinoids we can remove electrons from 5*f* as well as from *d* and due to this actinoids exhibit larger number of oxidation state than lanthanoids. Thus the correct answer is option (b)

39. (c) The titration of oxalic acid with $KMnO_4$ in presence of HCl gives unsatisfactory result because of the fact that $KMnO_4$ can also oxidise HCl along with oxalic acid. HCl on oxidation gives Cl_2 and HCl reduces $KMnO_4$ to Mn^{2+}

40. (b) Most of the Ln^{3+} compounds except La^{3+} and Lu^{3+} are coloured due to the presence of *f*-electrons.

41. (d)

42. (d) The configuration of Gd is [xe] $4f^7\,5d^1\,6s^2$.

43. (d) Fe^{3+} is easily hydrolysed than Fe^{2+} due to more positive charge.

44. (a)

(a) $V = 3d^3\,4s^2$; $V^{2+} = 3d^3$ = 3 unpaired electrons
$Cr = 3d^5\,4s^1$; $Cr^{2+} = 3d^4$ = 4 unpaired electrons
$Mn = 3d^5\,4s^2$; $Mn^{2+} = 3d^5$ = 5 unpaired electrons
$Fe = 3d^6\,4s^2$; $Fe^{2+} = 3d^6$ = 4 unpaired electrons
Hence the correct order of paramagnetic behaviour
$V^{2+} < Cr^{2+} = Fe^{2+} < Mn^{2+}$

(b) For the same oxidation state, the ionic radii generally decreases as the atomic number increases in a particular transition series. hence the order is
$Mn^{++} > Fe^{++} > Co^{++} > Ni^{++}$

(c) In solution, the stability of the compound depends upon electrode potentials, SEP of the transitions metal ions are given as
$Co^{3+} / Co = +1.97$, $Fe^{3+} / Fe = +0.77$;
$Cr^{3+} / Cr^{2+} = -0.41$, Sc^{3+} is highly stable as it does not show + 2 O. S.

(d) Sc – (+ 2), (+ 3)
Ti – (+ 2), (+ 3), (+ 4)
Cr – (+ 1), (+ 2), (+ 3), (+ 4), (+ 5), (+ 6)
Mn – (+ 2), (+ 3), (+ 4), (+ 5), (+ 6), (+ 7)
i.e. Sc < Ti < Cr = Mn

45. (d) $E^\circ_{Cr^{3+}/Cr^{2+}} = -0.41\,V$ $\quad E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77\,V$

$E^\circ_{Mn^{3+}/Mn^{2+}} = +1.57\,V$, $\quad E^\circ_{Co^{3+}/Co^{2+}} = +1.97\,V$

46. (d) (i) Haematite is Fe_2O_3 in which Fe is present in III oxidation state.

(ii) Magnetite (Fe_3O_4) is an equimolar mixture of FeO and Fe_2O_3.

Oxidation state of Fe in FeO is II.

Oxidation state of Fe in Fe_2O_3 is III.

EXERCISE 4

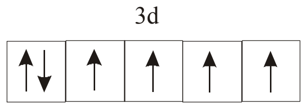
1. (c) The magnetic moment (μ) of a species is related to its number of unpaired electrons (n) in form of following expressions.

$$\mu = \sqrt{n(n+2)}\ B.M$$

The number of unpaired electrons in the given pairs are as follows:

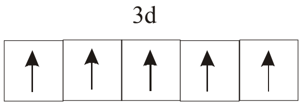
$$Fe^{2+} = 1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^6$$

or



Thus here n = 4.

$Fe^{3+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5$

or 

Thus here n = 5

$\overset{+}{NO}$ or $\overset{+}{\underset{xx}{N}} = \ddot{O}:$ n = 0

NO or $\overset{\times}{\underset{\times}{}}N = \overset{..}{O}:$ n = 1

The given combinations differ in the number of unpaired electrons. Hence these can be differentiated by the measurement on the solid state magnetic moment of nitroprusside ion.

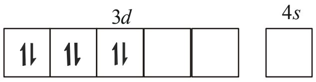
2. (b) $2Fe + 3Cl_2 \rightarrow 2FeCl_3$

3. (a) Stable oxidation state of Mn in alkaline medium is +6. So, MnO_2 is oxidised to K_2MnO_4 by atmospheric oxygen in KOH medium.
$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

4. (c) Magnetic moment $\mu = \sqrt{n(n+2)}$BM

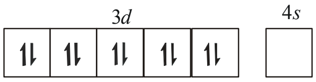
$1.73 = \sqrt{n(n+2)}$ $\therefore n = 1$, it has one unpaired electron hence electronic configuration is $[Ar]3d^1$ and electronic configuration for Z = 22 is $[Ar]3d^2 4s^2$. Hence charge on Ti is +3

5. (d) Fe^{2+} has electronic configuration



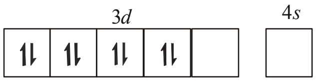
due to strong ligand

Ni has electronic configuration



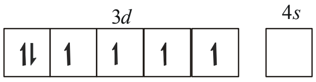
due to strong ligand

Ni^{2+} has electronic configuration



due to strong ligand

Co^{3+} has electronic configuration



No pairing of electrons

due to weak ligand hence $[CoF_6]^{3-}$ is paramagnetic.

6. (a) $Fe^{++} + 6KCN \rightarrow [Fe(CN)_6]^{4-} + 6K^+$

7. (c) The reaction at $500^\circ C$ is $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

8. (c) $Cu^{++} + 4NH_4OH \rightarrow \underset{\text{deep blue comp}}{[Cu(NH_3)_4]^{2+}} + 4H_2O$

9. (a) Ans (a) See text

10. (d) The statement (d) is correct.

11. (a) $2CuSO_4 + 4KI \rightarrow Cu_2I_2 + 2K_2SO_4 + I_2$ (not given by KCl).
Fehling solution gives Cu_2O with reducing substances

$CuSO_4 \xrightarrow[\Delta]{\text{strong}} CuO + SO_3$

12. (b) $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$ takes place in Bessemer convertor

13. (a) (see extraction of copper)

14. (b) $Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$. Cu^{2+} will give blue solution. Cu is below in ECS than K and Zn hence no reaction with them

15. (c) There is no reaction between $NaNO_3$ and AgCl

$AgCl + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaCl$

$AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl + 2H_2O$

$4AgCl + 2Na_2CO_3 \rightarrow 4NaCl + 4Ag + 2CO_2 + O_2$

16. (d) Developing in photography involves decomposition of AgBr

$C_6H_4(OH)_2 + 2AgBr \rightarrow C_6H_4O_2 + 2HBr + 2Ag$

17. (b) $Ag_2S + 4NaCN + 2O_2 \rightarrow 2Na[Ag(CN)_2] + Na_2SO_4$
X is S and Y is O_2

18. (a) $2AgNO_3 + Na_2S_2O_3 \rightarrow Ag_2S_2O_3 + 2NaNO_3$

19. (d) NO_3^- ions are reduced by nascent hydrogen

$\text{Metal} + HNO_3 \rightarrow \text{Metal nitrate} + H$

$HNO_3 + 8H \rightarrow N_2O + 5H_2O$

20. (c) Both MnO_2 and $KMnO_4$ used for the preparation of chlorine by the action of Conc. HCl

$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$

$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

Chlorine is not obtained by dil HCl

$Ag_2S_2O_3 + H_2O \rightarrow \underset{\text{Black ppt}}{Ag_2S} + H_2SO_4$

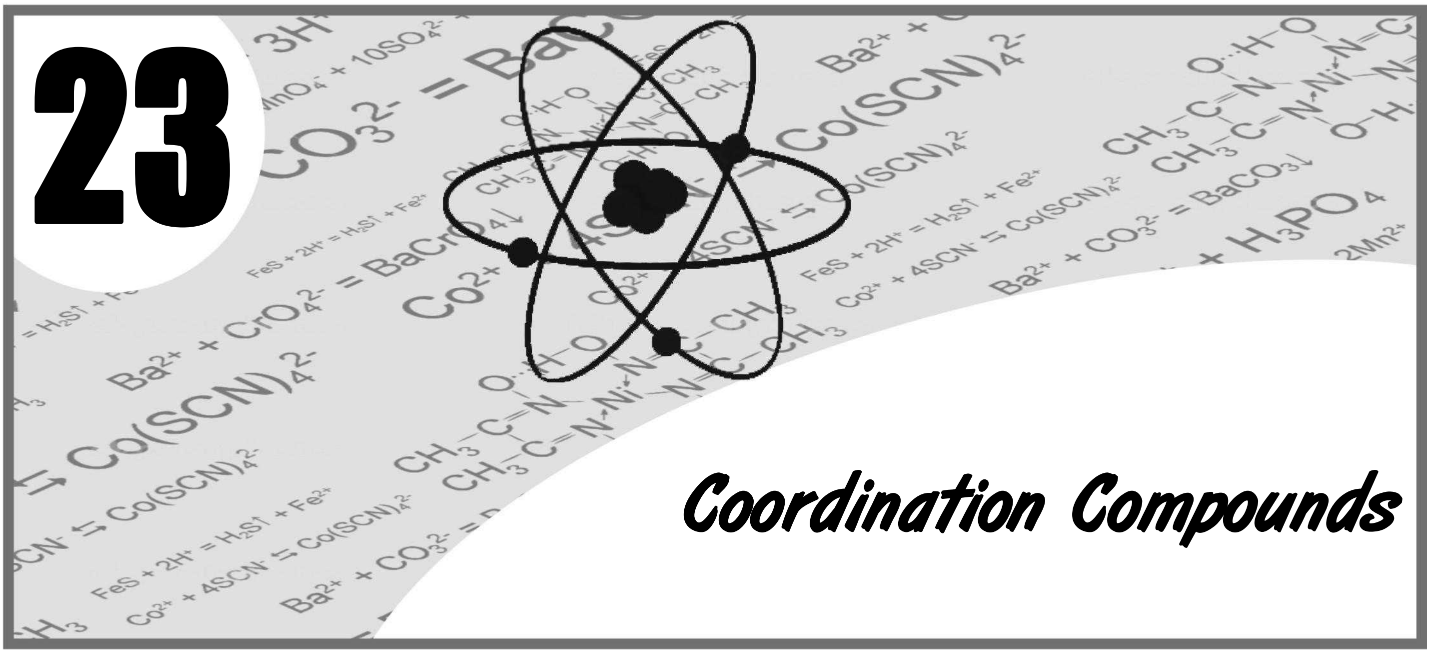
21. (b) $1M\ KMnO_4 \equiv 5N\ KMnO_4 \equiv 5N\ FeSO_4$
$\therefore \underset{KMnO_4}{10 \times 1M} \equiv \underset{KMnO_4}{10 \times 5N} \equiv \underset{FeSO_4}{10 \times 5N}$

22. (a) $Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

one mol of Sn^{2+} provide 2 mol of e^- which will reduce $1/3 Cr_2O_7^{2-}$

23. (a) $CrO_3 + 2NaOH \rightarrow Na_2CrO_4 + H_2O$



23

Coordination Compounds

DOUBLE SALTS :

The addition compounds which retain their identity in solid form only and not in solution are known as double salts eg carnallite.

$$KCl.MgCl_2.6H_2O \longrightarrow K^+ + Cl^- + Mg^{2+}(aqs)$$

In aqueous solution carnallite shows the properties of K^+, Mg^{2+} and Cl^- ions

COORDINATION COMPOUNDS :

The addition compounds which retain their identity in solid as well as in solution. Such compounds contain a complex ion formed by the combination of a metal atom and other species having lewis base character eg.

$$K_4[Fe(CN)_6](s) \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

Since the complex ion contains a number of coordinate bonds they are also known as coordination compounds.

SOME DEFINITIONS :

(i) ***Complex -*** A central metal atom /ion surrounded by a set of ligands

(ii) ***Ligand -*** An ion or a molecule that can have an independent existence and can donate a pair of electrons. It can be negative ion, neutral molecule or positive cation (though rare in nature)

(iii) ***Coordination compound -*** A neutral complex or ionic compound in which atleast one of the ions is a complex formed between a lewis acid ($\bar{e}$ -acceptor) and lewis base $(\bar{e} - \text{pair doner})$ eg

$$Ni(ClO_4)_2 + 6NH_3 \rightarrow [Ni(NH_3)_6](ClO_4)_2$$

Ni = lewis acid centre, NH_3 = Lewis base

Complex ion is always written in square brackets

(iv) ***Coordination number -*** Number of ligand donor atoms (not number of ligands) in a coordination compound (or complex) or number of electron pairs arising from ligand donor atoms to which the metal is directly bonded. Coordination number range from 1 to 12 (> 12 for some f-block element.

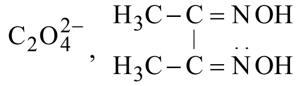
(v) ***Types of ligands***

(a) ***Unidentate*** - Which binds to a metal through a single point of attachment eg $\ddot{N}H_3$, Br etc.

$\ddot{N}H_3$	$H_2\ddot{O}$	$\ddot{P}H_3$	NO	CO	CS
$C_5H_5\ddot{N}$,	$(C_6H_5)_3\ddot{P}$,	X^- (Cl,Br,I)	$:OH^-$	$:CN^-$	O^{2-},
O_2^{2-},	CO_3^{2-},	NO_2^-,	SO_4^{2-},	SCN^-,	CH_3COO^-,
S^{2-},	$S_2O_3^{2-}$,	NO_3^-,	SO_3^{2-},	NH_2^-,	NH^{2-}

(b) **Bidentate -** Which binds to a metal through two points eg

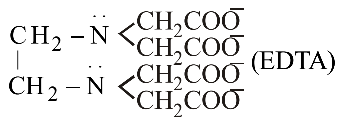
$$H_2\ddot{N} - CH_2 - CH_2\ddot{N}H_2 \text{ (binds through N)}$$



$$C_2O_4^{2-}, \quad \begin{array}{l} H_3C-C=\ddot{N}OH \\ \quad\;\;\; | \\ H_3C-C=\ddot{N}OH \end{array}$$

(c) **Polydentate -** Several donor atoms are present in one molecule

(Dentate- derived from teeth)



$$\begin{array}{l} CH_2-\ddot{N} < \begin{array}{l} CH_2COO^- \\ CH_2COO^- \end{array} \\ | \\ CH_2-\ddot{N} < \begin{array}{l} CH_2COO^- \\ CH_2COO^- \end{array} \end{array} \text{(EDTA)}$$

(vi) ***Chelate complex -*** It is formed when a bi or polydentate ligand uses two or more donor atoms to bind to one metal atom ("chelate" derived from claw)

Most common elements to act as donor atoms are N, P, O, S halides and C (in organic metallic compounds) *(vii)* ***Bridging ligands*** **-** Such ligands can bind to more than one metal atom

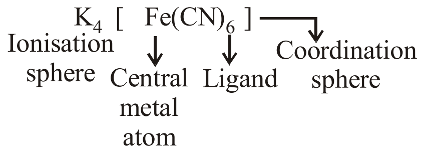
(viii) ***Homoleptic ligand*** **-** Metal bound to only one type of donor group

(ix) ***Heteroleptic ligand*** **-** Metal bound to more than one type donor group

(x) ***Co-ordination sphere*** **-** The combination of central metal atom and ligands written in "square brackets" is called the coordination sphere

(xi) ***Ionisation sphere*** **-** The portion present outside the square bracket is called ionisation sphere

Species present in the coordination sphere are non ionisable and species present in the ionisation sphere are ionisable.



(xii) ***Oxidation number*** **-** Charge carried by the central metal atom

(xiii) ***Effective atomic number (EAN)*** **-** It can be obtained from the following simple expression

EAN = Z – O.N + 2 (CN)

Where Z = Atomic number of central metal atom

O.N. = Oxidation number of central metal atom

CN = Coordination number of central metal atom.

It is equal to the number of monodentate ligands, twice the number of bidentate ligands and so on.

WERNER'S THEORY :

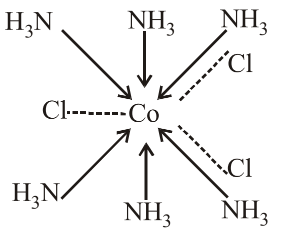
According to Werner's theory metals have two types of linkages (valencies)

1. ***Primary linkages*** **-** Which are satisfied by the negative ions, ionisable and their number is equal to the O . N of central metal atom.

   They are always represented by dotted lines

2. ***Secondary linkages*** **-** Which are satisfied by the negative, neutral or a positive species (ligands) and their number is equal to the coordination number of the central metal atom. These are non ionisable and represented by complete lines.

   Every metal atom has a tendency to satisfy both the valencies. On the basis of Werner's theory the structure of $CoCl_3 . 6NH_3$ can be represented as follows :



$$\rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$$

NOMENCLATURE OF COORDINATION COMPOUNDS :

Nomenclature of coordination compounds follows different rules which are as follows.

1. Name the cation, then anion
2. Non ionic compounds are given one-word name
3. Name ligands
   (a) Ligands are named first and central atom last
   (b) Ligands are named in alphabetical order
   (c) Neutral ligands are named the same as the molecule (except aqua and ammine)
   (d) Anionic ligands are named by adding - O to the stem of the name (chloride becomes chloro)
   (e) The ligand name is preceeded by a numerical prefix to indicate how many are present
   di, tri, tetra, penta, hexa
4. In a neutral or cationic complex, the name of the central metal atom is followed by its oxidation number in Roman numerals in parentheses
5. In anionic complex, the suffix- **ate** is added to the name of central metal, followed by its oxidation number in Roman numerals in parentheses
6. In case of bridging ligand the word μ (mu) is written before the name of ligand

Formula and names of some ligands

H_2O aqua	OH^-	hydroxo	$-NC^-$	Isocyano
CO carbonyl	F^-	fluoro	$-SCN^-$	thiocyanato
NH_3 ammine	Br^-	bromo	NO_3^-	nitrato
NO nitrosyl	CN^-	cyano	$-ONO^-$	nitrito
C_6H_5 Phenyl	$-NCS^-$	Isothiocyanato	NH^{2-}	imido
C_5H_5N Pyridine	SO_4^2	Sulphato	O_2^{2-}	peroxo
PH_3 Phosphine	NO_2^-	nitro	NH_2^-	Amido
$P(C_6H_5)_3$ Triphenylphosphine	CO_3^{2-}	Carbonato	N^{3-}	nitrido
$H_2N. CSNH_2$ Thiourea	O^{2-}	oxo	S^{2-}	sulphido
$H_2N. CH_2. CH_2. NH_2$ ethylene diammine	Cl^-	chloro	$C_2O_4^{2-}$	oxalato
	I^-	iodo	CH_3COO^-	acetato

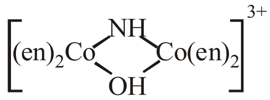
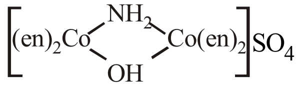
ligands carrying positive charge have ending of **–ium**

$\overset{+}{NO_2}$ nitronium

$\overset{+}{NO}$ nitrosonium

$(NH_2NH_3)^+$ hydrazinium

Name of some complex compounds - Following the above rules here are names of some complex compounds.

$[Cr(H_2O)_5Cl]SO_4$	Pentaaquachlorochromium (III) Sulphate
$[Cr(H_2O)_4Cl_2]Cl$	Tetraaquadichlorochromium (III) Chloride
$K_2[PtCl_4]$ (II)	Potassiumtetrachloroplatinate
$[Co(en)_2Cl_2]Cl$	Dichlorobis (ethylene-diammine) cobalt (III) Chloride
$[Pt^{IV}(NH_3)_4Cl_2]\,[Pt^{II}Cl_4]$	Tetraamminedichloro platinum (IV) tetrachloroplatinate (II)
 $\left[(en)_2Co\overset{NH}{\underset{OH}{\langle\rangle}}Co(en)_2\right]^{3+}$	Bisethylenediaminecobalt (III) -μ-amido -μhydroxobis ethylenediaminecobalt (III) ion
$[Fe(H_2O)_4(C_2O_4)]_2SO_4$	Tetraaquaoxalato iron (III) sulphate
$[Ag(NH_3)_2]Cl$	Diamminesilver (I) chloride
$[Cu(NH_3)_4]SO_4$	Tetramminecopper (II) sulphate
$[Ni(CN)_4]^{2-}$	Tetracyanonickelate (II) ion
K_2HgI_4	Potassiumtetraiodomercurate (II)
$[Cr(NH_3)_6]\,[Co(C_2O_4)_3]$	Hexammine chromiun (III) trioxalato cobaltate (III)
 $\left[(en)_2Co\overset{NH_2}{\underset{OH}{\langle\rangle}}Co(en)_2\right]SO_4$	Bis (ethylenediammine) cobalt (III) μ - amido μ - hydroroxo bis (ethylene diammine) cobalt (III) sulphate

ISOMERISM IN COORDINATION COMPOUNDS :

Isomers - two or more forms of a compound having the same composition

(i) ***Structural Isomers*** - (have different bonding) . They are of the following types

(ii) ***Ionization Isomers*** - Exchange ion between ligand and anion eg.

$[Co(NH_3)_4ClBr]Cl$ and $[Co(NH_3)_4Cl_2]Br$

$[Pt(NH_3)_3Cl]NO_2$ and $[Pt(NH_3)_3NO_2]Cl$

(iii) ***Hydration Isomers***-Exchange water as ligand and hydrate

$[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2.H_2O$ and $[Cr(H_2O)_4Cl_2]Cl_2.H_2O$

$[Co(NH_3)_5H_2O]Cl_3$ and $[Co(NH_3)_5Cl]Cl_3.H_2O$

(iv) ***Linkage Isomers*** - ligands that can bond at more than one atomic site

(ambidentate) $:CN^-$ $:NC^-$

$[Cr(H_2O)_5CN]^{2+}$ and $[Cr(H_2O)_5NC]^{2+}$

$:NCS^-$ and $:SCN^-$

$[Co(NH_3)_5NCS]^{2+}$ and $[Co(NH_3)_5SCN]^{2+}$

$:NO_2^-$ and $:\underset{..}{\overset{..}{O}}-\overset{..}{N}=\underset{..}{\overset{..}{O}}$

$[Pt(NH_3)_3NO_2]^+$ and $[Pt(NH_3)_3ONO]^+$

(v) ***Coordination Isomerism*** - Occurs when cationic and anionic complexes of different metal ions are present in a salt. Interchange of ligand between the complexes give isomers eg

$[Co(NH_3)_6][Cr(CN)_6]$ is an isomer of $[Co(CN)_6][Cr(NH_3)_6]$

(vi) ***Ligand isomerism***-Occurs when more than one isomer of the ligand is possible eg 1, 2 diamino propane and 1,3-diamino propane.

(vii) ***Polymerisation Isomerism*** - The isomers have the same empirical formula but different molecular weights eg.

$[Co(NO_2)_3(NH_3)_3]$ and $[Co(NH_3)_6][Co(NO_2)_6]$.

Triamminetrinitrocobalt (III)

Hexamminec obalt (III)
Hexanitrocobalt (III)

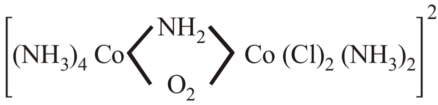
The molecular weight of the second is twice as that of the first.

(viii) ***Valence Isomerism*** - In this the same coordinating group is held by different types of valence bonds. The valence state of the central metal atom then differ in the two isomers. eg.

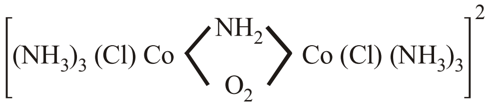
$[Co(NO)(NH_3)_5]^{2+}$ and $[Co(NH_3)_5(NO)]^{2+}$.

In the first compound the NO group is a negative group and oxidation state of Co is +3. In the second compound the NO group is neutral and oxidation state of Co is +2.

(ix) ***Coordination position isomerism*** - In this coordinating groups occupy different positions and the isomerism occurs generally in bridged complex. eg.



$\left[(NH_3)_4\,Co\overset{NH_2}{\underset{O_2}{\langle\rangle}}Co\,(Cl)_2\,(NH_3)_2\right]^{2+}$ and



$\left[(NH_3)_3\,(Cl)\,Co\overset{NH_2}{\underset{O_2}{\langle\rangle}}Co\,(Cl)\,(NH_3)_3\right]^{2+}$

(x) ***Stereo isomerism*** - It is due to different spatial arrangement of atoms and groups in a molecule. It is of two types.

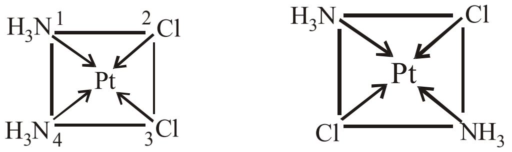
(a) ***Geometrical*** - It is due to different geometrical arrangements of ligands around central metal atom and is shown by

(I) Square planar complexes of the type

MA_2X_2 ; $MABX_2$; $MABXY$

Type $MA_2X_2^-$

$[Co(NH_3)_2Cl_2]$, $[Pt(NH_3)_2Cl_2]$



Pale yellow Cis isomer

Dark yellow trans isomer

Positions 1,2 and 1,4 are cis while 1,3 and 2,4 are trans.

Type $MABX_2$ - $[Co(NH_3)_2ClBr]$

Cis

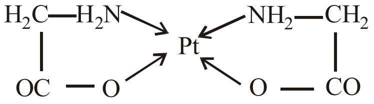
Trans

Type MABXY -

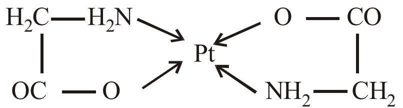
Example is $[Pt(NH_3)(NH_2OH)(NO_2)(py)]NO_2$. Its three isomers are possible.

Type $M(AA^1)_2$ - Where AA^1 is unsymmetrical bidentate eg

$[Pt(Gly)_2]$, here gly = $H_2\ddot{N}CH_2CO\bar{O}$



Cis - isomer

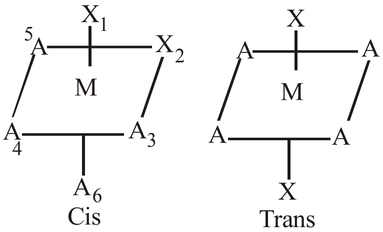


Trans - isomer

(II) **Octahedral of the type** : MA_4XY, MA_4X_2 MA_3X_3 $MA_2X_2Y_2$. $M(AA)_2X_2$ and M(ABCDEF). In the last type 15 geometrical isomers are possible.

AA= symmetrical bidentate eg

Type MA_4X_2 - $[Pt(NH_3)_4Cl_2]^{2+}$, $[Co(NH_3)_4Cl_2]^+$, $[Pt(NH_3)_2Cl_4]$

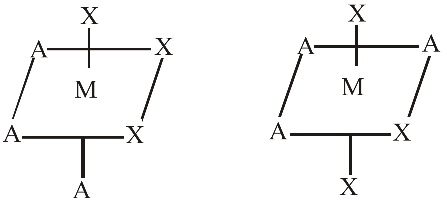


Cis

Trans

Note : The positions 1,6 and 2,4 and 3,5 are trans.

Type MA_3X_3 - $[Pt(NH_3)_3Cl_3]^+$, $[Co(NH_3)_3Cl_3]$

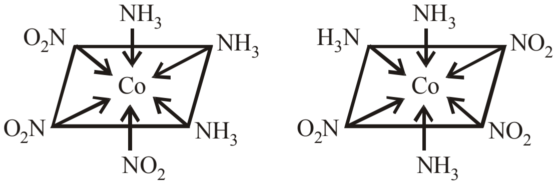


Fac (facial)

Mer (meridranal)

The geometrical isomerism is not possible in square planar MA_4, MAB_3 and tetrahedral MA_4, MA_2B_2 and MABCD and Octahedral MA_6, MA_5B.

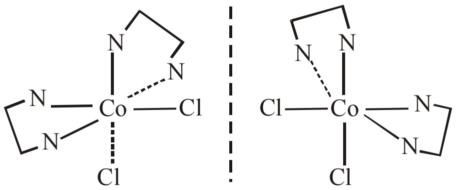
Facial (fac) meridional (mer) isomerism - The octahedral coordination compounds of the type MA_3B_3 eg. $Co(NO_2)_3(NH_3)_3$ exhibit this type of geomerical isomerism of each trio of donor atoms occupy adjacent positions at the corners of an octahedral face the isomer is known as facial (fac) isomerism. When the positions are around the meridian of the octahedron we have meridional (mer) isomer.



Fac.

Mer.

(b) **Optical isomerism -** Non superimposable mirror images are called optical isomers and may be described as "chiral'. They are also called enantiomers and they rotate plane polarised light in opposite directions.



Optical isomerism - It is given by octahedral complexes of the type

$M(AA')_3$ (Cis or trans) $M(AA)_3$; $M(AA)_2B_2$ (Cis not trans) ; $M(AA)_2BC$ (Cis form) ; $M(AA)B_2C_2$, $MA_2B_2C_2$ (Cisform), MA_2B_2CD, MA_2BCDE, MABCDEF.

All exist in three forms two optically active and one optically inactive. Examples are

$[Co(en)_3]^{3+}$, $[Co(en)_2Cl_2]^+$, $[Rh(en)_2Cl_2]^+$,

$[Co(en)_2ClBr]^+$, $[Co(en)_2(NH_3)_2Cl_2]^+$

Tetrahedal Complexes - Tetrahedral complexes of the type $(M(AA^1)_2$ show optical activity. Examples are Bis(benzoylacetonato) Be (ii) and Bis (glycinato) Ni (ii)

Tetrahedral complexes can have optical isomers if all four ligands are different eg MABCD

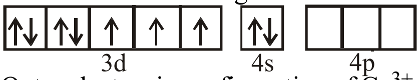
VALENCE BOND THEORY :

Features of this theory are

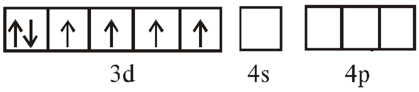
1. Uses hybrid orbitals to hold the donated electron pairs for the formation of the coordinate bonds.
2. Can explain the structure and magnetic properties eg consider the ions

$\left[Co(CN)_6\right]^{3-}$ or $\left[Co(NH_3)_6\right]^{3+}$

Outer electronic configuration of Co At . No. 27

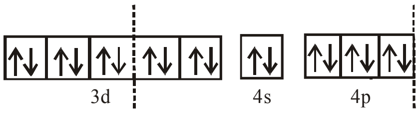


Outer electronic configuration of Co^{3+}



(CN^- and NH_3 are strong ligands and do pairing of electrons).

The coordination number is six. We need six empty atomic orbitals to accomodate electrons donated by CN or NH_3.

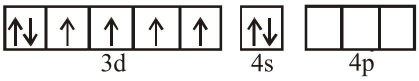


d^2sp^3 hybridisation

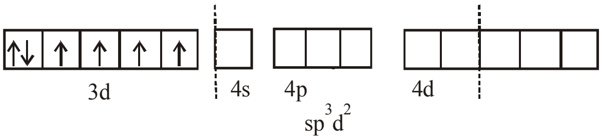
d^2sp^3 hybridisation is octahedral. As shown above there is no unpaired electron hence the complex ions are diamagnetic in nature. It is inner complex since d atomic orbitals come from inside and low spin complex

Second example - Structure of $\left[Fe(H_2O)_6\right]^{2+}$

Outer electronic configuration of Fe(At. No 26)



Outer electronic configuration of Fe^{2+}

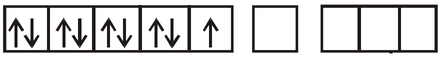


The coordination number is six. We need six empty valence atomic orbitals.

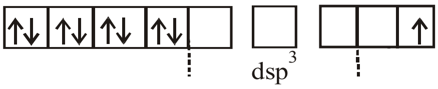
H_2O is a weak ligand, pairing of electrons is not possible hence hybridisation sp^3d^2. Hence $\left[Fe(H_2O)_6\right]^{2+}$ is octahedral, paramagnetic in nature, outer complex and high spin complex.

Third example - Structure of $\left[CuX_4\right]^{2-}$

Cu^{2+} has electronic configuration

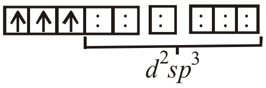
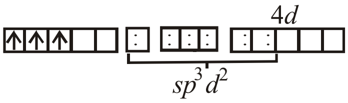
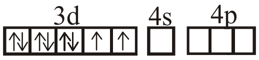
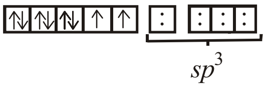
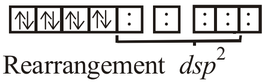


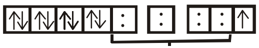
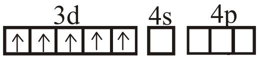
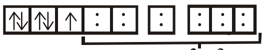
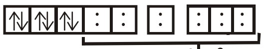
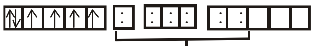
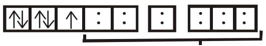
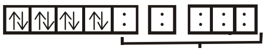
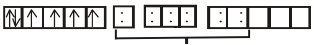
Since the coordination number is 4, we need four hybrid atomic orbitals. Hybridisation should be sp^3 but X-ray analysis reveals the presence of four ligands in the same plane hence hybridisation should be square planar. For this Cu^{2+} should have the configuration.



Hence $\left[CuX_4\right]^{2-}$ is square planar, paramagnetic and inner complex.

Geometry (shape) and magnetic nature of some of the complexes
(Application of valence bond theory)

Atom/Ion/ Complex	*Configuration*	*Oxidation state of metal*	*Type of Hybridization*	*Geometry shape*	*No. of unpaired electrons*	*Magnetic property*
$Cr^{3+}(d^3)$		+3			3	Paramagnetic
$[Cr(NH_3)_6]^{3+}$		+3	d^2sp^3(Inner)	Octahedral	3	Paramagnetic
$[Cr(H_2O)_6]^{3+}$		+3	sp^3d^2 (Outer)	Octahedral	3	Paramagnetic
$Ni^{2+}(d^8)$		+2			2	Paramagnetic
$[NiCl_4]^{2-}$		+2	sp^3	Tetrahedral	2	Paramagnetic
$[Ni(CN)_4]^{2-}$		+2	dsp^2	Square planar	0	Diamagnetic

Ni(d^8s^2)		0			2	Paramagnetic
[Ni(CO)$_4$]	 Rearrangement sp^3	0	sp^3	Tetrahedral	0	Diamagnetic
Cu^{2+}(d^9)					1	Paramagnetic
[CuCl$_4$]$^{2-}$	 dsp^2	+2	dsp^2	Square planner	1	Paramagnetic
[Cu(NH$_3$)$_4$]$^{2+}$	 dsp^2 One electron is shifted from 3d to 4p-obrital	+2	dsp^2	Square planar	1	Paramagnetic
Mn^{2+}(d^5)		+2			5	Paramagnetic
[Mn(CN)$_6$]$^{4-}$	 Rearrangement d^2sp^3	+2	d^2sp^3(Inner)	Octahedral	1	Paramagnetic
[MnCl$_4$]$^{2-}$	 sp^3	+2	sp^3	Tetrahedral	5	Paramagnetic
Fe^{2+}(d^6)		+2			4	Paramagnetic
[Fe(CN)$_6$]$^{4-}$	 Rearrangement d^2sp^3	+2	d^2sp^3 (Inner)	Octahedral	0	Diamagnetic
[Fe(H$_2$O)$_6$]$^{2+}$	 sp^3d^2	+2	sp^3d^2 (Outer)	Octahedral	4	Paramagnetic
[Fe(NH$_3$)$_6$]$^{2+}$	 sp^3d^2	+2	sp^3d^2 (Outer)	Octahedral	4	Paramagnetic
Fe^{3+}(d^5)		+3			5	Paramagnetic
[Fe(CN)$_6$]$^{3-}$	 d^2sp^3	+3	d^2sp^3 (Inner)	Octahedral	1	Paramagnetic
Fe		0		Trigonal	4	Paramagnetic
[Fe(CO)$_5$]	 dsp^3	0	dsp^3 (Inner)	Bipyramidal	0	Diamagnetic
Co^{3+}(d^6)		+3			4	Paramagnetic
[CoF$_6$]$^{3-}$	 sp^3d^2	+3	sp^3d^2 (Outer)	Octahedral	4	Paramagnetic
[Co(NH$_3$)$_6$]$^{3+}$	 Rearrangement d^2sp^3	+3	d^2sp^3 (Inner)	Octahedral	0	Diamagnetic
Co^{2+}(d^7)		+2			3	Paramagnetic
[Co(H$_2$O)$_6$]$^{2+}$	 sp^3d^2	+2	sp^3d^2 (Outer)	Octahedral	3	Paramagnetic

Limitations of valence bond theory are following

1. It does not explain the relative stability of complexes.
2. It can not explain colour and spectra
3. The relative stability of structural isomers.

CRYSTAL FIELD THEORY :

Crystal field theory (CFT) was proposed by Bethe and Ven Vleck. It gives satisfactory explanation for the proporties and bonding in co-ordination compounds. The main points of this theory are following :-

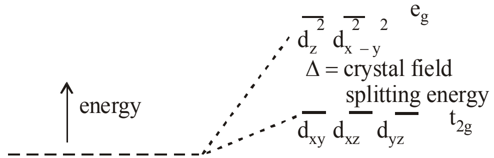
(i) The attraction between the central metal and ligands in the complexes is considered to be purely electrostatic
Thus bonding in the complex may be ion-ion attraction or ion dipole attraction.

(ii) Ligands are treated as point of negative charges

(iii) There is no interaction between metal orbitals and ligand orbitals

(iv) The d-orbitals present in metal have the same energy in the free state. This is called degenerate state of d-orbital. But, when a complex is formed the ligands destroy the degeneracy of these orbitals. This effect is Known as **Crystal field splitting** of d- orbitals.

It accounts for both the colour and the magnetic properties of complexes. It is based on d- orbital energy level splitting



d orbitals of the free metal ion splitting of d-orbitals of the metal ion in an octahedral field of ligands

The size of Δ depends on -

(i) The nature of the ligand "Spectro chemical series" Δ decreases as shown below

$I^- < Br^- < Cl^- < OH^- < F^- < C_2O_4^{2-} < H_2O < CNS^- <$
weak ligands

$< NH_3 < en < NO_2^- < CN^- < CO$
strong ligands

(ii) The oxidation state of the metal Δ is greater for M^{3+} than for M^{2+}

(iii) The row of the metal in the periodic table. For a given ligand and oxidation state of the metal, Δ increases going down in a group eg.
Δ is greater in $[Ru(NH_3)_6]^{3+}$ than in $[Fe(NH_3)_6]^{3+}$

Effect of strong field ligands and weak field ligands– Strong field ligands forces the electrons of central metal for pairing and the complex formed is known as low spin complex. While weak field ligands do not forces the electron of central atom for pairing and the compelx formed is known as high spin complex. For example– In $[Ni(CN)_4]$, CN is a strong field ligand which forces electrons of Ni^{2+} for pairing

Ni^{2+}; [Ar] $3d^8$	↑↓	↑↓	↑↓	↑	↑

$[Ni(CN)_4]^{2-}$

	3d					4s	4p		
∴ [Ar]	↑↓	↑↓	↑↓	↑↓	:	:	:	:	

electrons provided by $4CN^-$

Hybridisation: dsp^2 (square planar)

In $[NiCl_4]^{2-}$, Cl^- is a weak field ligand which do not forces electrons of Ni^{2+} for pairing

$[Ni\,Cl_4]^{2-}$ ∴ [Ar]

3d					4s	4p		
↑↓	↑↓	↑↓	↑	↑	:	:	:	:

Hybridisation sp^3 ∴ tetrahedral

COLOURS OF METAL COMPLEXES :

It is due to electronic transitions between t_{2g} and e_g energy levels. The energy of an electron is increased by absorbing light energy and it moves to a higher energy level.

Energy of a photon = Energy difference between the ground state and an excited state

$$E = h\nu = h\frac{c}{\lambda}$$

h = Planck's constant ($6.63x10^{-34}$ J.sec.) υ = frequency of light. E = energy of photon (measured with UV. or visible spectroscopy)

MAGNETIC PROPERTIES OF METAL COMPLEXES :

- Paramagnetic - unpaired electrons
- Diamagnetic - no unpaired electrons
- Determined from crystal field splitting diagrams

STABILITY OF COORDINATION COMPOUNDS IN SOLUTION :

Consider the following equilibrium between undissociated complex ion and dissociated ion.

$$[MLn]^{b+} \rightleftharpoons M^{a+} + nL^{x-}$$

The equilribrium constant $K_c = \dfrac{[M^{a+}][L^{x-}]^n}{[(MLn)^{b+}]}$

The smaller the value of K_c, the greater is the stability of complex ion and vice versa. The reciprocal of equilibrium constant is called stability constant.

$$K_s = \frac{1}{K_c} = \frac{[MLn]^{b+}}{[M^{a+}][L^{x-}]^n}$$

The higher the value of K_s, the more is the stability of complex ion. The value of K_s depends on.

1. **Nature of central metal atom -** The more the polarizing power of the central metal ion the more is the stability of complex ion.

   The polarising power $\phi = \dfrac{\text{charge}}{\text{radius}}$

   Thus complex of Fe^{3+} is more stable then Fe^{2+}

2. **Nature of ligand -** Since ligand is a Lewis base the more the basic character of ligand the more is the stability of complex ion. Thus complex ion of $F^-$is more stable than that of $\bar{Cl}$ or $\bar{Br}$

   Chelating ligands give much larger values of stability constant.

$$[Ni(H_2O)_6]^{2+} \xrightarrow{6NH_3} [Ni(NH_3)_6]^{2+}, K_f = 4x10^8$$

$$[Ni(H_2O)_6]^{2+} \xrightarrow{3en} [Ni(en)_3]^{2+}, K_f = 2x10^{18}$$

Perfect or penetrating complexes : They are fairly stable and dissociate negligibly or not at all e.g.

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

Imperfect or normal complexes : The complex ion is reversibly dissociated

$$K_2[Cd(CN)_4] \rightleftharpoons 2K^+ + [Cd(CN)_4]^{2-} \rightleftharpoons Cd^{2+} + 4CN^-$$

IMPORTANCE OF COORDINATION COMPOUNDS :

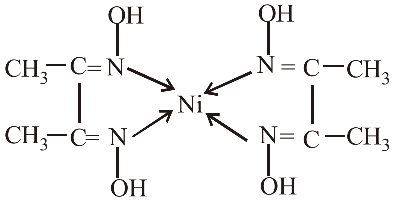
1. **Biological processes**

   Haemoglobin - Oxygen carrier is a complex of Iron (II)

   Chlrorophyll - Green colouring matter of plants is a complex of Mg

   Vitamin B_{12} - It is a complex of cobalt

2. **Analytical chemistry -** Many metal ions are quantitatively estimated by complex formation eg Cu^{++}, Ni^{2+}, Fe^{3+}, Al^{3+}



Red precipitate of nickel with dimethyl glyoxime

- Separation of Ag^+ and Hg_2^{2+}, Ag^+ form soluble complex

  $$\underset{\text{Soluble complex}}{AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl + 2H_2O}$$

$$Hg_2Cl_2 + NH_4OH \rightarrow \underbrace{Hg(NH_2)Cl}_{\text{Black insoluble}} + Hg + HCl + H_2O$$

3. **Metallurgical processes**

   (a) Bauxite ore of aluminium is purified by soluble complex formation

   $$Al_2O_3 + 3H_2O + 2OH^- \rightarrow 2\ Al(OH)_4$$

   Impurites of Fe_2O_3 are left behind in solution.

   (b) Extraction of silver and gold by cyanide process involves complex formation

   $$Ag^+(aq) + 2NaCN(aq) \rightarrow Na[Ag(CN)_2](aq) + Na^+$$

   $$Au^+(aq) + 2NaCN(aq) \rightarrow Na[Au(CN)_2](aq) + Na^+$$

   (c) Nickel is purified by Mond's process forming volatile nickel carbonyl

   $$Ni + 4CO \rightarrow Ni(CO)_4 \xrightarrow{\Delta} Ni + 4CO$$

4. **Photography -** Excess of AgBr is removed by complex formation

$$AgBr(s) + 3\ Na_2S_2O_3\ (aq) \rightarrow Na_3\ [Ag(S_2O_3)_2]\ (aq) + NaBr\ (aq)$$

5. **Miscellaneous uses**
   - K $[Ag(CN)_2]$ complex of silver is used in silver plating
   - EDTA (ethylene diammine tetra acetate) is used for the estimation of Mg^{2+} and Ca^{2+} ions and for removal of hardness of water
   - $[Pt(NH_3)_2Cl_2]$ known as cisplatin is used in the treatment of cancer

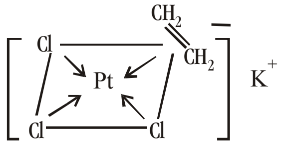
ORGANOMETALLIC COMPOUNDS :

The organic compounds having metal atom directly attached to the carbon are known as organometallic compounds. They can be

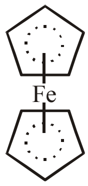
1. **Sigma bonded -**
   - R - Mg - X Alkyl magnesium halide commonly known as Grignard's reagent
2. **π-bonded**

   $(CH_3)_4$ Sn (Tetramethyl tin), $(C_2H_5)_2$ Zn (Diethyl Zinc), n–C_4H_9Li (n–butyl lithium)

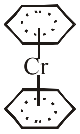
   K $[PtCl_3–\eta^2–(C_2H_4)]$ (Zeise's salt)



Fe$[\eta^5– C_5H_5]_2$ Ferrocene



Cr$[\eta^6– C_6H_6]_2$ Dibenzene chromium



SYNTHESIS OF ORGANOMETALLIC COMPOUNDS:

1. **Synthesis of Grignard's reagent -** By reaction between an alkyl halide and Mg in presence of ether

   $$R - X + Mg \xrightarrow{\text{ether}} R - Mg - X$$

   Other metals like Li, Na, Zn, Cd can also be used.

2. **Synthesis of other organometallic** compounds using Grignand's reagent

   $$PbCl_4 + 4C_2H_5Mg - Br \xrightarrow{\text{ether}} (C_2H_5)_4Pb + 4MgBrCl$$

   $$PCl_3 + 3C_6H_5MgCl \xrightarrow{\text{ether}} P(C_6H_5)_3 + 3MgCl_2$$

3. **Preparation of π complexes**

   Zeise's salt :-

   $$H_2C = CH_2 + K_2PtCl_4 \rightarrow [PtCl_3(C_2H_4)]^- K^+ + KCl$$

   Dibenzene chromium :-

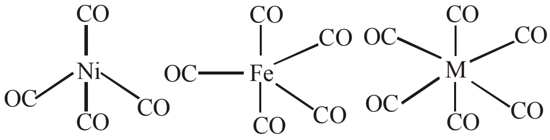
   $$2C_6H_6 + Cr(vapour) \rightarrow [(C_6H_6)_2Cr]$$

   Ferrocene :-

   $$2C_5H_5MgBr + FeCl_2 \rightarrow [(C_5H_5)_2Fe] + 2MgBrCl$$

Metal carbonyls :

The compounds of carbon monoxide with certain transition metals are known as metal carbonyls

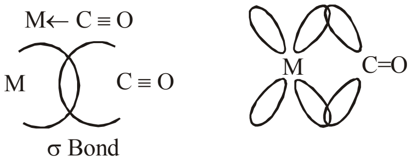


M= Cr, Mo, W

Polynuclear metal carbonyls are also known e.g. $Fe_3(CO)_{12}$ $Mn_2(CO)_{10}$

The metal carbon bond in carbonyls may be represented as

M← C≡ O. Due to some back bonding by sidewise overlapping between d orbitals of metal and empty π-orbitals of carbons, the M–C bond length is somewhat shorter and C–O bond is longer than triple bond.



Preparation of metal carbonyls - By passing CO over heated metal eg

$$Ni + 4CO \xrightarrow{320-340\,K} Ni(CO)_4$$

$$Fe + 5CO \longrightarrow Fe(CO)_5$$

Uses of organometallic compounds.

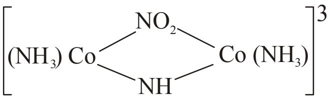
1. Grignard's reagent is employed for the synthesis of number of organic compounds eg alcohols, aldehydes, ketones, esters etc.
2. Nickel is purified by Monds, process forming $Ni(CO)_4$.
3. **Zeigler Natta** Catalyst which is mixture of triethyl aluminium and titanium Chloride (Al $(C_2H_5)_3$ + $TiCl_3$) is used for polymerisation of ethene.
4. Tetraethyl lead is used as antiknock compound $Pb(C_2H_5)_4$.
5. **Wilkinson's catalyst** $(Ph_3P)_3$ RhCl. for selective hydrogenation .
6. C_2H_5HgCl (ethyl mercury chloride) as fungicide.

Exercise-1 | NCERT Based Questions

Very Short/Short Answer Questions

1. What is the oxidation state of Co in complex $[Co(NH_3)_2(NO_2)Cl][Au(CN)_2]$?

2. Write IUPAC name of complex,



.

3. When copper sulphate solution is mixed with liquid ammonia (in molar ratio of 1 : 4), the resultant solution does not give the test of Cu^{2+} ion. Why?

4. How many moles of Cl^- ions are formed by one mole of each of the following in aqueous solution :

(*a*) $K_2[PtCl_6]$

(*b*) $[Pt(NH_3)_3Cl_3]Cl$

(*c*) $[Pt(NH_3)_4Cl_2]Cl_2$

5. How is tetrabutyl lead is prepared?

6. Among $Ag(NH_3)_2Cl$, $[Ni(CN)_4]^{2-}$ and $[CuCl_4]^{2-}$, which

(*a*) has square planar geometry?

(*b*) remains colourless in aqueous solution and why?

[Ag (Z = 47), Ni (Z = 28), Cu (Z = 29)].

7. Assign the formula to complex formed by Fe^{2+} with following ligands:

(*a*) three cyanide ion and three ammonia molecules.

(*b*) one hydroxy ion and two ammonia molecules and three chloride ions.

8. Answer the following questions referring to $[Al(H_2O)_6]^{3+}$:

(*a*) Coordination number of Al

(*b*) Oxidation state of Al

(*c*) Hybridisation involved in complex formation

(*d*) Shape of complex ion

(*e*) Paramagnetic or diamagnetic

9. Give (*a*) linkage isomer of $[Cr(CN)(H_2O)_5]^{2+}$

(*b*) ionisation isomer of $[PtCl_2(NH_3)_4]Br_2$

(*c*) coordination isomer of $[Pt(NH_3)_4][CuCl_4]$

10. Mention the application of organometallic compounds in the following areas:

(*a*) Homogeneous catalysis

(*b*) Heterogeneous catalysis

(*c*) Organic synthesis.

11. Arrange the following complexes in order of increasing electrical conductivity:

$[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_4Cl_2]Cl$.

12. Write the correct formula for the following compounds :

(*a*) $CrCl_3{\cdot}6H_2O$ (violet, with three chloride ions/unit formula)

(*b*) $CoCl_3{\cdot}6H_2O$ (light green colour with two chloride ions/unit formula)

(*c*) $CrCl_3{\cdot}6H_2O$ (dark green colour with one chloride ion (unit formula)

13. Write the name, the state of hybridization, the shape and the magnetic behaviour of the following complexes:

$$[CoCl_4]^{2-},\ \left[Ni(CN)_4\right]^{2-},\ \left[Cr(H_2O)_2(C_2O_4)_2\right]^-$$

(At. No.: Co = 27, Ni = 28, Cr = 24)

14. Write the name, stereochemistry and magnetic behaviour of the following:

(At nos. Mn = 25, Co = 27, Ni = 28)

(i) $K_4\left[Mn(CN)_6\right]$

(ii) $\left[Co(NH_3)_5Cl\right]Cl_2$

(iii) $K_2\left[Ni(CN)_4\right]$

15. Write the name, the structure and the magnetic behaviour of each one of the following complexes:

(i) $\left[Pt(NH_3)Cl(NO_2)\right]$

(ii) $\left[Co(NH_3)_4Cl_2\right]Cl$

(iii) $Ni(CO)_4$

[Al nos, Co = 27, Ni = 28, Pt = 78)

16. Write the IUPAC names of the following coordination compounds:

(i) $\left[Cr(NH_3)_3Cl_3\right]$

(ii) $K_3\left[Fe(CN)_6\right]$

(iii) $\left[CoBr_2(en)_2\right]^+$, (en = ethylenediamine)

Multiple Choice Questions

17. An example of double salt is

(a) Bleaching powder (b) $K_4[Fe(CN)_6]$

(c) Hypo (d) Potash alum

18. The number of unpaired electrons in the complex ion $[CoF_6]^{3-}$ is (Atomic no.: Co = 27)

(a) zero (b) 2

(c) 3 (d) 4

19. Hybridization of Ag in the linear complex $[Ag(NH_3)_2]^+$ is :

(a) dsp^2 (b) sp

(c) sp^2 (d) sp^3

20. Ammonia will not form complex ions with

(a) Ag^+ (b) Cd^{2+}

(c) Cu^{2+} (d) Pb^{2+}

21. Which statement is incorrect?

(a) $Ni(CO)_4$ – Tetrahedral, paramagnetic

(b) $[Ni(CN)_4]^{2-}$ – Square planar, diamagnetic

(c) $Ni(CO)_4$ – Tetrahedral, diamagnetic

(d) $[NiCl_4]^{2-}$ – Tetrahedral, paramagnetic

22. Which one of the following octahedral complexes will not show geometric isomerism?
(A and B are monodentate ligands)

(a) $[MA_5B]$ (b) $[MA_2B_4]$

(c) $[MA_3B_3]$ (d) $[MA_4B_2]$

23. Considering H_2O as a weak field ligand, the number of unpaired electrons in $[Mn(H_2O)_6]^{2+}$ will be (At. no. of Mn = 25)

(a) three (b) five

(c) two (d) four

24. The complex, $[Pt(Py)(NH_3)BrCl]$ will have how many geometrical isomers ?

(a) 3 (b) 4

(c) 0 (d) 2

25. On mixing conc. NH_4OH to a Cu^{2+} salt, the following blue complex is formed :

(a) $[Cu(NH_4)_4]^{2+}$ (b) $[Cu(NH_3)_2]^{2+}$

(c) $[Cu(NH_3)_4]^{2+}$ (d) $[Cu(NH_4)_2]^{2+}$

26. A square planar complex is formed by hybridisation of which atomic orbitals?

(a) s, p_x, p_y, d_{yz} (b) $s, p_x, p_y, d_{x^2-y^2}$

(c) s, p_x, p_y, d_{z^2} (d) s, p_y, p_z, d_{xy}

Exercise-2 | CONCEPTUAL MCQs

1. Which of the following is odd one out ?

(a) potassium ferricyanide

(b) ferrous ammoniumsulphate

(c) potassium ferrocyanide

(d) tetraamminecopper (II) sulphate

2. $CuSO_4$ dissolves in NH_3 due to formation of

(a) $Cu(OH)_2$ (b) $[Cu(NH_3)_4]SO_4$

(c) $[Cu(NH_3)_4(OH)_2]$ (d) CuO

3. $K_4[Fe(CN)_6]$ is a

(a) double salt (b) complex compound

(c) neutral molecule (d) None of these

4. AgCl is soluble in NH_4OH solution. The solubility is due to formation of

(a) AgOH (b) Ag_2O

(c) $[Ag(NH_3)_2]^+$ (d) NH_4Cl

5. Some salts although containing two different metallic elements give test for only one of them in solution. Such salts are

(a) complex (b) double salts

(c) normal salts (d) None of these

6. In the compound lithium tetrahydridoalumninate, the ligand is

(a) Al^+ (b) H

(c) H^- (d) None of these

7. In which of the following coordinate compounds the central metal atom obeys the EAN rule.

(a) $K_3[Fe(CN)_6]$ (b) $K_4[Fe(CN)_6]$

(c) $[Cu(NH_3)_4]SO_4$ (d) All of these

8. The EAN of iron in $[Fe(CN)_6]^{3-}$ is

(a) 34 (b) 36

(c) 37 (d) 35

9. Coordination number of Ni in $[Ni(C_2O_4)_3]^{4-}$ is

(a) 3 (b) 6

(c) 4 (d) 5

10. The coordination number of Fe(II) in oxyhaemoglobin is

(a) 6 (b) 4

(c) 8 (d) 10

11. Correct formula of the complex formed in the brown ring test for nitrates is

(a) $FeSO_4.NO$ (b) $[Fe(H_2O)_5NO]^{2+}$

(c) $[Fe(H_2O)_5NO]^+$ (d) $[Fe(H_2O)_5NO]^{3+}$

12. According to Lewis, the ligands are

(a) acidic in nature

(b) basic in nature

(c) some are acidic and others are basic

(d) neither acidic nor basic

13. According to the postulates of Werner for coordination compounds

(a) primary valency is ionizable

(b) secondary valency is ionizable

(c) primary and secondary valencies are non-ionizable

(d) only primary valency is non-ionizable.

14. In $[Co(NH_3)_6]Cl_3$, the number of covalent bonds is

(a) 3 (b) 6

(c) 9 (d) 18

15. When $AgNO_3$ is added to a solution of $Co(NH_3)_5Cl_3$, the precipitate of AgCl shows two ionisable chloride ions. This means :

(a) Two chlorine atoms satisfy primary valency and one secondary valency

(b) One chlorine atom satisfies primary as well as secondary valency

(c) Three chlorine atoms satisfy primary valency

(d) Three chlorine atoms satisfy secondary valency

16. The formula dichlorobis (urea) copper (II) is

(a) $[Cu\{O=C(NH_2)_2\}_2]Cl_2$ (b) $[CuCl_2\{O=C(NH_2)_2\}_2]$

(c) $[Cu\{O=C(NH_2)_2\}Cl]Cl$ (d) $[CuCl_2\{O=C(NH_2)_2\}H_2]$

17. Chemical formula for iron (III) hexacyanoferrate (II) is

(a) $Fe[Fe(CN)_6]$ (b) $Fe_3[Fe(CN)_6]$

(c) $Fe_3[Fe(CN)_6]_4$ (d) $Fe_4[Fe(CN)_6]_3$

18. IUPAC name of $Na_3[Co(NO_2)_6]$ is

(a) sodium cobaltinitrite

(b) sodium hexanitritocobaltate (III)

(c) sodium hexanitrocobalt (III)

(d) sodium hexanitrocobaltate (III)

19. Ligand in a complex salt are

(a) anions linked by coordinate bonds to a central metal atom or ion

(b) cations linked by coordinate bonds to a central metal or ion

(c) molecules linked by coordinate bonds to a central metal or ion

(d) ions or molecules linked by coordinate bonds to a central atom or ion

20. The IUPAC name of $K_3[Ir(C_2O_4)_3]$ is

(a) potassium trioxalatoiridium (III)

(b) potassium trioxalatoiridate (III)

(c) potassium tris (oxalato) iridium (III)

(d) potassium tris (oxalato) iridate (III)

21. In Zeigler- Natta polymerisation of ethylene, the active species is

(a) $AlCl_3$ (b) Et_3Al

(c) CH_2CH_2 (d) Ti^{III}

22. The hypothetical complex chloro-diaquatriamminecobalt (III) chloride can be represented as

(a) $[CoCl(NH_3)_3(H_2O)_2]Cl_2$

(b) $[Co(NH_3)_3(H_2O)Cl_3]$

(c) $[Co(NH_3)_3(H_2O)_2Cl]$

(d) $[Co(NH_3)_3(H_2O)_3]Cl_3$

23. The oxidation state of Fe in $K_4[Fe(CN)_6]$ is

(a) +2 (b) +6

(c) +3 (d) +4

24. Which of the following complex will show geometrical as well as optical isomerism (en=ethylenediammine)

(a) $Pt(NH_3)_2Cl_2$ (b) $[Pt(NH_3)Cl_4]$

(c) $[Pt(en)_3]^{4+}$ (d) $[Pt(en)_2Cl_2]$

25. The number of geometrical isomers from $[Co(NH_3)_3(NO_2)_3]$ is

(a) 2 (b) 3

(c) 4 (d) 0

26. The total number of possible isomers of the complex compound $[Cu^{II}(NH_3)_4][Pt^{II}Cl_4]$ is

(a) 3 (b) 6

(c) 5 (d) 4

27. A coordination complex compound of cobalt has molecular formula containing five ammonia molecules, one nitro group and two chlorine atoms for one cobalt atom. One mole of this compound produces three mole ions in an aqueous solution. On reacting this solution, with excess of $AgNO_3$ solution two moles of AgCl get precipitated. The ionic formula of this complex would be

(a) $[Co(NH_3)_4NO_2Cl]\,[(NH_3)Cl]$

(b) $[Co(NH_3)_5Cl]\,[Cl(NO)_2]$

(c) $[Co(NH_3)_5(NO_2)]Cl_2$

(d) $[Co(NH_3)_5][(NO_2)_2Cl_2]$

28. The number of isomers exhibited by $[Cr(NH_3)_3Cl_3]$ is

(a) 2 (b) 3

(c) 4 (d) 5

29. For the square planar complex [M (a) (b) (c) (d)] (where M = central metal and a, b, c and d are monodentate ligands), the number of possible geometrical isomers are

(a) 1 (b) 2

(c) 3 (d) 4

30. Which of the following will exhibit optical isomerism ?

(a) $[Cr(en)(H_2O)_4]^{3+}$

(b) $[Cr(en)_3]^{3+}$

(c) *trans*-$[Cr(en)(Cl_2)(NH_3)_2]^+$

(d) $[Cr(NH_3)_6]^{3+}$

31. Which of the following will give maximum number of isomers?

(a) $[Co(NH_3)_4Cl_2]$ (b) $[Ni(en)(NH_3)_4]^{2+}$

(c) $[Ni(C_2O_4)(en)_2]$ (d) $[Cr(SCN)_2(NH_3)_4]^{2+}$

32. The compounds $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$ constitutes a pair of

(a) coordination isomers (b) linkage isomers
(c) ionization isomers (d) optical isomers

33. Which of the following compounds exhibits linkage isomerism ?

(a) $[Co(en)_2]Cl_3$ (b) $[Co(NH_3)_6][Cr(en)_3]$
(c) $[Co(en)_2NO_2Cl]Br$ (d) $[Co(NH_3)_5Cl]Br_2$

34. Both geometrical and optical isomerisms are shown by

(a) $[Co(en)_2Cl_2]^+$ (b) $[Co(NH_3)_5Cl]^{2+}$
(c) $[Co(NH_3)_4Cl_2]^+$ (d) $[Cr(ox)_3]^{3-}$

35. Which one of the following will not show geometrical isomerism ?

(a) $[Cr(NH_3)_4Cl_2]Cl$ (b) $[Co(en)_2Cl_2]Cl$
(c) $[Co(NH_3)_5NO_2]Cl_2$ (d) $[Pt(NH_3)_2Cl_2]$

36. A similarity between optical and geometrical isomerism is that

(a) each gives equal number of isomers for a given compound
(b) if in a compound one is present then so is the other
(c) both are included in stereoisomerism
(d) they have no similarity

37. The type of isomerism present in nitropentaamminechromium (III) chloride is

(a) optical (b) linkage
(c) ionization (d) polymerization

38. Which of the following has square planar structure?

(a) $[Ni(CO)_4]$ (b) $[NiCl_4]^{2-}$
(c) $[Ni(CN)_4]^{2-}$ (d) $\left[Ni(H_2O)_6\right]^{2+}$

39. The unpaired electrons in $Ni(CO)_4$ are

(a) zero (b) one
(c) three (d) four

40. Which of the following species represent the example of dsp^2 – hybridisation ?

(a) $[Fe(CN)_6]^{3-}$ (b) $[Ni(CN)_4]^{2-}$
(c) $[Zn(NH_3)_4]^{2+}$ (d) $[FeF_6]^{3-}$

41. The correct structure of $Fe(CO)_5$ is (Z=26 for Fe)

(a) octahedral (b) tetrahedral
(c) square pyramidal (d) trigonal pyramidal

42. The shape of $[Cu(NH_3)_4]^{2+}$ is

(a) tetrahedral (b) square planar
(c) pyramidal (d) octahedral

43. Which one of the following is an example of octahedral complex ?

(a) $[FeF_6]^{3-}$ (b) $[Zn(NH_3)_4]^{2+}$
(c) $[Ni(CN)_4]^{2-}$ (d) $[Cu(NH_3)_4]^{2+}$

44. Which of the following is paramagnetic ?

(a) $[Fe(CN)_6]^{4-}$ (b) $[Ni(CO)_4]$
(c) $[Ni(CN)_4]^{2-}$ (d) $[CoF_6]^{3-}$

45. The valency of Cr in the complex $[Cr(H_2O)_4Cl_2]^+$ is

(a) 1 (b) 3
(c) 5 (d) 6

46. Which of the following is expected to be a paramagnetic complex ?

(a) $[Ni(H_2O)_6]^{2+}$ (b) $[Ni(CO)_4]$
(c) $[Zn(NH_3)_4]^{2+}$ (d) $[Co(NH_3)_6]^{3+}$

47. Which statement is incorrect ?

(a) $[Ni(CO)_4]$ – Tetrahedral, paramagnetic
(b) $[Ni(CN)_4]^{2-}$ – Square planar, diamagnetic
(c) $[Ni(CO)_4]$ – Tetrahedral, diamagnetic
(d) $[NiCl_4]^{2-}$ – Tetrahedral, paramagnetic

48. The geometry of the compound $[Pt(NH_3)_2Cl_2]$ is

(a) square planar (b) pyramidal
(c) tetrahedral (d) octahedral

49. The shape of cuprammonium ion is

(a) octahedral (b) tetrahedral
(c) trigonal (d) square planar

50. Which of the following species represent the example of dsp^2 - hybridisation ?

(a) $[Fe(CN)_6]^{3-}$ (b) $[Ni(CN)_4]^{2-}$
(c) $[Ag(CN)_2]^-$ (d) $[Co(CN)_6]^{3-}$

51. Consider the following complex $[Co(NH_3)_5CO_3]ClO_4$. The coordination number, oxidation number, number of *d*-electrons and number of unpaired *d*-electrons on the metal are respectively

(a) 6, 3, 6, 0 (b) 7, 2, 7, 1
(c) 7, 1, 6, 4 (d) 6, 2, 7, 3

52. Atomic numbers of Cr and Fe are respectively 24 and 26. Which of the following is paramagnetic with the spin of the electron ?

(a) $[Cr(CO)_6]$ (b) $[Fe(CO)_5]$
(c) $[Fe(CN)_6]^{4-}$ (d) $[Cr(NH_3)_6]^{3+}$

53. Which of the following will exhibit maximum ionic conductivity ?

(a) $K_4[Fe(CN)_6]$ (b) $[Co(NH_3)_6]Cl_3$
(c) $[Cu(NH_3)_4Cl_2]$ (d) $[Ni(CO)_4]$

54. Which of the following is organo-metallic compound ?

(a) $Ti(C_2H_4)_4$ (b) $Ti(OC_2H_5)_4$
(c) $Ti(OCOCH_3)_4$ (d) $Ti(OC_6H_5)_4$

55. Which is not π - bonded complex ?

(a) Zeise's salt (b) Ferrocene
(c) Dibenzene chromiun (d) Tetraethyl lead

Exercise-3 | PAST COMPETITION MCQs

1. Which of the following will give a pair of enantiomorphs? **[CBSE-PMT 2007]**
(a) $[Cr(NH_3)_6][Co(CN)_6]$
(b) $[Co(en)_2Cl_2]Cl$
(c) $[Pt(NH_3)_4][PtCl_6]$
(d) $[Co(NH_3)_4Cl_2]NO_2$. (en $=NH_2CH_2CH_2NH_2$)

2. The d electron configurations of Cr^{2+}, Mn^{2+}, Fe^{2+} and Ni^{2+} are $3d^4$, $3d^5$, $3d^6$ and $3d^8$ respectively. Which one of the following aqua complexes will exhibit the minimum paramagnetic behaviour? **[CBSE-PMT 2007]**
(a) $[Fe(H_2O)_6]^{2+}$ (b) $[Ni(H_2O)_6]^{2+}$
(c) $[Cr(H_2O)_6]^{2+}$ (d) $[Mn(H_2O)_6]^{2+}$
(At. No. Cr = 24, Mn = 25, Fe = 26, Ni = 28)

3. Which of the following complexes exhibits the highest paramagnetic behaviour ? **[CBSE-PMT 2008]**
(a) $[V(gly)_2(OH)_2(NH_3)_2]^+$ (b) $[Fe(en)(bpy)(NH_3)_2]^{2+}$
(c) $[Co(ox)_2(OH)_2]^{2-}$ (d) $[Ti(NH_3)_6]^{3+}$
where gly = glycine, en = ethylenediamine and bpy = bipyridyl moities)
(At.nos Ti = 22, V = 23, Fe = 26, Co = 27)

4. In which of the following coordination entities the magnitude Δ_0 (CFSE in octahedral field) will be maximum? **[CBSE-PMT 2008]**
(a) $[Co(H_2O)_6]^{3+}$ (b) $[Co(NH_3)_6]^{3+}$
(c) $[Co(CN)_6]^{3-}$ (d) $[Co(C_2O_4)_3]^{3-}$
(At. No. Co = 27)

5. Which of the following **does not** show optical isomerism? **[CBSE-PMT 2009]**
(a) $[Co(NH_3)_3Cl_3]^0$ (b) $[Co(en)Cl_2(NH_3)_2]^+$
(c) $[Co(en)_3]^{3+}$ (d) $[Co(en)_2Cl_2]^+$
(en = ethylenediamine)

6. Which of the following complex ions is expected to absorb visible light? **[CBSE-PMT 2009]**
(a) $[Ti(en)_2(NH_3)_2]^{4+}$ (b) $[Cr(NH_3)_6]^{3+}$
(c) $[Zn(NH_3)_6]^{2+}$ (d) $[Sc(H_2O)_3(NH_3)_3]^{3+}$
(At. no. Zn = 30, Sc = 21, Ti = 22, Cr = 24)

7. Which of the following complex ion is not expected to absorb visible light ? **[CBSE-PMT 2010]**
(a) $[Ni(CN)_4]^{2-}$ (b) $[Cr(NH_3)_6]^{3+}$
(c) $[Fe(H_2O)_6]^{2+}$ (d) $[Ni(H_2O)_6]^{2+}$

8. Crystal field stabilization energy for high spin d^4 octahedral complex is: **[CBSE-PMT 2010]**
(a) $-1.8\ \Delta_0$ (b) $-1.6\ \Delta_0 + P$
(c) $-1.2\ \Delta_0$ (d) $-0.6\ \Delta_0$

9. The existence of two different coloured complexes with the composition of $[Co(NH_3)_4Cl_2]^+$ is due to : **[CBSE-PMT 2010]**
(a) linkage isomerism (b) geometrical isomerism
(c) coordination isomerism (d) ionization isomerism

10. Which one of the following complexes is not expected to exhibit isomerism? **[CBSE-PMT 2010]**
(a) $[Ni(en)_3]^{2+}$ (b) $[Ni(NH_3)_4(H_2O)_2]^{2+}$
(c) $[Pt(NH_3)_2Cl_2]$ (d) $[Ni(NH_3)_2Cl_2]$

11. Of the following complex ions, which is diamagnetic in nature? **[CBSE-PMT 2011]**
(a) $[NiCl_4]^{2-}$ (b) $[Ni(CN)_4]^{2-}$
(c) $[CuCl_4]^{2-}$ (d) $[CoF_6]^{3-}$

12. The complexes $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ are the examples of which type of isomerism? **[CBSE-PMT 2011]**
(a) Linkage isomerism (b) Ionization isomerism
(c) Coordination isomerism (d) Geometrical isomerism

13. The complex, $[Pt(py)(NH_3)BrCl]$ will have how many geometrical isomers ? **[CBSE-PMT 2011]**
(a) 3 (b) 4 (c) 0 (d) 2

14. The *d*-electron configurations of Cr^{2+}, Mn^{2+}, Fe^{2+} and Co^{2+} are d^4, d^5, d^6 and d^7, respectively. Which one of the following will exhibit minimum paramagnetic behaviour? **[CBSE-PMT 2011]**
(a) $[Mn(H_2O)_6]^{2+}$ (b) $[Fe(H_2O)_6]^{2+}$
(c) $[Co(H_2O)_6]^{2+}$ (d) $[Cr(H_2O)_6]^{2+}$
(At, nos. Cr = 24, Mn = 25, Fe = 26, Co = 27)

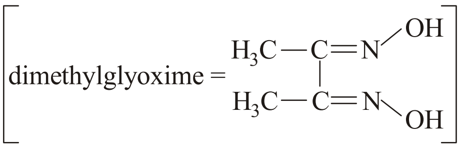
15. Which of the following carbonyls will have the strongest C – O bond ? **[CBSE-PMT 2011 M]**
(a) $[Mn(CO)_6]^+$ (b) $[Cr(CO)_6]$
(c) $[V(CO)_6]^-$ (d) $[Fe(CO)_5]$

16. Which of the following complex compounds will exhibit highest paramagnetic behaviour? **[CBSE-PMT 2011M]**
(At. No. : Ti = 22, Cr = 24, Co = 27, Zn = 30)
(a) $[Ti(NH_3)_6]^{3+}$ (b) $[Cr(NH_3)_6]^{3+}$
(c) $[Co(NH_3)_6]^{3+}$ (d) $[Zn(NH_3)_6]^{2+}$

17. Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour ? **[CBSE-PMT 2012 S]**
(a) $[Ni(NH_3)_6]^{2+}$ (b) $[Zn(NH_3)_6)]^{2+}$
(c) $[Cr(NH_3)_6]^{3+}$ (d) $[Co(NH_3)_6]^{3+}$

18. Red precipitate is obtained when ethanol solution of dimethylglyoxime is added to ammoniacal Ni(II). Which of the following statements is not true ? **[CBSE-PMT 2012 M]**

(a) Red complex has a square planar geometry.
(b) Complex has symmetrical H-bonding
(c) Red complex has a tetrahedral geometry.
(d) Dimethylglyoxime functions as bidentate ligand.



dimethylglyoxime = $H_3C-C(=N-OH)-C(=N-OH)-CH_3$

19. Low spin complex of d^6-cation in an octahedral field will have the following energy : **[CBSE-PMT 2012 M]**

(a) $\frac{-12}{5}\Delta_0 + P$ (b) $\frac{-12}{5}\Delta_0 + 3P$

(c) $\frac{-2}{5}\Delta_0 + 2P$ (d) $\frac{-2}{5}\Delta_0 + P$

(Δ_0= Crystal Field Splitting Energy in an octahedral field, P = Electron pairing energy)

20. An excess of $AgNO_3$ is added to 100 mL of a 0.01 M solution of dichlorotetraaquachromium (iii) chloride. The number of moles of AgCl precipitated would be : **[NEET 2013]**

(a) 0.002 (b) 0.003
(c) 0.01 (d) 0.001

21. A square planar complex is formed by hybridisation of which atomic orbitals? **[AIEEE 2002]**

(a) s, p_x, p_y, d_{yz} (b) $s, p_x, p_y, d_{x^2-y^2}$
(c) s, p_x, p_y, d_{z^2} (d) s, p_y, p_z, d_{xy}

22. $CH_3 - Mg - Br$ is an organometallic compound due to **[AIEEE 2002]**

(a) Mg – Br bond (b) C – Mg bond
(c) C – Br bond (d) C – H bond.

23. The most stable ion is **[AIEEE 2002]**

(a) $[Fe(OH)_3]^{3-}$ (b) $[Fe(Cl)_6]^{3-}$
(c) $[Fe(CN)_6]^{3-}$ (d) $[Fe(H_2O)_6]^{3+}$.

24. One mole of the complex compound $Co(NH_3)_5Cl_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to yield two moles of AgCl (s). The structure of the complex is **[AIEEE 2003]**

(a) $[Co(NH_3)_3Cl_3]. 2\,NH_3$ (b) $[Co(NH_3)_4Cl_2]\,Cl\,.\,NH_3$
(c) $[Co(NH_3)_4Cl]\,Cl_2.\,NH_3$ (d) $[Co(NH_3)_5Cl]\,Cl_2$

25. In the coordination compound, $K_4[Ni(CN)_4]$, the oxidation state of nickel is **[AIEEE 2003]**

(a) 0 (b) +1
(c) +2 (d) –1

26. The coordination number of a central metal atom in a complex is determined by **[AIEEE 2004]**

(a) the number of ligands around a metal ion bonded by sigma and pi-bonds both
(b) the number of ligands around a metal ion bonded by pi-bonds
(c) the number of ligands around a metal ion bonded by sigma bonds
(d) the number of only anionic ligands bonded to the metal ion.

27. Which one of the following complexes is an outer orbital complex ? **[AIEEE 2004]**

(a) $[Co(NH_3)_6]^{3+}$ (b) $[Mn(CN)_6]^{4-}$
(c) $[Fe(CN)_6]^{4-}$ (d) $[Ni(NH_3)_6]^{2+}$
(Atomic nos. : Mn = 25; Fe = 26; Co = 27, Ni = 28)

28. Coordination compounds have great importance in biological systems. In this context which of the following statements is **incorrect** ? **[AIEEE 2004]**

(a) Cyanocobalamin is B_{12} and contains cobalt
(b) Haemoglobin is the red pigment of blood and contains iron
(c) Chlorophylls are green pigments in plants and contain calcium
(d) Carboxypeptidase - A is an enzyme and contains zinc.

29. Which one of the following has largest number of isomers ? **[AIEEE 2004]**

(a) $[Ir(PR_3)_2H(CO)]^{2+}$ (b) $[Co(NH_3)_5Cl]^{2+}$
(c) $[Ru(NH_3)_4Cl_2]^+$ (d) $[Co(en)_2Cl_2]^+$
(R = alkyl group, en = ethylenediamine)

30. The correct order of magnetic moments (spin only values in B.M.) is **[AIEEE 2004]**

(a) $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$
(b) $[MnCl_4]^{2-} > [Fe(CN)_6]^{4-} > [CoCl_4]^{2-}$
(c) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$
(d) $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$
(Atomic nos. : Mn = 25, Fe = 26, Co = 27)

31. The oxidation state Cr in $[Cr(NH_3)_4Cl_2]^+$ is **[AIEEE 2005]**

(a) 0 (b) + 1
(c) + 2 (d) + 3

32. The IUPAC name of the coordination compound $K_3[Fe(CN)_6]$ is **[AIEEE 2005]**

(a) Tripotassium hexacyanoiron (II)
(b) Potassium hexacyanoiron (II)
(c) Potassium hexacyanoferrate (III)
(d) Potassium hexacyanoferrate (II)

33. Which of the following compounds shows optical isomerism? **[AIEEE 2005]**

(a) $[Co(CN)_6]^{3-}$ (b) $[Cr(C_2O_4)_3]^{3-}$
(c) $[ZnCl_4]^{2-}$ (d) $[Cu(NH_3)_4]^{2+}$

34. Which one of the following cyano complexes would exhibit the lowest value of paramagnetic behaviour ? **[AIEEE 2005]**

(a) $[Co(CN)_6]^{3-}$ (b) $[Fe(CN)_6]^{3-}$
(c) $[Mn(CN)_6]^{3-}$ (d) $[Cr(CN)_6]^{3-}$
(At. Nos : Cr = 24, Mn = 25, Fe = 26, Co = 27)

35. The value of the 'spin only' magnetic moment for one of the following configurations is 2.84 B.M. The correct one is **[AIEEE 2005]**

(a) d^5 (in strong ligand field)
(b) d^3 (in weak as well as in strong fields)
(c) d^4 (in weak ligand fields)
(d) d^4 (in strong ligand fields)

36. The IUPAC name for the complex $[Co(NO_2)(NH_3)_5]Cl_2$ is : **[AIEEE 2006]**

(a) pentaammine nitrito-N-cobalt(II) chloride
(b) pentaammine nitrito-N-cobalt(III) chloride
(c) nitrito-N-pentaamminecobalt(III) chloride
(d) nitrito-N-pentaamminecobalt(II) chloride

37. In $Fe(CO)_5$, the Fe – C bond possesses **[AIEEE 2006]**

(a) ionic character (b) σ-character only
(c) π-character (d) both σ and π characters

38. How many EDTA (ethylenediaminetetraacetic acid) molecules are required to make an octahedral complex with a Ca^{2+} ion? **[AIEEE 2006]**

(a) One (b) Two
(c) Six (d) Three

39. Which of the following has a square planar geometry? **[AIEEE 2007]**

(a) $[PtCl_4]^{2-}$ (b) $[CoCl_4]^{2-}$ (c) $[FeCl_4]^{2-}$ (d) $[NiCl_4]^{2-}$
(At. nos.: Fe = 26, Co = 27, Ni = 28, Pt = 78)

40. The coordination number and the oxidation state of the element 'E' in the complex $[E\,(en)_2\,(C_2O_4)]NO_2$ (where (en) is ethylene diamine) are, respectively, **[AIEEE 2008]**

(a) 6 and 2 (b) 4 and 2 (c) 4 and 3 (d) 6 and 3

41. In which of the following complexes of the Co (at. no. 27), will the magnitude of Δ_o be the hightest? **[AIEEE 2008]**

(a) $[Co(CN)_6]^{3-}$ (b) $[Co(C_2O_4)_3]^{3-}$
(c) $[Co(H_2O)_6]^{3+}$ (d) $[Co(NH_3)_6]^{3+}$

42. Which of the following has an optical isomer **[AIEEE 2009]**

(a) $[Co(en)(NH_3)_2]^{2+}$ (b) $[Co(H_2O)_4(en)]^{3+}$
(c) $[Co(en)_2(NH_3)_2]^{3+}$ (d) $[Co(NH_3)_3Cl]^+$

43. Which of the following pairs represent linkage isomers? **[AIEEE 2009]**

(a) $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$
(b) $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$
(c) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$
(d) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

44. A solution containing 2.675 g of $CoCl_3 . 6\,NH_3$ (molar mass = 267.5 g mol^{-1}) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 4.78 g of AgCl (molar mass = 143.5 g mol^{-1}). The formula of the complex is **[AIEEE 2010]**
(At. mass of Ag = 108 u)

(a) $[Co(NH_3)_6]Cl_3$ (b) $[CoCl_2(NH_3)_4]Cl$
(c) $[CoCl_3(NH_3)_3]$ (d) $[CoCl(NH_3)_5]Cl_2$

45. Which one of the following has an optical isomer? **[AIEEE 2010]**

(a) $[Zn(en)(NH_3)_2]^{2+}$ (b) $[Co(en)_3]^{3+}$
(c) $[Co(H_2O)_4(en)]^{3+}$ (d) $[Zn(en)_2]^{2+}$
(en = ethylenediamine)

46. Which one of the following complex ions has geometrical isomers ? **[AIEEE 2011]**

(a) $[Ni(NH_3)_5Br]^+$ (b) $[Co(NH_3)_2(en)_2]^{3+}$
(c) $[Cr(NH_3)_4(en)_2]^{3+}$ (d) $[Co(en)_3]^{3+}$
(en = ethylenediamine)

47. Which of the following facts about the complex $[Cr(NH_3)_6]Cl_3$ is wrong? **[AIEEE 2011]**

(a) The complex involves d^2sp^3 hybridisation and is octahedral in shape.
(b) The complex is paramagnetic.
(c) The complex is an outer orbital complex
(d) The complex gives white precipitate with silver nitrate solution.

48. Among the ligands NH_3, en, CN^- and CO the correct order of their increasing field strength, is : **[AIEEE 2011]**

(a) $NH_3 < en < CN^- < CO$
(b) $CN^- < NH_3 < CO < en$
(c) $en < CN^- < NH_3 < CO$
(d) $CO < NH_3 < en < CN^-$

49. Which among the following will be named as dibromidobis (ethylene diamine) chromium (III) bromide? **[AIEEE 2012]**

(a) $[Cr(en)_3]Br_3$ (b) $[Cr(en)_2Br_2]Br$
(c) $[Cr(en)Br_4]^-$ (d) $[Cr(en)Br_2]Br$

50. Which of the following complex species is not expected to exhibit optical isomerism ? **[JEE M 2013]**

(a) $[Co(en)_3]^{3+}$ (b) $[Co(en)_2Cl_2]^+$
(c) $[Co(NH_3)_3Cl_3]$ (d) $[Co(en)(NH_3)_2Cl_2]^+$

51. Among the following metal carbonyls, the C–O bond order is lowest in **[IIT-JEE 2007]**

(a) $[Mn(CO)_6]^+$ (b) $[Fe(CO)_5]$
(c) $[Cr(CO)_6]$ (d) $[V(CO)_6]^-$

52. The IUPAC name of $[Ni(NH_3)_4][NiCl_4]$ is **[IIT-JEE 2008]**

(a) Tetrachloronickel (II) - tetraamminenickel (II)
(b) Tetraamminenickel (II) - tetrachloronickel (II)
(c) Tetraamminenickel (II) - tetrachloronickelate (II)
(d) Tetrachloronickel (II) - tetrachloronickelate (0)

53. Both $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic. The hybridisations of nickel in these complexes, respectively, are **[IIT-JEE 2008]**

(a) sp^3, sp^3 (b) sp^3, dsp^2 (c) dsp^2, sp^3 (d) dsp^2, sp^2

54. The spin only magnetic moment value (in Bohr magneton units) of $Cr(CO)_6$ is **[IIT-JEE 2009]**

(a) 0 (b) 2.84 (c) 4.90 (d) 5.92

55. The ionisation isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is **[IIT-JEE 2010]**

(a) $[Cr(H_2O)_4(O_2N)]Cl_2$

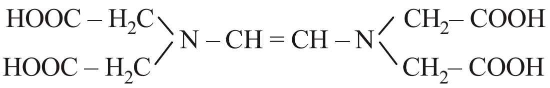
(b) $[Cr(H_2O)_4Cl_2](NO_2)$

(c) $[Cr(H_2O)_4Cl(ONO)]Cl$

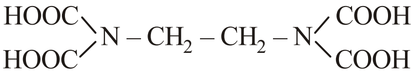
(d) $[Cr(H_2O)_4Cl_2(NO_2)].H_2O$

56. The correct structure of ethylenediaminetetraacetic acid (EDTA) is **[IIT-JEE 2010]**

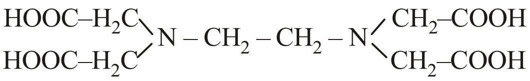
(a)



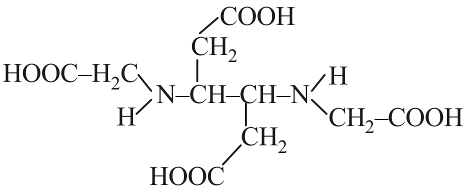
(b)



(c)



(d)



57. The complex showing a spin-only magnetic moment of 2.82 B.M. is : **[IIT-JEE 2010]**

(a) $Ni(CO)_4$ (b) $[NiCl_4]^{2-}$

(c) $Ni(PPh_3)_4$ (d) $[Ni(CN)_4]^{2-}$

58. Among the following complexes (**K**–**P**)

$K_3[Fe(CN)_6]$ (**K**), $[Co(NH_3)_6]Cl_3$ (**L**), $Na_3[Co(oxalate)_3]$ (**M**), $[Ni(H_2O)_6]Cl_2$ (**N**), $K_2[Pt(CN)_4]$ (**O**) and $[Zn(H_2O)_6](NO_3)_2$ (**P**) the diamagnetic complexes are **[IIT-JEE 2011]**

(a) K, L, M, N (b) K, M, O, P

(c) L, M, O, P (d) L, M, N, O

59. As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is : **[IIT-JEE 2012]**

(a) Tetraaquadiaminecobalt (III) chloride

(b) Tetraaquadiamminecobalt (III) chloride

(c) Diaminetetraaquacoblat (II) chloride

(d) Diamminetetraaquacobalt (III) chloride

60. $[NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2]$ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively **[IIT-JEE 2012]**

(a) tetrahedral and tetrahedral

(b) square planar and square planar

(c) tetrahedral and square planar

(d) square planar and tetrahedral

61. Consider the following complex ions, P, Q and R.

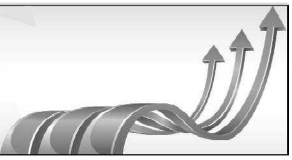
$P = [FeF_6]^{3-}$, $Q = [V(H_2O)_6]^{2+}$ and $R = [Fe(H_2O)_6]^{2+}$

The correct order of the complex ions, according to their spin-only magnetic moment values (in B.M.) is **[JEE Advanced 2013]**

(a) $R < Q < P$ (b) $Q < R < P$

(c) $R < P < Q$ (d) $Q < P < R$

Exercise-4 | Applied MCQs



1. Which one is the most likely structure of $CrCl_3 . 6H_2O$ if 1/3 of total chlorine of the compound is precipitated by adding $AgNO_3$

(a) $CrCl_3 . 6H_2O$

(b) $[Cr(H_2O)_3Cl_3] . (H_2O)_3$

(c) $[CrCl_2(H_2O)_4]Cl . 2H_2O$

(d) $[CrCl(H_2O)_5]Cl_2 . H_2O$

2. Which will give a white precipitate with $AgNO_3$ in aqueous solution

(a) $[Co(NH_3)_5Cl](NO_2)_2$ (b) $[Pt(NH_3)_6]Cl_4$

(c) $[Pt(en)Cl_2]$ (d) $[Cu(NH_3)_4]SO_4$

3. Pick a poor electrolytic conductor complex in solution

(a) $K_2[PtCl_6]$ (b) $[Co(NH_3)_3](NO_2)_3$

(c) $K_4[Fe(CN)_6]$ (d) $[Co(NH_3)_4]SO_4$

4. Which is correct in the case of $[Fe(CN)_6]^{4-}$ complex ?

(a) Diamagnetic (b) Octahedral

(c) d^2sp^3 - hybridisation (a) All are correct

5. IUPAC name of $Na_3[Co(ONO)_6]$ is

(a) Sodium cobaltinitrite

(b) Sodium hexanitrito cobaltate (III)

(c) Sodium hexanitrocobalt (III)

(d) Sodium hexanitritocobaltate (II)

6. Which has highest paramagnetism

(a) $[Cr(H_2O)_6]^{3+}$ (b) $[Fe(H_2O)_6]^{2+}$

(c) $[Cu(H_2O)_6]^{2+}$ (d) $[Zn(H_2O)_6]^{2+}$

7. Which is not true ligands metal complex ?

(a) Larger the ligand, the more stable is the metal - ligand complex

(b) Highly charged ligand forms stronger bonds

(c) Larger the permanent dipole moment of ligand , the more stable is the bond.

(d) Greater the ionisation potential of central metal, the stronger the bond

8. In solid $CuSO_4.5H_2O$ copper is coordinated to

(a) 4 water molecules (b) 5 water molecules

(c) one sulphate molecule (d) one water molecule

9. The catalyst used for the polymerization of olefins is

(a) Ziegler - Natta catalyst (b) Wilkinson's catalyst

(c) Pd- catalyst (d) Zeise's salt catalyst

10. Which of the following hydrate is diamagnetic?

(a) $[Mn(H_2O)_6]^{2+}$ (b) $[Cu(H_2O)_6]^{3+}$

(c) $[Co(NH_3)_6]^{3+}$ (d) $[Co(H_2O)_6]^{2+}$

11. The geometry of $Ni(CO)_4$ and $Ni(PPh_3)_2Cl_2$ are

(a) both square planar

(b) tetrahedral and square planar

(c) both tetrahedral

(d) None of these

12. Which of the following is paramagnetic ?

(a) $[Co(NH_3)_6]^{3+}$ (b) $[Ni(CO)_4]$

(c) $[Ni(Cl)_4]^{2-}$ (d) $[Ni(CN)_4]^{2-}$

13. Which of the following compounds is not coloured?

(a) $Na_2[CuCl_6]$ (b) $Na_2[CdCl_4]$

(c) $K_4[Fe(CN)_6]$ (d) $K_3[Fe(CN)_6]$

14. Which is paramagnetic ?

(a) $[Ni(H_2O)_6]^{2+}$ (b) $[Fe(CN)_6]^{4-}$

(c) $[Ni(CO)_4]$ (d) $[Ni(CN)_4]^{2-}$

15. In the complexes $[Fe(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$, $[Fe(C_2O_4)_3]^{3-}$ and $[FeCl_6]^{3-}$, more stability is shown by

(a) $[Fe(H_2O)_6]^{3+}$ (b) $[Fe(CN)_6]^{3-}$

(c) $[Fe(C_2O_4)_6]^{3-}$ (d) $[FeCl_6]^{3-}$

16. The most stable complex among the following is

(a) $K_3[Al(C_2O_4)_3]$ (b) $[Pt(en)_2]Cl$

(c) $[Ag(NH_3)_2]Cl$ (d) $K_2[Ni(EDTA)]$

17. In the silver plating of copper, $K[Ag(CN)_2]$ is used instead of $AgNO_3$. The reason is

(a) a thin layer of Ag is formed on Cu

(b) more voltage is required

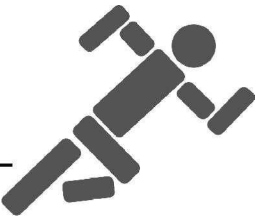
(c) Ag^+ ions are completely removed from solution

(d) less availability of Ag^+ ions, as Cu cannot displace Ag from $[Ag(CN)_2]^-$ ion.

18. Which of the following organometallic compound is σ and π -bonded ?

(a) $[Fe(\eta^5-C_5H_5)_2]$ (b) $[PtCl_3(\eta^2-C_2H_4)]$

(c) $[Co(CO)_5NH_3]^{2+}$ (d) $Al(CH_3)_3$



Hints & Solutions

EXERCISE 1

1. Co has + 3 oxidation state.
2. Tetraamminecobalt (III) – μ-imido-μ-nitro tetrammine cobalt (III) ion.
3. A complex is formed, $[Cu(NH_3)_4]^{2+}$ which does not dissociate to form Cu^{2+} ion.
4. (*a*) Zero. (*b*) One mole of Cl^- (*c*) 2 moles of Cl^-.
6. (*a*) $[Ni(CN)_4]^{2-}$
   (*b*) $[Ag(NH_3)_2]^+ Cl^-$ remains colourless in a solution.
7. (*a*) $[Fe(CN)_3(NH_3)_3]^-$
   (*b*) $[Fe(OH)(NH_3)_2Cl_3]^{2-}$
8. (*a*) Six. (*b*) +3.
   (*c*) sp^3d^2 hybridisation. (*d*) Octahedral.
   (*e*) Diamagnetic.
9. (*a*) $[Cr(NC)(H_2O)_5]^{2+}$
   (*b*) $[PtBr_2(NH_3)_4]Cl_2$
   (*c*) $[Cu(NH_3)_4][PtCl_4]$
12. (*a*) $[Cr(H_2O)_6]Cl_3$
    (*b*) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$
    (*c*) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

17. (d) **18. (d)** **19. (b)**
20. (d) **21. (a)** **22. (a)**
23. (b) **24. (a)** **25. (c)**
26. (b)

EXERCISE 2

1. **(b)** Ferrous ammonium sulphate $[FeSO_4](NH_4)_2SO_4 6H_2O$ is a double salt. While all others are complex compounds
2. **(b)** $CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$
3. **(b)** $K_4[Fe(CN)_6]$ is a complex compound
4. **(c)** AgCl form soluble complex with NH_4OH which is $[Ag(NH_3)_2]^+$
5. **(a)** Salt may be complex salt. Metal atom present in the coordination sphere appears in the form of complex ion and not as simple cation
6. **(c)** Lithium tetrahydridoaluminate is $Li[AlH_4]$ and the ligand is H^-
7. **(c)** $K_4[Fe(CN)_6]$ obeys the EAN rule
8. **(d)** EAN is given by : Atomic number of central metal atom + 2 x C.N. – O.S.
   ∴ EAN of Fe in $[Fe(CN)_6]^{3-}$ is 26+12–3 =35
9. **(b)** Coordinate number is = 2 (number of bindentate ligands
   ∴ C.N. of Ni = (2 × 3) = 6
10. **(a)** The C. N. of Fe(II) in oxyhaemoglobin is 6
11. **(b)** In the ring test the complex formed is $[Fe(H_2O)_5NO]^{2+}$
12. **(b)** In the complex formation the ligands whether negative, neutral or positive always donate electrons to the central metal atom hence they act as Lewis bases.
13. **(a)** The primary valencies are ionisable and represented by dotted line.
14. **(d)** The number of ammonia molecules is 6. Each ammonia molecule contains 3 covalent bonds between N and H. Therefore the number of covalent bonds is 18.
15. **(a)** Since the precipitate of AgCl shows two ionisable chloride ion the complex must have the structure.

$$[Co(NH_3)_5Cl]Cl_2 + 2AgNO_3 \rightarrow [Co(NH_3)_5Cl](NO_3)_2 + 2AgCl$$

Hence two chlorine atoms satisfy the primary valency and one, secondary valency

16. **(b)** $[CuCl_2\{O{=}C(NH_2)_2\}_2]$ this is dichlorobis(urea) copper (II) (see rules for naming a complex compound)
17. **(d)** Chemical formula of iron (III) hexacynaoferrate (II) is $Fe_4[Fe(CN)_6]_3$
18. **(d)** IUPAC name of $Na_3[Co(NO_2)_6]$ is sodium hexanitro cobaltate (III)
19. **(c)** $K[Co(CN)_4]$ let the O. N. of Co be x then $1\times(+1)+1(+x)+4(-1) = 0 \Rightarrow x = +3$
20. **(b)** IUPAC name of $K_3[Ir(C_2O_4)_3]$ is potassium trioxalato iridate (III)
21. **(d)** In Ziegler Natta catalyst the active species the Ti^{III}
22. **(a)** The complex chlorodiaquatriammine cobalt (III) chloride can have the structure $[CoCl(NH_3)_3(H_2O)_2]Cl_2$
23. **(a)** O. S of Fe in $K_4[Fe(CN)_6]$. Let O. S. of Fe be x then $4\times(+1)+1\times(+x)+6\times(-1) = 0 \therefore x = +2$
24. **(d)** $[Pt(en)_2Cl_2]$ is a complex of the type $M(AA)_2B_2$ which is octahedral Such compounds exhibit optical and geometrical isomerism both

25. (a) $[Co(NH_3)_3(NO_2)_3]$ is of the type MA_3B_3. They give two geometrical Isomers

26. (d) For $[Cu^{II}(NH_3)_4][Pt^{II}Cl_4]$ four isomers are possible which are $[Cu(NH_3)_4]$ $[PtCl_4]$, $[CuCl_4][Pt(NH_3)_4]$, $[PtCl_3(NH_3)][Cu(NH_3)_3Cl]$ and $[Pt(NH_3)_3Cl]$ $[Cu(NH_3)Cl_3]$

27. (c) Since the complex with $AgNO_3$ solution gives two moles of AgCl it must have two ionisable Cl atoms. Hence the complex is $[Co(NH_3)_5NO_2]Cl_2$. On ionisation it will give three moles of ion viz $[Co(NH_3)_5NO_2]^{2+} + 2Cl^-$

28. (d) $[Cr(NH_3)_3Cl_3]$ is of the type MA_3B_3 and exists in two isomeric forms.

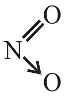
29. (d) Square planar complex of the formula Mabcd give three geometrical isomers

30. (b)

31. (d) The complex ion $[Cr(SCN)_2(NH_3)_4]^{2+}$ can exhibit geometrical and linkage isomerism

32. (c) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$ are ionisation isomers

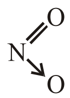
33. (c) The complex compound $[Co(en)_2NO_2Cl]$ Br can have NO_2 group differently linked to central metal atom –


or $O-N=O$

34. (a) The compounds of the type $M(AA)_2B_2$ exhibit both geometrical and optical isomerism

35. (c) Octahedral complex of the type MA_5B do not show geometrical isomerism

36. (c) Similarity between optical and geometrical isomerism is that both are included in stereo isomerism

37. (b) The compound is $[Cr(NH_3)_5NO_2]Cl_2$ and can exhibit linkage isomerism due to NO_2 group (–  or $O-N=O$)

38. (c) Electronic configuration of Ni^{2+} is [Ar] $3d^8 4s^0 4p^0$. CN^- is strong ligand and will do pairing of electrons so will have one d orbital left empty. C. N. is 4 so dsp^2 hybridisation will take place which is square planar, $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are tetrahedral.

39. (a) $Ni(CO)_4$. The O. S. of Ni is Zero. Electronic configuration is [Ar] $3d^8 4s^2 4p^0$. In presence of strong ligand CO the paring of electrons take place and electronic configuration will be [Ar] $3d^{10} 4s^0 4p^0$. Hence unpaired electrons is zero .

40. (b)

41. (d) $Fe(CO)_5$ (Z=26) O. S. of Fe is zero . Electronic configuaration is [Ar]] $3d^6$, $4s^2 4p^0$. After pairing of electrons of d and s orbitals, we have one d atomic orbital empty. C. N. is 5 so hybridisation is dsp^3 which is trigonal bipyramidal.

42. (b) Shape of $[Cu(NH_3)_4]^{2+}$ is square planar.

43. (a) $[FeF_6]^{3-}$ the C. N. is 6 hence it is octahedral

44. (d) Fe^{2+} electronic configuration is [Ar] $3d^6$. Since CN is strong field ligand d electrons are paired . In $Ni(CO)_4$ O. S. of Ni is zero electronic configuration is [Ar} $3d^8$ $4s^2$. In presence of CO it is [Ar] $3d^{10} 4s^0$, electrons are paired. Electronic configuration of Ni^{2+} [Ar]$3d^8 4s^0$, due to CN^- ligand all electrons are paired. Co^{3+} is [Ar] $3d^6$ since F is weak ligand hence paramagnetic.

45. (b) The valency is given by O. S. In $[Cr(H_2O)_4Cl_2]^+$. O. S. of Cr is +3 hence valency of Cr is +3

46.(a)

A,Ni^{2+}	B,Ni	C,Zn^{2+}	D,Co^{3+}
E.C.[Ar]$3d^8$	[Ar]$3d^8$,	[Ar]$3d^{10}$	[Ar]$3d^6$
$4s^0$	$4s^2$	$4s^0$	$4s^0$
H_2O weak ligand	CO strong	NH_3 strong	NH_3 strong ligand
No pairing of electrons	Pairing of electrons	Pairing of electrons	Pairing of electrons
Paramagnetic	Diamagnetic	Diamagnetic	Diamagnetic

47. (a) $Ni(CO)_4$ is tetrahedral but not paramagnetic. It is diamagnetic

48. (a) $[Pt(NH_3)_2Cl_2]$ O.S. of Pt +2; electronic configuration of Pt^{+2} = $[Xe]4f^{14} 5d^8$. Ligand NH_3 results in pairing of d electrons leaving one d orbital empty therefore hybridisation is dsp^2 square planar

49. (d) Shape of cuprammonium ion $[Cu(NH_3)_4]^{2+}$ is square planar dsp^2 hybridisation

50. (b) $[Ni(CN)_4]^{2-}$ dsp^2,

51. (a) $[Co(NH_3)_5CO_3]ClO_4$ Six monodentate ligands are attached to Co hence C. N. of Co = 6;

O. N. = x + 5 × (0) + 1 × (–2) + 1× (–1) = 0 ∴ x = + 3 ; electronic configuration of Co^{3+}[Ar] $3d^6 4s^0$ hence number of d electrons is 6. All d electrons are paired due to strong ligand hence unpaired electron is zero.

52. (d)	$[Cr(CO)_6]$	$Fe(CO)_5$	$[Fe(CN)_6]^{4-}$	$[Cr(NH_3)_6]^{3+}$
O.S. of M	0	0	+2	+3
E.C.	[Ar] $3d^5 4s^1$	[Ar] $3d^6 4s^2$	[Ar] $3d^6$	[Ar] $3d^3$
Pairing of e^-	Pairing of e^-	Pairing of e^-	Pairing of e^-	Pairing of e^-
	Diamagnetic	Paramagnetic	Diamagnetic	Diamagnetic

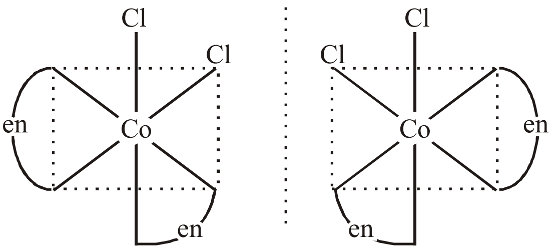
53. (a) $K_4[Fe(CN)_6]$ in solution furnishes $4K^+ + [Fe(CN)_6]^{4-}$ five ions and exhibits maximum ionic conductivity.

54. (a) $Ti(C_2H_4)_4$ is an organometallic compound due to Ti directly attached to C- atom

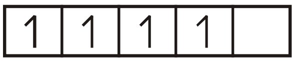
55. (d) Tetraethyl lead $Pb(C_2H_5)_4$ is not π bonded complex. It is σ bonded organometallic compound

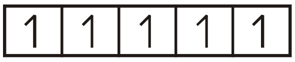
EXERCISE 3

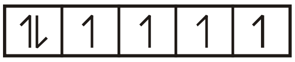
1. **(b)** Non superimposable mirror images are called optical isomers and may be described as "chiral'. They are also called enantiomers and rotate plane polarised light in opposite directions.

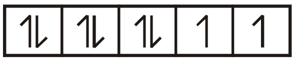


2. **(b)** Lesser is the number of unpaired electrons smaller will be the paramagnetic behaviour. As Cr^{++}, Mn^{++}, Fe^{++} and Ni^{++} contains.

$Cr^{++}(3d^4)$ =

= 4 unpaired e^-.

$Mn^{++}(3d^5)$=

= 5 unpaired e^-.

$Fe^{++}(3d^6)$ =

= 4 unpaired e^-.

$Ni^{++}(3d^8)$ =

= 2 unpaired e^-.

As Ni^{++} has minimum no. of unpaired e^- thus this is least paramagnetic.

3. **(c)**

4. **(c)** In octahedral field the crystal field splitting of d- orbitals of a metal ion depends upon the field produced by the ligands. In general ligands can be arranged in a series in the order of increasing fields and splittings which they produce around a central metal ion. A portion of the series is given below.

cyanide > ethylene - diamine > ammonia > pyridine > thiocyanate > water > oxalate > hydroxide > fluoride > chloride > bromide > iodide.

Out of the given ligands water, ammonia, cyanide and oxalate, we can find from the above series of ligands that the maximum splitting will occur in case of cyanide (CN^-) i.e. the magnitude of Δ_0 will be maximum in case of $[Co(CN)_6]^{3+}$.

5. **(a)** The octahedral coordination compounds of the type MA_3B_3 exhibit fac-mer isomerism.

6. **(b)** Since Cr^{3+} in the complex has unpaired electrons in the d orbital, hence it will absorb visible light and will be coloured

$Ti = [Ar]3d^2\,4s^2$; $Ti^{4+} = 3d^0$
$Cr = [Ar]\,3d^5\,4s^1$; $Cr^{3+} = 3d^3$
$Zn = [Ar]\,3d^{10}\,4s^2$; $Zn^{2+} = 3d^{10}$
$Sc = [Ar]\,3d^1\,4s^2$; $Sc^{3+} = 3d^0$

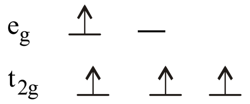
7. **(a)** $[Ni(CN)_4]^{2-}$: Number of unpaired electrons = 0

$[Cr(NH_3)_6]^{3+}$: Number of unpaired electrons = 3

$[Fe(H_2O)_6]^{2+}$: Number of unpaired electrons = 4

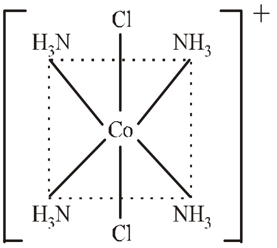
$[Ni(H_2O)_6]^{2+}$: Number of unpaired electrons = 2

8. **(d)** d^4 in high spin octahedral complex

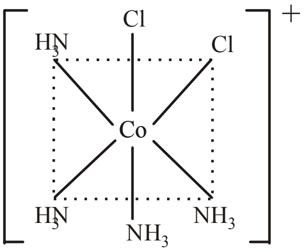


$CFSE = (-0.4x + 0.6y)\Delta_0$
Where, $x \rightarrow$ electrons in t_{2g} orbital
$y \rightarrow$ electrons in e_g orbital
$CFSE = [0.6 \times 1] + [-0.4 \times 3] = -0.6\ \Delta_0$

9. **(b)**



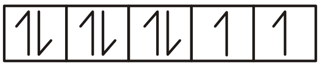
trans (green)



cis (violet)

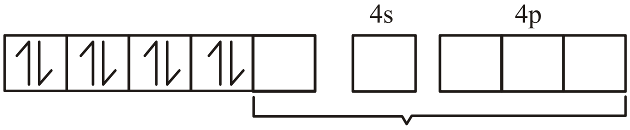
10. **(d)** In $\left[Ni(NH_3)_2Cl_2\right]$, Ni^{2+} is in sp^3 hybridisation, thus tetrahedral in shape. Hence the four ligands are not different to exhibit optical isomerism. In tetrahedral geometry all the positions are adjacent to one another $\therefore$ geometrical isomerism is not possible.

11. **(b)** $Ni^{++} = 3d^8\,4s^0$



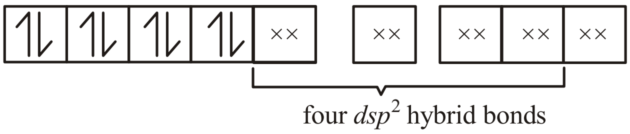
Since, the coordination number of Ni in this complex is 4, the configuration of Ni^{++} at first sight shows that the complex is paramagnetic with two unpaired electron. However, experiments show that the complex is diamagnetic. This is possible when the 3d electrons rearrange against the Hund's rule as shown below. This is in accordance with the fact that the ligand involved here is strong i.e., CN^- ion.

Ni^{++} (after rearrangement)



Hence, now dsp^2 hybridization involving one $3d$, one $4s$ and two $4p$ orbitals, takes place leading to four dsp^2 hybrid orbitals, each of which accepts four electron pairs from CN^- ion forming $[Ni(CN)_4]^{2-}$ ion.

$[Ni(CN)_4]^{2-}$

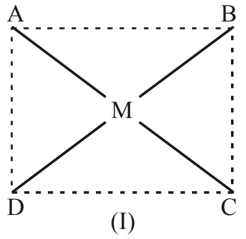


Thus, the complex is diamagnetic as it has no unpaired electron.

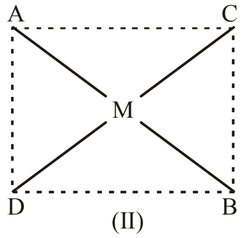
12. (c) Coordination isomerism occurs when cationic and anionic complexes of different metal ions are present in a salt. The two isomers differ in the distribution of ligands in cation and anion e.g.,

$[Co(NH_3)_6][Cr(CN)_6]$ is an isomer of $[Co(CN)_6][Cr(NH_3)_6]$

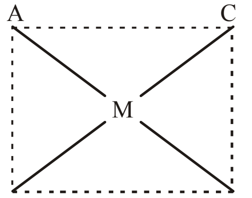
13. (a) Complexes of the type M_{ABCD} may exist in three isomeric forms.



(I)



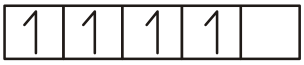
(II)

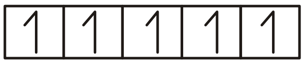


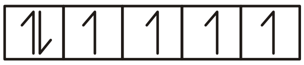
(III)

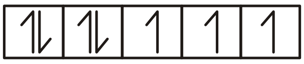
Similarly, $[Pt(py)(NH_3)BrCl]$ may exist in three isomeric form in which

$M = Pt, A = Py, B = NH_3, C = Br, D = Cl.$

14. (c) Cr^{2+} d^4  4

Mn^{2+} d^5  5

Fe^{2+} d^6  4

Co^{2+} d^7  3

Minimum paramagnetic behaviour = $[Co(H_2O)_6]^{2+}$

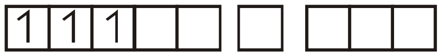
15. (a) As positive charge on the central metal atom increases, the less readily the metal can donate electron density into the π* orbitals of CO ligand (donation of electron density into π* orbitals of CO result in weakening of C – O bond). Hence, the C – O bond would be strongest in $[Mn(CO)_6]^+$.

16. (b)

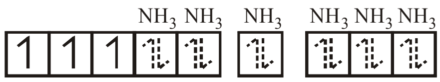
(a) $[Ti(NH_3)_6]^{3+}$: $3d^1$ configuration and thus has one unpaired electron.

(b) $[Cr(NH_3)_6]^{3+}$: In this complex Cr is in +3 oxidation state.

$Cr^{3+} : 3d^3 4s^0$

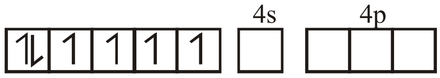


It has 3 unpaired electrons thus complex is paramagnetic

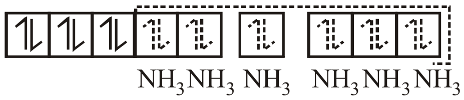


(c) $[Co(NH_3)_6]^{3+}$: In this complex cobalt ion is in + 3 oxidation state with $3d^6$ configuration.

$Co^{3+}, [Ar]3d^6$



$[Co(NH_3)_6]^{3+}$



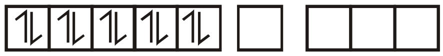
(inner orbital or d^2sp^3 hybrid orbital, low spin complex)

∴ diamagnetic

(d) In this complex Zn exists as

Zn^{++} ion

Zn^{++} ion : $3d^{10} 4s^0$



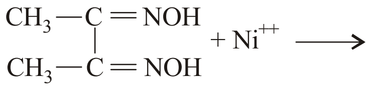
Zn^{++} ion in $[Zn(NH_3)_4]^{2+}$

Due to presence of paired electrons complex is diamagnetic in nature.

17. (a) $[Ni(NH_3)_6]^{2+}$

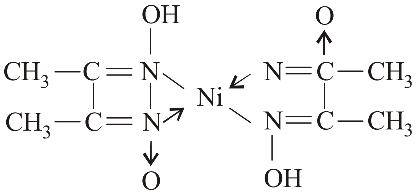
$Ni^{2+} = 3d^8$, according to CFT $= t_{2g}^6 e_g^2$ therefore, hybridisation is sp^3d^2 and complex is paramagnetic.

18. **(c)** Nickel ions are frequently detected by the formation of red precipitate of the complex of nickel dimethylglyoxime, when heated with dimethylglyoxime.



$$\begin{matrix} CH_3-C=NOH \\ | \\ CH_3-C=NOH \end{matrix} + Ni^{++} \longrightarrow$$

Dimethylglyoxime



Nickel dimethylglyoxime

19. **(b)** $d^6 - t_{2g}^{\;2,2,2}\; e_g^{\;0,0}$ (in low spin)

$$C.F.S.E = -0.4 \times 6\Delta_0 + 3P$$

$$= -\frac{12}{5}\,\Delta_0 + 3P$$

20. **(d)** $[Cr(H_2O)_4Cl_2]\,Cl + AgNO_3 \longrightarrow AgCl + [Cr(H_2O)_4Cl_2]NO_3$

$$\text{Molarity} = \frac{\text{wt}}{\text{mol. mass}} \times \frac{1000}{\text{vol.}}$$

$$\frac{\text{wt}}{\text{mol. mass}} = \text{molarity} \times \frac{\text{vol.}}{1000} = \frac{0.01 \times 100}{1000}$$

$$= 0.001$$

21. **(b)** A square planer complex is formed by hybridisation of s, p_x, p_y and $d_{x^2-y^2}$ atomic orbitals

22. **(b)** Bond between C of organic molecule and metal atom.

23. **(b)** A more basic ligand forms stable bond with metal ion, Cl^- is most basic amongst all.

24. **(d)** $Co\,(NH_3)_5Cl_3 \rightleftharpoons [Co(NH_3)_5Cl]^{+2} + 2Cl^-$

∴ Structure is $[Co\,(NH_3)_5\,Cl]\,Cl_2$.

25. **(a)** $4(+1) + x + (-1) \times 4 = 0$

$\Rightarrow 4 + x - 4 = 0$

$x = 0$

26. **(c)** The coordination number of central metal atom in a complex is equal to number of monovalent ligands, twice the number of bidentate ligands and so on, around the metal ion bonded by coordinate bonds

27. **(d)** Hybridisation

$$\underset{d^2sp^3}{[Fe(CN)_6]^{4-}},\ \underset{d^2sp^3}{[Mn(CN)_6]^{4-}},$$

$$\underset{d^2sp^3}{[Co(NH_3)]^{3+}},\underset{sp^3d^2}{[Ni(NH_3)_6]^{2+}}$$

Hence $[Ni(NH_3)_6]^{2+}$ is outer orbital complex

28. **(c)** Chlorophyll contains Mg and not Ca

29. **(d)** isomers

$$\underset{\text{cis and trans}}{[Ru(NH_3)_4Cl_2]^+},\underset{\text{none}}{[Co(NH_3)_5Cl]^{2+}},$$

$$\underset{\text{cis and trans}}{[Ir(PR_3)_2H(CO)]^{2+}},\underset{\text{cis and trans and optical isomers}}{[Co(en)_2Cl_2]^+}$$

30. **(c)** Number of unpaired electrons

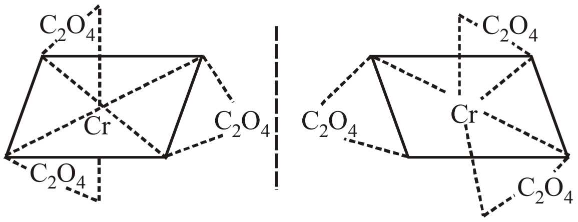
$$\underset{\text{zero}}{[Fe(CN)_6]^{4-}},\underset{\text{three}}{[CoCl]^{2-}},\underset{\text{five}}{[MnCl_4]^{2-}}$$

The greater the number of unpaired electrons, the higher the value of magnetic moment

31. **(d)** The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is + 3.

32. **(c)** $K_3[Fe(CN)_6]$ is potassium hexacyano ferrate (III).

33. **(b)**



Non-superimposable mirror images, hence optical isomers.

34. **(a)**

	No. of unpaired electron
a) Co^{3+}	4
b) Fe^{3+}	1
c) Mn^{3+}	4
d) Cr^{3+}	3

Lower the number of unpaired electrons in a substance, the lower is its magnetic moment in Bohr – Magneton and lower shall be its paramagnetism

35. **(d)** d_5 —— strong ligand field

[⇅][⇅][↑] [ ][ ]
t_{2g} e_g

$\mu = \sqrt{n(n+2)} = \sqrt{3} = 1.73BM$

d^3— in weak as well as in strong field

[↑][↑][↑] [ ][ ]
t_{2g} e_g

$\mu = \sqrt{3(5)} = \sqrt{15} = 3.87\,B.M.$

d^4– in weak ligend field

[↑][↑][↑] [↑][ ]
t_{2g} e_g

$\mu = \sqrt{4(6)} = \sqrt{24} = 4.89$

d^4– in strong ligand field

[⇅][↑][↑] [ ][ ]
t_{2g} e_g

$\mu = \sqrt{2(4)} = \sqrt{8} = 2.82$

36. **(b)** $[Co(NO)_2(NH_3)_5]Cl_2$
pentaamminenitro-N-cobalt (III) chloride

37. **(d)** Due to some backbonding by sidewise overlapping between d-orbitals of metal and p-orbital of carbon, the F–C bond has σ and π character.

38. **(a)** EDTA is hexadentate (four donor O atoms and 2 donor N atoms and for the formation of octahedral complex one molecule is required

$Ca^{++} + [H_2EDTA^-] \longrightarrow [Ca(EDTA)]^{2-} + 2H^+$

39. **(a)** Complexes with dsp^2 hybridisation are square planar. So, $[PtCl_4]^{2-}$ is square planar in shape.

40. **(d)** In the given complex we have two bidentate ligands (i.e en and C_2O_4), so coordination number of E is 6

$(2 \times 2 + 1 \times 2 = 6)$

Let the oxidation state of E in complex be x, then

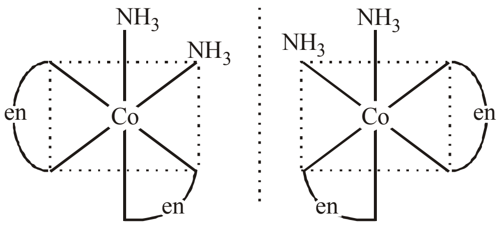
$[x + (-2) = 1]$ or $x - 2 = 1$

or $x = +3$, so its oxidation state is + 3

Thus option (d) is correct.

41. **(a)** In octahedral complex the magnitude of Δ_0 will be highest in a complex having strongest ligand. Out of the given ligands CN^- is strongest. So, Δ_0 will be highest for $[Co(CN)_6]^{3-}$. Thus option (a) is correct.

42. **(c)**



Enantiomers of $cis\text{-}\left[Co(en)_2(NH_3)_2\right]^{3+}$

43. **(a)** The SCN^- ion can coordinate through S or N atom giving rise to linkage isomerism

$M \leftarrow SCN$ thiocyanato

$M \leftarrow NCS$ isothiocyanato.

44. **(a)** $\underset{2.675g}{CoCl_3.6NH_3} \longrightarrow x\,Cl^-$

$x\,Cl^- + AgNO_3 \longrightarrow \underset{4.78g}{x\,AgCl \downarrow}$

Number of moles of the complex

$= \frac{2.675}{267.5} = 0.01$ moles

Number of moles of AgCl obtained

$= \frac{4.78}{143.5} = 0.03$ moles

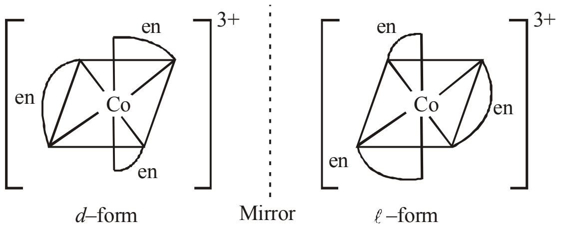
∴ No. of moles of AgCl obtained
= 3 × No. of moles of complex

$\therefore n = \frac{0.03}{0.01} = 3$

∴ $3Cl^-$ ions are precipitable

Hence the formula of the complex is $[Co(NH_3)_6]Cl_3$

45. **(b)** Option (b) shows optical isomerism $[Co(en)_3]^{3+}$

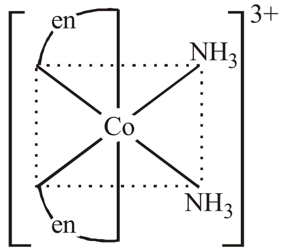


Complexes of Zn^{++} cannot show optical isomerism as they are tetrahedral complexes with plane of symmetry.

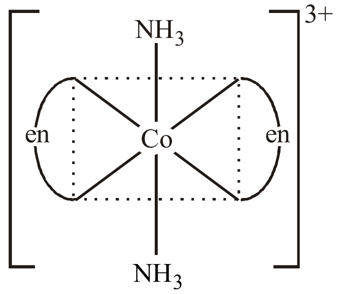
$[Co(H_2O)_4(en)]^{3+}$ have two planes of symmetry hence it is also optically inactive.

$[Zn(en)_2]^{2+}$ cannot show optical isomerism

46. **(b)**



cis



trans-

47. **(c)** $[Cr(NH_3)_6]Cl_3$ is an inner orbital complex, because in this complex inner d-orbital is used for hybridisation (d^2sp^3)

48. **(a)** Ligands can be arranged in a series in the orders of increasing field strength as given below :

Weak field ligands :

$I^- < Br^- < S^{2-} < SCN < Cl^- < N_3^-, F^-$
$< \text{Urea}, OH^- < \text{oxalate}$

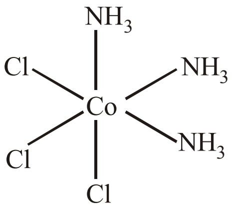
Strong field ligands

$O^{--} < H_2O < NCS^- < EDTA < Py, NH_3 <$
$en = SO_3^- < \text{bipy, Phen} < NO_2^- < CH_3^-$
$< C_6H_5^- < CN^- < CO$

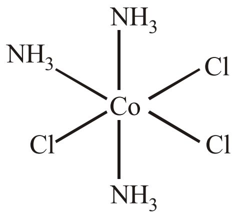
Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands.

49. (b) $[Cr(en)_2Br_2]Br$
dibromidobis (ethylenediamine) chromium (III) bromide.

50. (c) Octahedral coordination entities of the type Ma_3b_3 exhibit geometrical isomerism. The compound exists both as facial and meridional isomers, both contain plane of symmetry



fac-

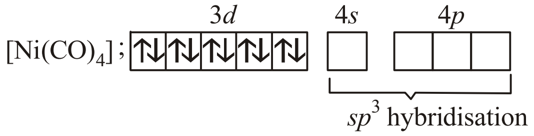


mer

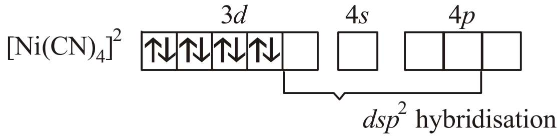
51. (d) An anionic carbonyl complex can delocalise more electron density to antibonding pi-orbital of CO and hence, lowers the bond order.

52. (c) The correct IUPAC name of the given compound is tetramminenickel (II) - tetrachloronickelate (II) thus (c) is the correct answer.

53. (b) In carbonyls O.S. of metal is zero
In $[Ni(CO)_4]$, the oxidation state of nickel is zero. Its configuration in $Ni(CO)_4$ is

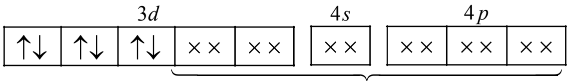


In $[Ni(CN)_4]^{2-}$ the oxidation state of Ni is 2+ and its configuration is



Thus the hybridisations of nickel in these compounds are sp^3 and dsp^2 respectively.
Hence (b) is the correct answer.

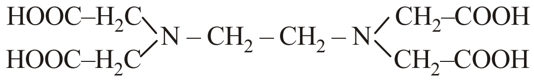
54. (a) Chromium in $Cr(CO)_6$ is in zero oxidation state and has $[Ar]^{18}\ 3d^5 4s^1$ as the electronic configuration. However, CO is a strong ligand, hence pairing up of electrons takes place leading to following configuration in $Cr(CO)_6$.



Since the complex has no unpaired electron, its magnetic moment is zero.

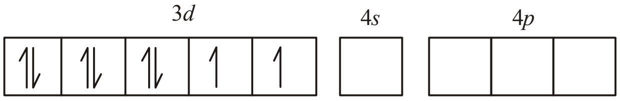
55. (b) Ionisation isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is $[Cr(H_2O)_4Cl_2]NO_2$.

56. (c) The correct structure of EDTA is

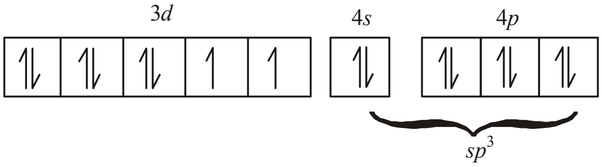


57. (b) $[NiCl_4]^{2-}$, O.S. of Ni = +2

$Ni(28) = 3d^8\ 4s^2$



Cl^- being weak ligand it cannot pair up the two electrons present in $3d$ orbital



No. of unpaired electrons = 2

Magnetic moment, $\mu = 2.82$ BM.

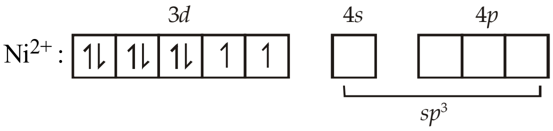
58. (c)

Complex	No. of electrons in outer *d* orbital	No. of unpaired electron (s)
$[Fe(CN)_6]^{3-}$	$3d^5$	1 (CN^- causes pairing of electrons)
$[Co(NH_3)_6]^{3+}$	$3d^6$	0
$[Co(oxal.)_3]^{3-}$	$3d^6$	0
$[Ni(H_2O)_6]^{2+}$	$3d^8$	2
$[Pt(CN)_4]^{2-}$	$5d^8$	0 (CN^- causes pairing of electrons)
$[Zn(H_2O)_6]^{2+}$	$3d^{10}$	0

Thus L, M, O and P are diamagnetic.

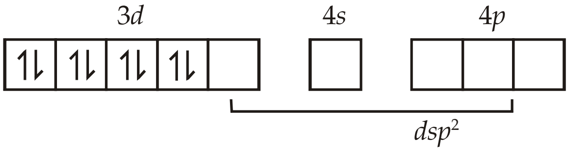
59. (d) $[Co(H_2O)_4(NH_3)_2]Cl_3$
= Diamminetetraaquacobalt (III) chloride.

60. (c) In both states (paramagnetic and diamagnetic) of the given complex, Ni exists as Ni^{2+} whose electronic configuration is $[Ar]\ 3d^8 4s^0$.



In the above paramagnetic state the geometry of the complex is sp^3 giving tetrahedral geometry.

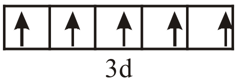
The diamagnetic state is achieved by pairing of electrons in $3d$ orbital.



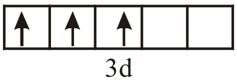
Thus the geometry of the complex will be dsp^2 giving square planar geometry.

61. **(b)** The electronic configuration of central metal ion in complex ions P, Q and R are

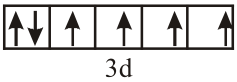
$P = [FeF_6]^{3-}; Fe^{3+}$:



$Q = [V(H_2O)_6]^{2+}; V^{2+}$



$R = [Fe(H_2O)_6]^{2+}; Fe^{2+}$



Higher the no. of unpaired electron(s), higher will be magnetic moment.
Thus the correct order of spin only magnetic moment is
$Q < R < P$

EXERCISE 4

1. **(c)** The ions present in the ionisation sphere are precipited Hence $[CrCl_2(H_2O)_4]Cl.2H_2O$ contains 1/3 Cl in ionisation sphere to be precipited by $AgNO_3$ as AgCl

2. **(b)** $\left[Pt\left(NH_3\right)_6\right]Cl_4 \rightleftharpoons \left[Pt\left(NH_3\right)_6\right]^{4+} + 4Cl^-$;

$Ag^+ + C\bar{l} \rightarrow AgCl$ (ppt)

3. **(d)** The complex furnishing least number of ions in solution will be poor electrolytic conductor.

4. **(d)** $[Fe(CN)_6]^{4-}$ complex ion contains $_{26}Fe^{2+}$ E.C is

$= 1s^2, 2s^2p^6, 3s^2p^6d^6$

(due to strong CN^- ligand, the electrons in 3d shell are paired)

C.N is 6 , hybridisation d^2sp^3 , octahedral, diamagnetic since no unpaired electron is present.

5. **(b)** $Na_3[Co(ONO)_6]$ IUPAC name is
sodium hexanitritocobaltate (III)

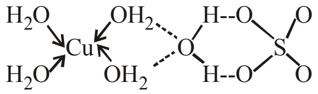
6. **(b)**

	$[Cr(H_2O)_6]^{3+}$	$[Fe(H_2O)_6]^{2+}$	$[Cu(H_2O)_6]^{2+}$	$[Zn(H_2O)_6]^{2+}$
EC	**$3d^3$**	**$3d^6$**	**$3d^9$**	**$3d^{10}$**
Unpaired electrons	3	4	1	0

More the number of unpaired electrons, more is the paramagnetic character.

7. **(a)** The larger the ligand, the less is the stablilty of metal ligand complex.

8. **(a)** Four water molecules are coordinated to copper.



9. **(a)** For polymerisation of alkenes Ziegler Natta catalyst $(Al(C_2H_5)_3 + TiCl_3)$ is used.

10. **(c)**

Mn^{2+}	Cu^{3+}	Co^{3+}	Co^{2+}
$[Ar]3d^5$	$[Ar]3d^8$	$[Ar]3d^6$	$[Ar]3d^7$
No pairing	No pairing	Pairing	No pairing
of e^-	of e^-	of e^-	of e^-
Paramagnetic	Paramagnetic	Diamagnetic	Paramagnetic

11. **(c)**

	$Ni(CO)_4$	$Ni(PPh_3)_2 Cl_2$
O.S.	Ni^0	Ni^{2+}
E.C.	$[Ar]3d^84s^2$	$[Ar]3d^84s^0$
	Pairing of e^-	No pairing of e^-
Hybridization	sp^3 (tetrahedral)	sp^3 (tetrahedral)

12. **(c)** $[NiCl_4]^{2-}$, Ni^{2+} $[Ar]3d^8$, Cl is weak ligand hence no pairing of of e^- in d atomic orbitals therefore it is paramagnetic.

13. **(b)** $Na_2[CdCl_4]$ does not contain any unpaired electron hence colourless

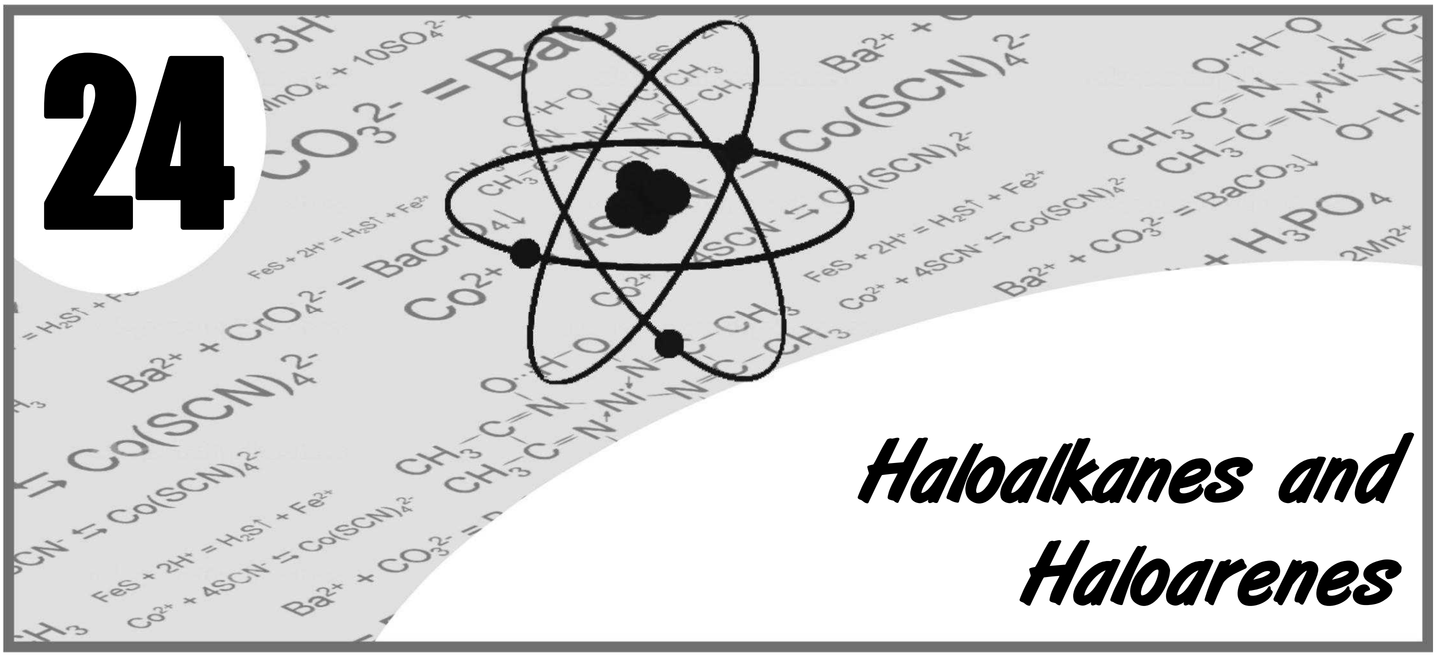
14. **(a)** $[Ni\ (H_2O)_6]^{2+}$ is paramagnetic.

15. **(c)** $[Fe(C_2O_4)_3]^{3-}$. The iron is present in the highest oxidation state Fe^{3+} and $C_2O_4^{2-}$ is a chelating ligand. Chelates are always form more stable complexes

16. **(d)** $K_2[Ni(EDTA)]$. Since EDTA is hexadentate and chelating and coordinates from six sides forming more stable complex

17. **(d)** In silver plating $K[Ag(CN)_2]$ is used which provides constant and required supply of Ag^+ ions as $Ag(CN)_2^-$ is very stable. But if $AgNO_3$ is used concentration of $[Ag^+]$ in solution will be very large. In that case Ag will be deposited at faster rate without any uniformity.

18. **(c)** In $[Co(CO)_5NH_3]^{2+}$ CO is bonded to cobalt through σ and π bonding



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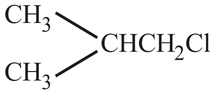
Haloalkanes and Haloarenes

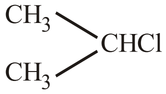
Halogen derivatives of alkanes, alkenes, alkynes and arenes are known as ***alkyl halides*** (haloalkenes), ***alkenyl halides*** (haloalkenes), ***alkynyl halides*** (haloalkynes) and *aryl halides* (halobenzenes), respectively. On the basis of the number of halogen atom, they are further classified as mono-, di-, tri- poly- and per-halohydrocarbons. The word ***perhalohydrocarbon*** means all the hydrogen atoms of the compound are replaced by corresponding number of halogen atoms.

Besides the nature and number of halogen atoms, alkyl halides may be classified into ***primary*** (1°), ***secondary*** (2°) and ***tertiary*** (3°) according to the nature of the carbon atom bearing halogen.



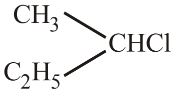
$(CH_3)_2CHCH_2Cl$

Isobutyl chloride (1°)
(–Cl present on 1°C)



$(CH_3)_2CHCl$

Isopropyl chloride (2°)
(–Cl on 2°C)



$(CH_3)(C_2H_5)CHCl$

sec. Butyl chloride (2°)
(–Cl on 2°C)

$(CH_3)_3CCl$

tert. Butyl chloride (3°)
(–Cl on 3°C)

Alkyl halides may show chain, position and optical isomerism; alkenyl halides may show geometrical; while aryl halides may show position isomerism.

PREPARATION :

(i) From alochols with HX, PX_3 (X = I, Br, Cl) or $SOCl_2$

$$R-OH + HX \longrightarrow RX$$

(a) Order of reactivity among HX : HI > HBr > HCl >> HF This is in accordance with the bond length, longer the H – X bond, weaker it will be.

(b) Order of reactivity among ROH : 3° > 2° > 1° > CH_3OH

(c) *tert*-Alcohols react with HX by S_N1 pathway, while primary alcohols react via S_N2, secondary may follow either or both of the paths (S_N1 and S_N2 are discussed later).

(d) Mixture of conc. HCl and anhydrous $ZnCl_2$ is used for differentiating three types of alcohols (3° > 2° > 1°) under the name of ***Lucas reagent***.

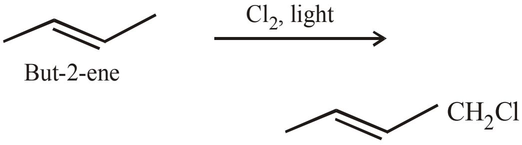
(e) Primary and secondary alcohols can best be converted to the corresponding chlorides (by $SOCl_2$), bromides (by PBr_3) and iodides, by PI_3 (P + I_2).

(f) $SOBr_2$ is less stable and SOI_2 does not exist, PBr_5 and PI_5 are highly unstable hence not used.

(ii) (a) Alkyl halides are generally not prepared by direct halogenation of alkanes because the reaction generally gives a mixture of several compounds. However, compounds containing only one type of hydrogen atom can be converted into monohalogeno products in good yield by taking excess of the concerned hydrocarbon; examples of such compounds are CH_4, CH_3CH_3, $(CH_3)_4C$, $C_6H_5CH_3$ etc.

(b) Since allylic hydrogen atoms are much more reactive than the vinylic hydrogen, former are easily replaced by halogen.

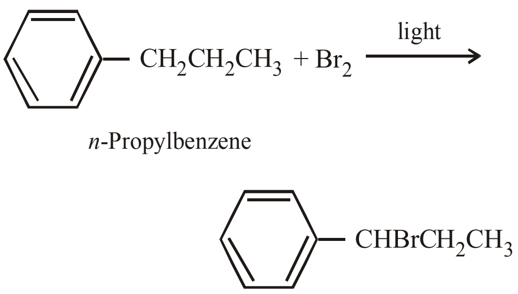
$$\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow{Cl_2,\ \text{light}} \underset{\text{Allyl chloride}}{ClCH_2CH=CH_2}$$



But-2-ene

1-Chlorobut-2-ene

(c) Benzylic hydrogens (hydrogen present on C attached directly to benzene) are more reactive, hence easily replaced than 1°, 2° or 3° hydrogen.



n-Propylbenzene

1-Bromo-1-phenylpropane

(d) Halogenation of hydrocarbons in presence of light, heat and absence of halogen carrier takes place through free-radical mechanism.

(e) More reactivity of benzylic and allylic hydrogens is due to stability of the corresponding free radical due to resonance.

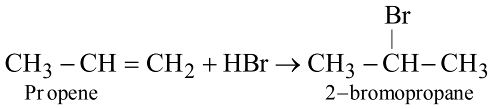
(f) Bromination at allylic and benzylic positions may best be carried by N-bromosuccinimide, **NBS** (***Wohl-Ziegler Reaction***).

(iii) Addition of hydrogen halides to alkenes is an example of electrophilic addition involving carbocations as intermediates (***ionic mechanism***).

Markownikoff's rule

(i) When an unsymmetrical alkene or alkyne reacts with unsymmetrical reagent, then negative part of reagent attach with that carbon atom which contains lesser number of hydrogen atom during the addition.

For example:



$$\underset{\text{Propene}}{CH_3-CH=CH_2}+HBr\rightarrow \underset{2\text{-bromopropane}}{CH_3-\overset{\overset{\displaystyle Br}{|}}{C}H-CH_3}$$

$$CH_2=CH_2+HBr\longrightarrow CH_3-CH_2Br$$

$$\underset{\substack{\text{Propene}\\ \text{(unsymmetrical alkene)}}}{CH_3CH=CH_2}+HBr\longrightarrow CH_3.CHBr.CH_3$$

(***Markownikoff's addition***)

(ii) Addition of HBr (not HCl, HI and HF) on alkenes in presence of peroxides takes place in ***anti-Markownikoff's way*** (***Peroxide effect***). Here addition takes place via ***free-radical mechanism.***

$$CH_3CH=CH_2+HBr\xrightarrow{\text{peroxide}}CH_3CH_2CH_2Br$$

(iv) Halide exchange method (*anti-Markownikoff's addition*) is considered to be best for alkyl fluorides and alkyl iodides.

For alkyl fluorides :

$$\underset{(X=Cl,Br,I)}{RCH_2X}+KF\xrightarrow[120°C]{\text{ethylene glycol}}RCH_2F+KX$$

Alkyl fluorides have lowest boiling point of all the alkyl halides, hence can be removed by distillation.

Swarts reaction

Alkyl chloride/ bromide is heated in presence of a metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3

CH_3–Br + AgF → CH_3F + AgBr

For alkyl iodides : **(Finkelstein reaction)**

$$\underset{(X=Cl,\,Br)}{CH_3CHXCH_3}+\underset{\text{Soluble in acetone}}{NaI}\xrightarrow{\text{acetone}}$$

$$CH_3CHICH_3+\underset{\text{Insoluble in acetone}}{NaX\downarrow}$$

(v) Hunsdiecker method (suitable for bromides) :

$$CH_3COOAg+Br_2\longrightarrow CH_3Br+CO_2+AgBr$$

(i) Reaction involves free radical mechanism.

(ii) Reaction gives an alkyl halide having one carbon atom less.

(iii) Yield of alkyl bromides follows the order : 1° > 2° > 3°.

(iv) Yield is very low in case of chlorides, while iodine in such cases react differently.

$$2RCOOAg+I_2\longrightarrow RCOOR+CO_2+2AgI$$

PHYSICAL PROPERTIES :

(i) Alkyl halides, although polar, are insoluble in water due to inability to form hydrogen bonds with water molecules.

(ii) Density :

RI > RBr > RCl (For the same R– or Ar– group)

$CH_3I > C_2H_5I > C_3H_7I$ (For the same halogen)

(iii) Methyl iodide is densest halide because contribution of alkyl part is minimum.

(iv) Boiling points :

(a) RI > RBr > RCl > RF (***When R is same***)

(b) $CH_3CH_2CH_2Cl > CH_3CH_2Cl > CH_3Cl$ (***For the same halide***)

(c) $CH_3CH_2CH_2CH_2Cl > CH_3CH_2CHClCH_3 > (CH_3)_2CHCH_2Cl > (CH_3)_3CCl$

(***For isomeric halides, b.p. decreases with the increase in branching***)

(v) Dipole moment : Except fluoride, dipole moment decreases with the decrease in electronegativity from Cl to I. Fluorides, although having highest electronegativity have lower dipole moment than chloride due to the very small size of F and hence very small C–F bond length which outweighs the effect of electronegativity (recall that $\mu = d \times e$). Thus the order for dipole moment is $CH_3Cl > CH_3F > CH_3Br > CH_3I$.

(vi) Stability order : R – F > R – Cl > R – Br > R – I

(***Similar to C – X bond length***)

CHEMICAL PROPERTIES :

1. *Nucleophilic substitution :*

(i) Alkyl halides undergo nucleophilic substitution very easily.

$$\mathbf{\overset{\delta+}{R}-\overset{\delta-}{X}+:Z\ (nucleophile)\longrightarrow R-Z+:X^-}$$

Source of :Z	***Product***	***R–Z and its Name***
Na^+OH^-	$R-OH$	Alcohols
H_2O (water)	$R-OH$	Alcohols
Na^+OR'	$R-OR'$	(*Williamson Ethers synthesis*)
I^-	$R-I$	Alkyl iodides
Source of :Z	***Product***	***R–Z and its Name***
$RCOO^-$	$R-OOCR'$	Esters
K^+CN^-	$R-CN$	Nitriles
AgCN (covalent)	$R-CN+R-NC$	Nitriles and Isonitriles
$K^+NO_2^-$	$R-O-N=O$	Alkyl nitrites
$AgNO_2$ (covalent)	$RONO+R-NO_2$	Nitrites and Nitroalkanes
K^+SH^-	$R-SH$	Thiols (Mercaptans)
$K^+SR'^-$	$R-SR'$	Thioethers (Sulphides)
N_3^-	$R-N=N^+=N^-$	Azides
NH_3	$R-NH_2$	Primary amines
$R'NH_2$	$R-NHR'$	Secondary amines
PPh_3	$[R-PPh_3]^+X^-$	Phosphonium salts
$R'C\equiv C^-$	$R'C\equiv C-R$	Alkynes
$Ar-H+AlCl_3$	$Ar-R$	Alkylbenzenes **(Friedel-Craft reaction)**
$^-CH(COOC_2H_5)_2$	$R-CH(COOC_2H_5)_2$	Malonic esters
$^{\delta-}R'-M^{\delta+}$	$R-R$	Alkanes **(Coupling)**
$H:^-$ (from $LiAlH_4$)	$R-H$	Alkanes **(Reduction)**

In case of AgCN and $AgNO_2$, two isomeric products are formed.

$$R-X+AgCN\longrightarrow \underset{\text{Alkyl nitrile}}{R-C\equiv N} + \underset{\text{Alkyl isonitrile (major)}}{RN\overset{\rightarrow}{=}C}$$

$$R-X+AgNO_2\longrightarrow \underset{\text{Nitroalkane}}{R-N\overset{\nearrow O}{\underset{\searrow O}{}}} + \underset{\text{Alkyl nitrite (minor)}}{R-O-N=O}$$

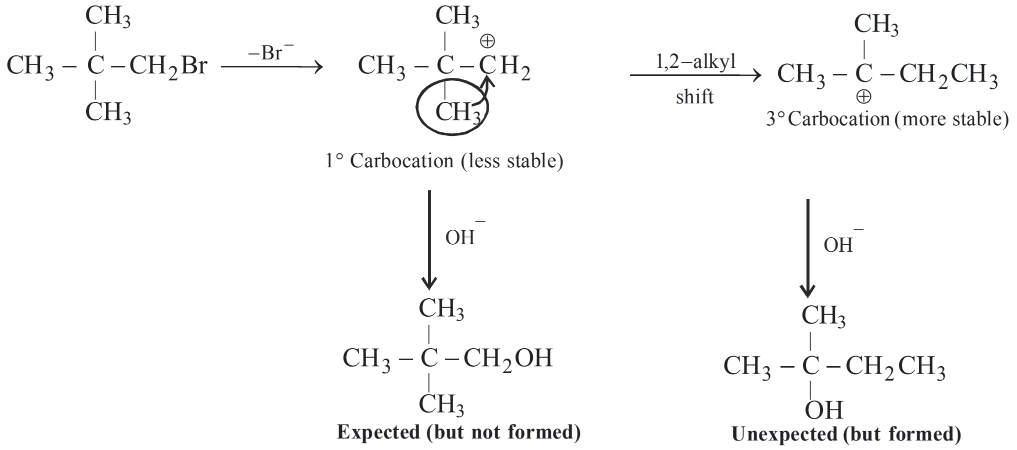
Nucleophilic substitution reactions occur either by S_N1 or S_N2 mechanism.

(ii) **S_N1 (Unimolecular nucleophilic substitution)** : Although it is a two step process, the rate of reaction depends only upon the **first (slow)** step which involves ionization of the alkyl halide to form carbocation. Hence rate of reaction depends only upon the concentration of the alkyl halides, $r=k[RX]$ and is independent of the concentration of the nucleophile which adds on the carbocation in the ***second (fast)*** step.

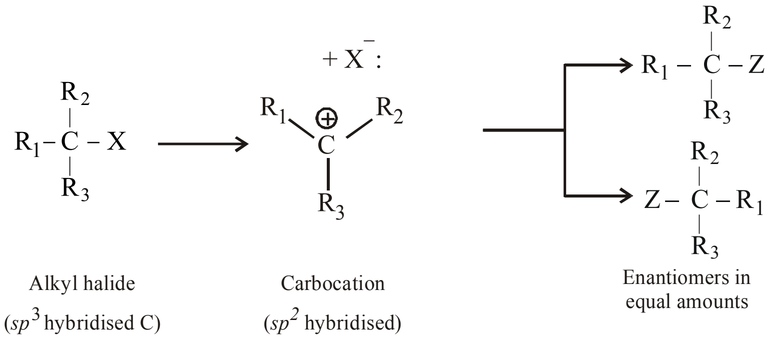
$$R-X\xrightarrow[\text{(slow)}]{-X^-}R^+\xrightarrow[\text{(fast)}]{:Z}R-Z$$

(a) In S_N1 mechanism, carbocations are formed as intermediate, hence more the stability of the intermediate carbocation, greater are chances for their formation and hence more reactive will be the parent alkyl halide for S_N1 reaction. Hence the order of reactivity of alkyl halides toward S_N1 reaction follows the order : 3° > 2° > 1°

(b) When the intermediate carbocation is capable of undergoing rearrangement, lesser stable carbocation (1° < 2° < 3°) rearranges to the more stable carbocation and hence under such conditions unexpected product is formed.

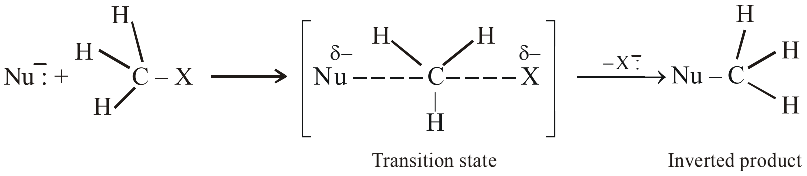


(c) If the alkyl halide is optically active, the product formed in S_N1 reaction is always a racemic mixture. This is due to the formation of carbocations as intermediates which, being planar (sp^2 hybridised) can be equally attacked by the nucleophile on either side of the face forming two enantiomers.

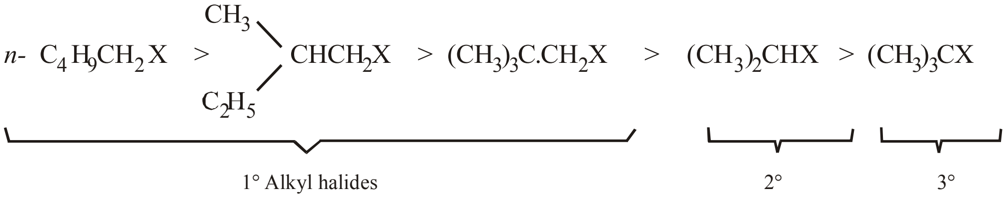


However, remember that the departing halide shields to some extent, the frontal attack of the carbocation, recemization is only partial and the inverted configuration predominates.

(iii) **S_N2** *(Bimolecular Nucleophilic Substitution) :* The rate of S_N2 reactions depends on the concentration of alkyl halide as well as nucleophile, *i.e.* $r = k\,[RX][Nu]$. This implies that both the reactants are involved in the rate-determining step, i.e. the reaction occurs in one step only or it is a *concerted reaction.* Concerted reactions occur through a transition state (an imaginary state in which both the reactant molecules are partially linked to each other).



Remember that the nucleophile attacks from the back side of the halide ion, bulkier the alkyl group present on the carbon bearing halogen lesser will be its tendency to undergo S_N2 reaction. Thus the reactivity of alkyl halides towards S_N2 mechanism is



$$\underbrace{n\text{-}C_4H_9CH_2X > \begin{matrix}CH_3\\ C_2H_5\end{matrix}\!\!>CHCH_2X > (CH_3)_3C.CH_2X}_{1^\circ\ \text{Alkyl halides}} > \underbrace{(CH_3)_2CHX}_{2^\circ} > \underbrace{(CH_3)_3CX}_{3^\circ}$$

Since the nucleophile attacks from the back side and the halide ion leaves from the front side, the product obtained will have an ***inverted configuration [Walden inversion].*** This implies that if the alkyl halide is optically active, the product will also be optically active, although the sign of rotation may be same or different. All primary alkyl halides undergo substitution via S_N2 pathway.

Remember :

(a) Polar solvents favour S_N1 reactions while non-polar solvents favour S_N2 reactions.

(b) Low concentration of nucleophile favours S_N1 reactions, while high concentration favours S_N2.

(c) Rate of reaction in S_N1 mechanism is independent of the nature of the attacking nucleophile because it is not involved in rate-determining step; while rate of S_N2 reactions depends upon the strength of the nucleophile. Strength of some common nucleophiles is

$:CN^- > :OR^- > :OH^- > CH_3COO^- > H_2O$

(d) Primary alkyl halides undergo S_N2 reactions, 3° halides S_N1, while 2° halides may undergo S_N2 and/or S_N1 mechanism.

2. ***Elimination reactions :***

(i) Alkyl halides lose a molecule of hydrogen halide *(dehydrohalogenation)* when heated with alcoholic potash. Dehydrohalogenation is a β-elimination reaction in which halogen and hydrogen atoms are lost from the two adjacent carbon atoms.

$$\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \quad \text{or} \quad \underset{\text{2-Bromopropane}}{CH_3CHBrCH_3}$$

$$\xrightarrow[\text{heat}]{\text{alc. KOH}} \underset{\text{Propene}}{CH_3CH = CH_2} + HBr$$

(ii) Dehydrohalogenation is governed by *Saytzeff rule* according to which more highly substituted alkene is the major product, *i.e.* hydrogen atom is lost from the carbon atom carrying minimum number of hydrogen atoms ***(poor becomes poorer).***

$$\underset{\text{2-Bromobutane}}{CH_3CH_2CHBrCH_3} \xrightarrow[\text{heat}]{\text{alc. KOH}}$$

$$\underset{\text{1-Butene (minor)}}{CH_3CH_2CH = CH_2} + \underset{\text{2-Butene (major)}}{CH_3CH = CHCH_3}$$

(iii) Ease of dehydrohalogenation among halides is : 3° > 2° > 1°

(iv) Elimination reactions dominate over substitution when strong Bronsted base [*e.g.* NH_2^-, Me_3CO^-, $\overline{O}C_2H_5$ etc.) is used and alkyl halide is 3° or 2°.

Remember:

(a) 1° Halides undergo S_N2 reactions except when a hindered strong base like Me_3CO^- is used.

(b) 2° Halides undergo S_N2 reactions with weak base like I^-, CN^-, $RCOO^-$ etc., and elimination reaction with strong base like RO^-.

(c) 3° Halides undergo S_N1 reaction in absence of a strong base and only solvent acts as a base/nucleophile (solvolysis), however in presence of strong base (^-OR) elimination reaction predominates.

3. ***Reaction with metals :***

(i) $R - X + 2Li \xrightarrow{\text{dry ether}} R - Li + LiX$

(ii) $R - X + Mg \xrightarrow{\text{dry ether}} R - MgX$

(Grignard reagent)

(iii) $4CH_3CH_2Cl + 4\ Pb/Na \xrightarrow{\text{dry ether}} \underset{\text{TEL}}{(C_2H_5)_4Pb} + 4NaCl + 3Pb$

(iv) $CH_3Cl + 2Na \xrightarrow{\text{dry ether}} \underset{\text{Very reactive}}{[CH_3Na]} \xrightarrow[\text{dry ether}]{CH_3Cl} CH_3CH_3$

(Wurtz reaction)

Tetraethyl lead, commonly known as TEL, is used as an ***anti-knocking agent*** in petrol.

(a) Solvent used must be perfectly anhydrous because even a trace of water or alcohol reacts with metals to form insoluble hydroxide or alkoxide that coat the surface of the metal. Moreover, water or alcohol may react with the product (organometallic compound) to form hydrocarbon.

(b) Alkyl lithiums react with copper halides to form higher alkanes **(Corey-House synthesis)**

$$2RLi \xrightarrow[(-LiI)]{CuI} R_2CuLi \xrightarrow[(1^\circ \text{ halide})]{R'X} R - R'$$

(c) Among alkyl halides, order of reactivity is I > Br > Cl > F.

(d) The reactivity of a metal toward an alkyl halide depends upon its reduction potential; more easily a metal is reduced, more reactive it is, *e.g.* Mg > Zn.

4. ***Reduction***

(a) $R - X + Zn + HX \longrightarrow R - H + ZnX_2$

In this reaction, zinc atoms transfer electrons to the carbon atom of the alkyl halide. Zinc is a good reducing agent because it has two electrons in an orbital far from the nucleus, which are readily donated to an electron acceptor.

(b) $R - X \xrightarrow{LiAlH_4} R - H$

(c) $R - X + H_2 \xrightarrow{Ni} R - H + HX$

(d) $R - X \xrightarrow{Mg} R - MgX \xrightarrow[\text{or } D_2O]{H_2O} RH \text{ (or RD)}$

(e) $R - I + HI \xrightarrow[423\text{ K}]{\text{red P}} R - H + I_2$

5. ***Halogenation :***

$$CH_3Cl \xrightarrow{Cl_2,\, hv} CH_2Cl_2 \xrightarrow{Cl_2,\, hv} CHCl_3 \xrightarrow{Cl_2,\, hv} CCl_4$$

6. ***Isomerisation :***

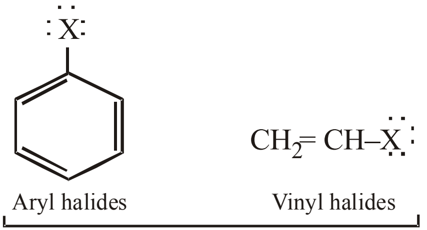
$$\underset{\text{1–Bromopropane}}{CH_3CH_2CH_2Br}\xrightarrow[\text{anhy. AlCl}_3]{573\text{ K}}\underset{\text{2–Bromopropane}}{CH_3CHBrCH_3}$$

ARYL AND ARYL SUBSTITUTED ALKYL HALIDES

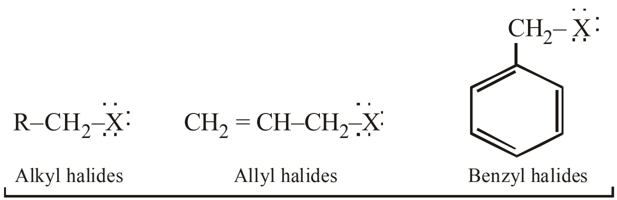
1. **Aryl halides** are the compounds having halogen atom directly attached to the aromatic ring. They are represented by the general formula Ar–X where Ar may be phenyl, substituted phenyl or other aromatic system, *e.g.* naphthyl.

   All compounds containing aromatic ring and a halogen atom should not be considered as aryl halides, *e.g.* benzyl chloride, $C_6H_5CH_2Cl$ because chlorine is not directly attached to the ring. Such ***compounds*** resemble alkyl halides in structure as well as in properties, hence grouped as ***aryl substituted alkyl halides.***

2. The carbon-halogen bonds of aryl halides are both shorter and stronger (due to possibility of resonance) than the carbon-halogen bonds of R–X and in this respect as well as in their chemical behaviour, they resemble vinyl halides ($CH_2 = CHX$) more than alkyl halides.



Halogen attached to C is sp^2 hybridised C, C–X bond is shorter and stronger because of partial double bond character due to delocalisation of electrons on halogens



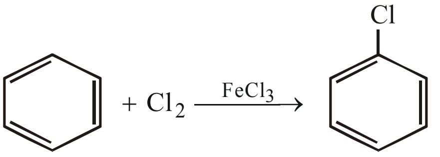
Halogen attached to sp^3 hybridised C. Delocalisation of electrons on halogen is not possible, hence C–X bond does not acquire double bond character, hence it is weaker and reactive.

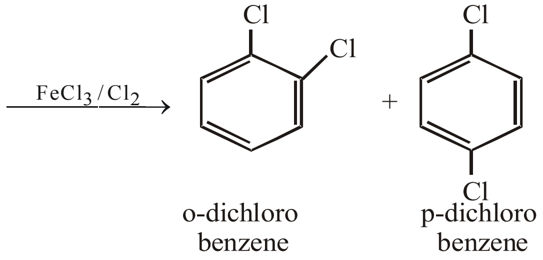
3. The strength of the C–X bonds causes aryl halides to react very slowly in reactions in which cleavage of C–X bond is rate determining, *i.e.* nucleophilic substitution.

PREPARATION :

By direct halogenation of aromatic hydrocarbons.

(a) ***Nuclear halogenation*** (suitable for aryl chlorides and bromides)





(i) Fluorination is difficult to control, while iodination is too slow to be useful. Moreover, iodination being reversible (because of reducing character of HI), the reaction requires the use of an oxidising agent like HNO_3, HIO_3, HgO etc.

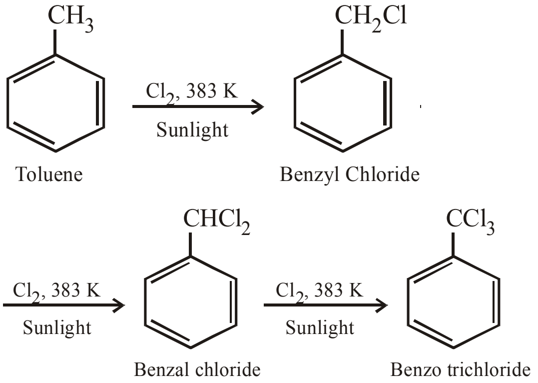
$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

(ii) Introduction of second –Cl is difficult as compared to first, because of electron withdrawing character of chlorine (deactivating nature of halogens).

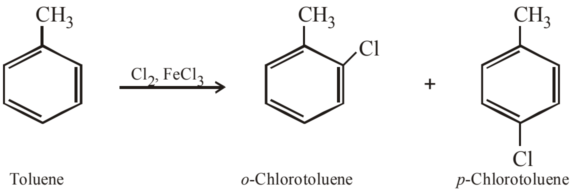
(iii) Nuclear halogenation is an ***electrophilic substitution reaction***.

(b) Side chain halogenation :

(i) Halogenation of higher arenes, *i.e.* other than benzene, in presence of light or heat and in the absence of a halogen carrier introduces halogen in the side chain.



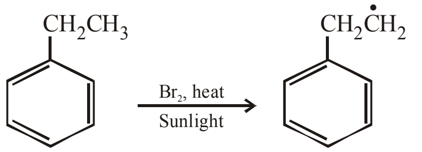
Remember halogenation of toluene at low temperature, in the absence of light and in presence of catalyst, gives nuclear substituted products.



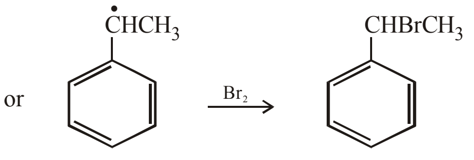
Generally, p-isomer predominates due to steric hindrance in the o-position.

(ii) Side chain halogenation occurs by ***free radical mechanism***.

(iii) In case, the side chain is larger than methyl group, side chain halogenation mainly occurs at the ***benzylic carbon*** (carbon directly attached to benzene nucleus). This is due to stability of benzylic free radical due to resonance.



2-phenylethyl radical
(less stable, 1° free radical,
2° benzylic radical)

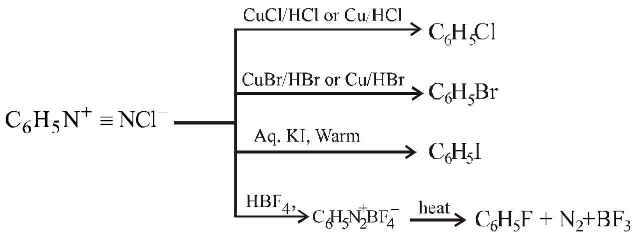


Benzylic free radical (more stable)

1-Bromo-1-phenylethane **(Major product)**

(iv) Side chain halogenation can also be carried out with SO_2Cl_2 in presence of light and a trace of peroxides or with NBS (N-bromosuccinimide) in presence of light and trace of peroxide like benzoyl peroxide.

2. By the decomposition of diazonium salts :



(i) When CuCl/HCl or CuBr/HBr is used, the reaction is called ***Sandmeyer reaction***. It is the halogen attached to cuprous halide which enters the ring.

(ii) When Cu/HCl or Cu/HBr is used, the reaction is called ***Gattermann reaction.***

(iii) Thermal decomposition of benzenediazonium tetrafluoroborate to give fluorobenzene is called *Balz-**Schiemann reaction.***

(iv) This method for preparing aryl halides is more important than direct halogenation of arenes in two respects.

(a) Fluorides and iodides can be easily prepared.

(b) Halogenation gives a mixture of o- and p- isomers which are difficult to separate.

3. Hunsdiecker method :

$$C_6H_5COOAg + Cl_2(\text{or } Br_2) \longrightarrow C_6H_5Cl + CO_2 + AgCl$$

4. Industrial method for chlorobenzen *(Raschig process)*

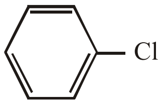
$$2C_6H_6 + 2HCl + O_2 \xrightarrow[500K]{CuCl_2} 2C_6H_5Cl + 2H_2O$$

Physical Properties :

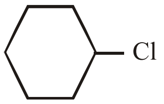
(i) Like alkyl halides, aryl halides are insoluble in water due to their incapability of forming H-bonds.

(ii) Aryl halides are less polar than alkyl halides because in aryl halides, halogen is present on sp^2 hybridised carbon which is more electronegative than the sp^3 hybridised carbon of alkyl halides or halocyclohexanes. Consequently, the electroneg ativity difference between C and Cl is low in aryl halides than in alkyl halides.

(iii) Possibility of resonance in chlorobenzene makes the C–Cl bond shorter and hence, its dipole moment is less than that of cyclohexyl chloride.



Chlorobenzene
(C–Cl bond is less polar
and shorter in length), μ = 1.7 D



Chlorocyclohexane
(C–Cl bond is more polar
and longer in length), μ = 2.2 D

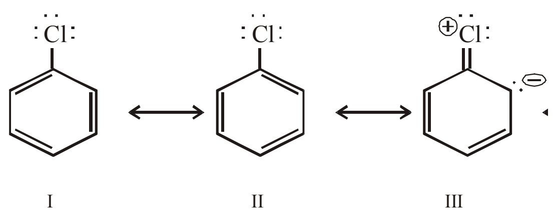
(iv) Although, the three isomeric dihalobenzenes have nearly same boiling points, the p-isomer has higher melting point than the o- and m-isomers. This is due to symmetrical nature of the *para* isomer due to which it is better packed in the crystal lattice. This explains why only the *para* isomer crystallises on cooling a solution containing *ortho* and *para* isomers.

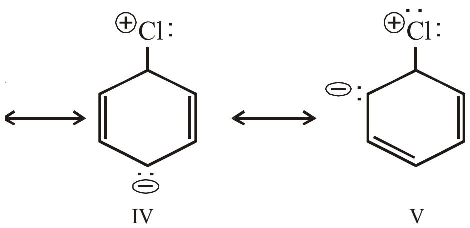
(v) Due to strong intercrystalline forces, *the higher melting point of para isomer is less soluble in a given solvent than the ortho isomer.*

Chemical Properties

1. Low reactivity towards nucleophilic substitution :

(i) Aryl halides (like vinyl halides) are less reactive towards nucleophilic substitutions under ordinary conditions (difference from alkyl halides). This low reactivity is due to *(a)* resonance effect, *(b)* sp^2 hybridisation of carbon atom holding the halogen atom and *(c)* less polarity of the C–X bond.





IV V

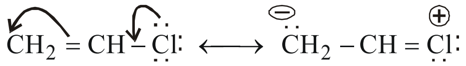
Resonating structures of chlorobenzene

Possibility of resonance in aryl halides produces two results

(a) Stabilisation of the molecule by delocalisation of electrons.

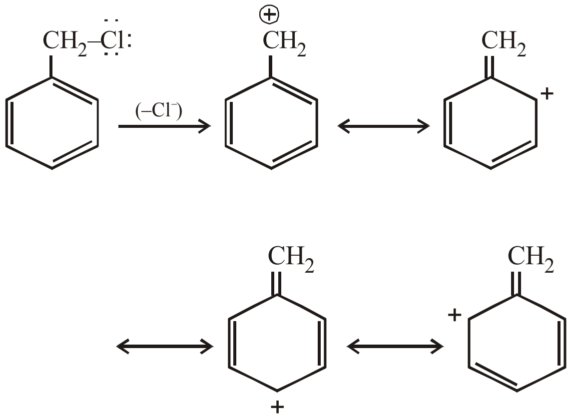
(b) The C–Cl bond acquires some double bond character (structures III, IV and V) and thus becomes shorter and stronger than the C–Cl bond in alkyl halides.

On the same ground, low reactivity of vinyl chloride is explained



$$CH_2=CH-\underset{\cdot\cdot}{\ddot{Cl}}: \longleftrightarrow \overset{\ominus}{\ddot{C}}H_2-CH=\overset{\oplus}{\underset{\cdot\cdot}{Cl}}:$$

(ii) Conversely, benzyl halides do not show delocalisation of electrons of the halogen atom, hence its halogen is quite reactive towards nucleophilic substitutions (similarity with alkyl halides). Moreover, benzyl halides are even more reactive than alkyl halides, because the carbocation (benzyl) formed after the removal of halide ion is stabilised by resonance (remember higher is the stability of a species, easier will be its formation).



Similar is the case of allyl carbocation formed from allyl halides.

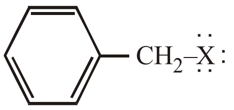
$$\underset{\text{Allyl bromide}}{CH_2=CHCH_2Br} \xrightarrow[(-Br^-)]{} CH_2=CH-\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2-CH=CH_2$$

(iii) Thus halogen derivatives can be categorised into two main groups on the basis of reactivity of the halogen atom.

(a) Those in which halogen is present on sp^3-hybridised carbon atom, such halogens and corresponding halides are highly reactive. For example,

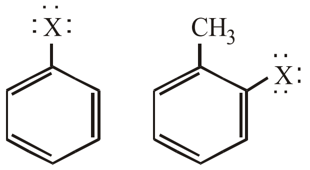
$R-CH_2-\underset{\cdot\cdot}{\ddot{X}}:$ Alkyl halides

$CH_2=CH-CH_2-\underset{\cdot\cdot}{\ddot{X}}:$ Allyl halides



Benzyl halides

(b) Those in which halogen is present on sp^2-hybridised carbon atom, such halogens are relatively inert. For example,

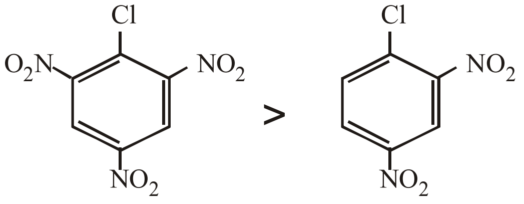


Aryl halides

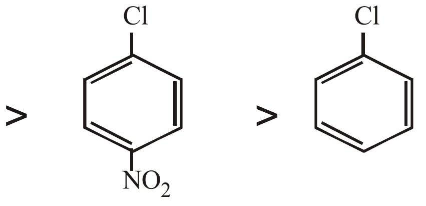
$CH_2=CH-X$

Vinyl halides

(iv) However, aryl halides having electron-withdrawing groups (like $-NO_2$, $-CN$, $-COOH$, $-SO_3H$ etc.) in ***ortho*** and ***para*** positions undergo nucleophilic substitution very easily. Further, greater the number of such groups in *o*- and *p*- positions, more rapid is the reaction and hence less vigorous conditions are required. Thus, reactivity of chlorine in the following compounds towards nucleophilic substitution follows the order.



2,4,6-Trinitrochlorobenzene 2,4-Diinitrochlorobenzene



p-Nitrochlorobenzene Chlorobenzene

Remember that the electron-withdrawing groups activate chlorine of chlorobenzene towards nucleophilic substitution, they deactivate the benzene nucleus towards electrophilic substitution.

(v) Since electron-withdrawing groups activate halogen toward nucleophilic substitution, electron-releasing groups (like –OH, $-NH_2$, $-OCH_3$, –R etc.) deactivate toward nucleophilic substitution.

(vi) Aromatic nucleophilic substitution proceeds through mechanisms different from the S_N2 and S_N1 mechanism of alkyl halides.

(a) Bimolecular mechanism is applicable to reactions of aryl halides having electron-withdrawing groups with the usual nucleophiles like NaOH, CH_3ONa etc. Here carbanion is formed as an intermediate.

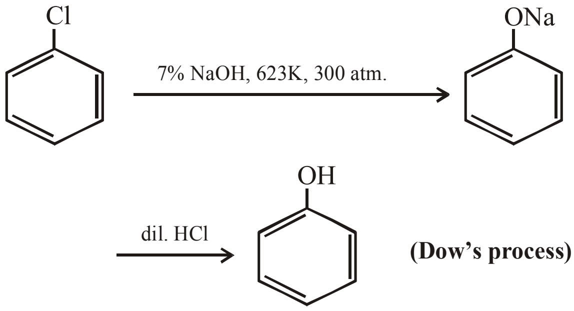
(b) Benzyne mechanism is applicable when aryl halides are treated with a strong base like NH_2^- or with the usual nucleophiles like NaOH, NH_3, CH_3ONa etc. under drastic conditions.

(vii) ***Relative reactivity of halogens towards nucleophilic substitution***. The order of reactivity of the halogen atom in aryl halides is opposite to that observed in alkyl halides ($R-I > R-Br > R-Cl > R-F$). In aromatic nucleophilic substitution, fluoride is the most reactive and iodide the least. $Ar-F > Ar-Cl > Ar-Br > Ar-I$

The unusually high reactivity of aryl fluorides (although having a strong C – F bond) is due to very high electronegativity of fluorine due to which it stabilises the carbanion, formed as intermediate during the reaction, most easily.

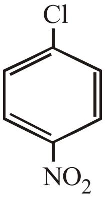
2. ***Important nucleophilic substitution reactions :***

(i)

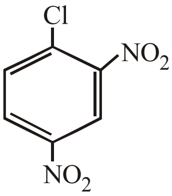


(Dow's process)

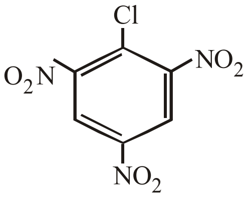
Note that introduction of $-NO_2$ group in *p*– and *o*– positions make the substitution of –Cl by –OH easier as it is evident by increased mild conditions.



Requires 15% NaOH and 433K

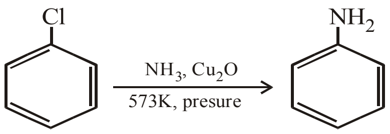


Requires weak base Na_2CO_3 and 403K

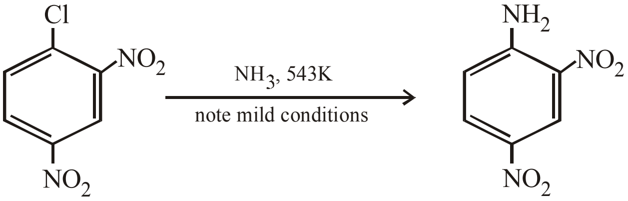


Undergoes hydrolysis even by warming with H_2O

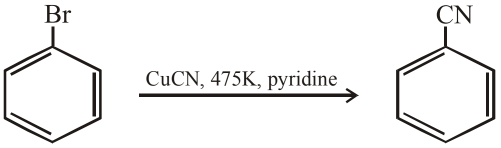
(ii)



(Dow's process)



(iii)



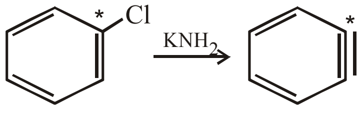
Benzonitrile

Benzyl chloride undergoes all the above reactions under mild conditions

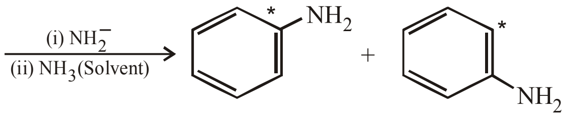
$$C_6H_5CH_2Cl \xrightarrow[\text{aq. KCN}]{\text{aq. } NH_3,\text{ aq. KOH}} C_6H_5-CH_2-Y$$

(where $-Y = -NH_2, -OH, -CN$)

(iv) However, simple aryl halides undergo nucleophilic substitution very easily by strong basic nucleophiles, like amide ion, *via* benzyne mechanism.



Chlorobenzene Benzyne



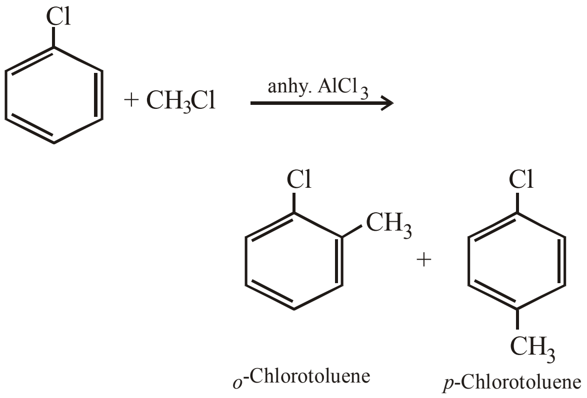
Aniline having C–NH_2 Aniline having C–NH_2

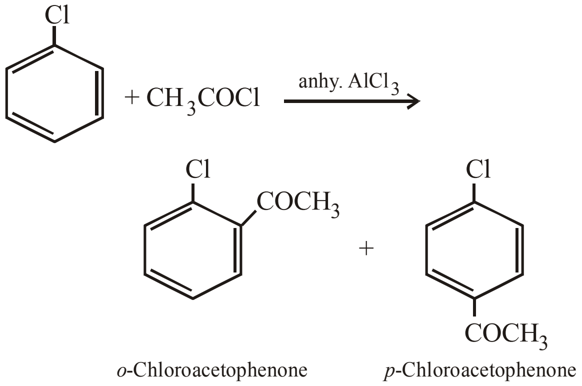
where $*$ ***indicates isotopically labelled carbon,*** *i.e. C-14.*

Benzyl chloride does not form benzyne intermediate.

(a) Remember triple bond of benzyne is different from the triple bond of alkynes, in benzyne one of the π bonds is formed by *p–p* overlap while the other by sp^2–sp^2 overlap.

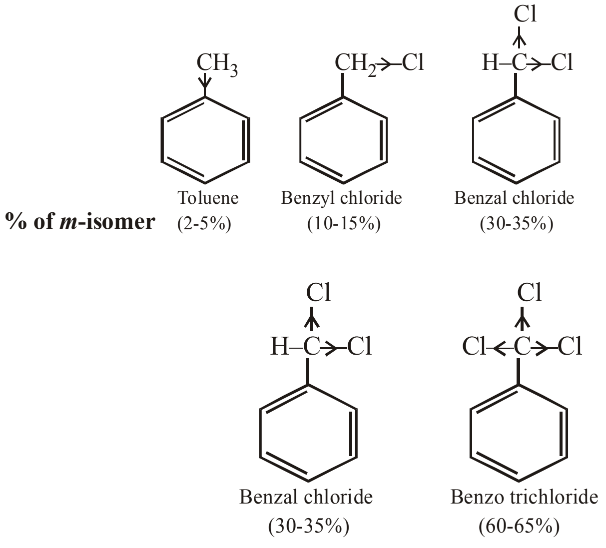
3. ***Electrophilic substitution :*** Remember that halogens are *deactivating* but *o, p*–directing. Thus chlorination, nitration, sulphonation and Friedel-Craft reaction forms a mixture of *o*- and *p*-chlorosubstituted derivatives, e.g.





However, unlike CH_3Cl, chlorobenzene does not undergo Friedel-Craft reaction with benzene. This is because of unstability of $C_6H_5^+$ cation.

Benzyl chloride also undergoes electrophilic substitution easily and mainly in the *o*- and *p*-positions. However, here percentage of *m*- too is significant (10-15%) as compared to that in toulene. Formation of *m*-isomer is due to the presence of Cl as $-CH_2 \rightarrow Cl$ which decreases the electron-releasing power of the parent methyl group due to its electron withdrawing nature. Thus we can explain the increased percentage of the *m*-isomer with the increase in number of Cl atoms in the $-CH_3$ group.



4. ***Other reactions :***

(i) ***Formation of Grignard reagent*** : Since chlorobenzene is less reactive than methyl chloride, THF (a higher boiling solvent) is used.

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + Mg \xrightarrow{\text{Tetrahydrofuran (THF)}} C_6H_5MgCl$$

(ii) ***Fittig reaction*** :

$$C_6H_5Cl + 2Na + ClC_6H_5 \xrightarrow{\text{dry ether}} \underset{\text{Diphenyl}}{C_6H_5C_6H_5}$$

(iii) ***Wurtz-Fittig reaction*** :

$$C_6H_5Cl + 2Na + ClCH_3 \xrightarrow{\text{dry ether}} \underset{\text{Toluene}}{C_6H_5CH_3}$$

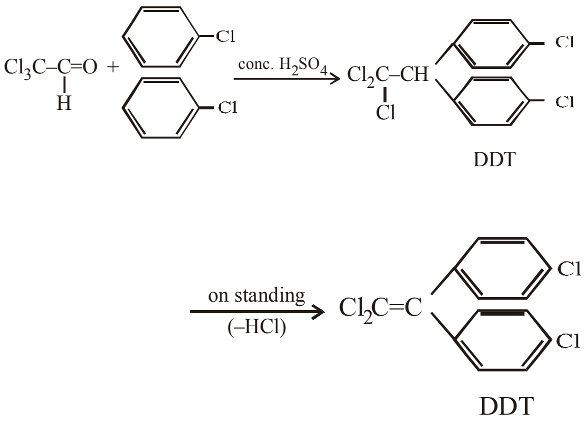
(iv) ***Ullmann reaction*** :

$$C_6H_5I + 2Cu + IC_6H_5 \xrightarrow{\text{heat}} \underset{\text{Diphenyl}}{C_6H_5C_6H_5}$$

(v) ***Reduction*** : $C_6H_5Cl + 2[H] \xrightarrow[\text{or Ni-Al/NaOH}]{\text{Zn/Cu}} \underset{\text{Benzene}}{C_6H_6}$

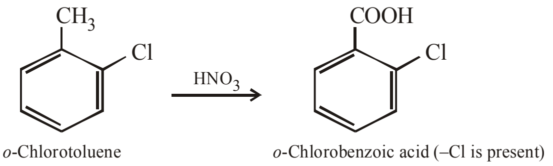
Benzyl chloride undergoes all the above reactions forming $C_6H_5CH_2MgCl$, $C_6H_5CH_2CH_2C_6H_5$ (dibenzyl), $C_6H_5CH_2CH_3$, $C_6H_5CH_2CH_2C_6H_5$ and $C_6H_5CH_3$ respectively.

(vi) Condensation with chloral to form DDT, 2,2-bis (4-chlorophenyl)–1, 1, 1-trichloroethane.

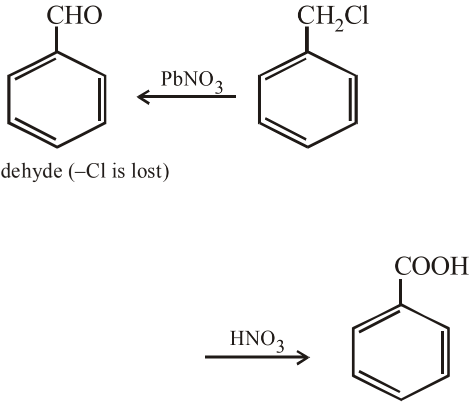


DDT is non-biodegradable and slowly loses a molecule of HCl to form another compound *p, p′*–dichlorodiphenyldichloroethene (DDE) which hinders with the egg shell formation of birds with the result eggs break off before hatching.

(vii) ***Oxidation of the side chain*** *:*



o-Chlorotoluene → *o*-Chlorobenzoic acid (–Cl is present)



Benzaldehyde (–Cl is lost)

Benzoic acid (–Cl is lost)

POLYHALOGEN DERIVATIVES

1. Dihalogen derivatives of alkanes may be ***vicinal*** (when two halogen atoms are present on adjacent carbon atoms), ***gem*** (when two halogen atoms are present on the same carbon atom) and α, ω (when two halogen atoms are present on the two terminal carbon atoms).

$$\underset{\substack{vicinal\text{–Dihalide}\\ \text{(Alkylene halides)}}}{CH_3CH_2CHClCH_2Cl} \qquad \underset{\substack{gem\text{–Dihalide}\\ \text{(Alkylidene halides)}}}{CH_3CH_2CH_2CHCl_2}$$

$$\underset{\substack{\alpha,\omega\text{–Dihalide}\\ \text{(Polymethylene dihalides)}}}{ClCH_2CH_2CH_2Cl}$$

2. **Preparation :**

(i) $CH_2=CH_2+Cl_2 \longrightarrow ClCH_2-CH_2Cl$

For *vic*-dihalides

(ii) $HOCH_2-CH_2OH \xrightarrow[\text{or } PCl_5]{HCl,\ 475K} ClCH_2-CH_2Cl$

For *vic*-dihalides

(iii) $CH\equiv CH \xrightarrow{HCl} CH_2=CHCl \xrightarrow{HCl} CH_3CHCl_2$

For *gem*-dihalides

(iv) $CH_3CHO \xrightarrow{PCl_5} CH_3CHCl_2+POCl_3$

For *gem*-dihalides

3. **Properties :**

(i) ***Dehydrohalogenation*** *:* Both give alkynes.

$$\underset{\text{Ethylene chloride}}{ClCH_2-CH_2Cl} \quad \text{or} \quad \underset{\text{Ethylidene chloride}}{CH_3CHCl_2} \xrightarrow{\text{alc. KOH}}$$

$$\underset{\text{Vinyl chloride}}{CH_2=CHCl} \quad \text{or} \xrightarrow[\text{preferably } NaNH_2]{\text{alc. KOH}} \underset{\text{Acetylene}}{HC\equiv CH}$$

(ii) ***Dehalogenation*** : Both give alkenes.

$$ClCH_2-CH_2Cl \quad \text{or} \quad CH_3CHCl_2 \xrightarrow[\text{heat}]{Zn/CH_3OH}$$

$$CH_2=CH_2+ZnCl_2$$

(iii) ***Hydrolysis*** *:* Two give different products.

$$\underset{\text{Ethylene chloride}}{ClCH_2-CH_2Cl}+2KOH\ (aq.) \longrightarrow$$

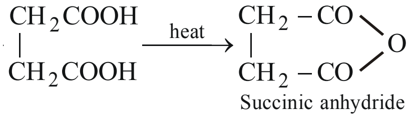
$$\underset{\text{Ethylene glycol}}{HOCH_2-CH_2OH}+2KCl$$

$$CH_3CHCl_2+2KOH\ (aq.) \xrightarrow[(-2\ KCl)]{}$$

$$\underset{\text{Unstable}}{CH_3CH(OH)_2} \xrightarrow[(-H_2O)]{} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

(iv) Reaction with aq. KCN followed by hydrolysis give different products.

$$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array} \xrightarrow{\text{aq. KCN}} \begin{array}{l} CH_2CN \\ | \\ CH_2CN \end{array} \xrightarrow{\text{hydrolysis}}$$



Succinic anhydride

$$\underset{\text{Ethylidene chloride}}{\begin{array}{l} CH_3 \\ | \\ CHCl_2 \end{array}} \xrightarrow{\text{aq. KCN}} \begin{array}{l} CH_3 \\ | \\ CH(CN)_2 \end{array} \xrightarrow{\text{hydrolysis}}$$

$$\underset{\text{Methylmalonic acid}}{\begin{array}{l} CH_3 \\ | \\ CH(COOH)_2 \end{array}} \xrightarrow{\text{heat}} \underset{\text{Propanoic acid}}{\begin{array}{l} CH_3 \\ | \\ CH_2COOH \end{array}}$$

Effect of heating on dicarboxylic acids : Dicarboxylic acids having two –COOH group on the same carbon atom give monocarboxylic acids, those having two –COOH groups on C_1 and C_2 or on C_1 and C_3 give anhydrides, those having two –COOH groups on C_1 and C_4 and C_1 and C_5 give cyclic ketones **(Blanc rule)**.

CHLOROFORM (TRICHLOROMETHANE) :

1. **Preparation :**

(i) $CH_4 + 3Cl_2 \xrightarrow[\text{controlled chlorination}]{\text{Sunlight}} CHCl_3 + 3HCl$

(ii) By distilling ethanol or acetone with a paste of bleaching powder *(laboratory and commercial method)*.

$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$

Cl_2, so obtained acts as a mild oxidising as well as chlorinating agent

From ethanol :

(a) $CH_3CH_2OH + Cl_2 \longrightarrow CH_3CHO + 2HCl$ ***(Oxidation)***

(b) $CH_3CHO + 3Cl_2 \longrightarrow CCl_3.CHO + 3HCl$ ***(Chlorination)***

(c) $2CCl_3.CHO + Ca(OH_2)$

$\longrightarrow \underset{\text{Chloroform}}{2CHCl_3} + (HCOO)_2Ca$ ***(Hydrolysis)***

From acetone :

(a) $CH_3COCH_3 + 3Cl_2$

$\longrightarrow CCl_3.CO.CH_3 + 3HCl$ ***(Chlorination)***

(b) $2CCl_3.CO.CH_3 + Ca(OH)_2 \longrightarrow$

$2CHCl_3 + (CH_3COO)_2Ca$ ***(Hydrolysis)***

(iii) $CCl_4 + 2[H] \xrightarrow{\text{Fe+steam}} CHCl_3 + HCl$

(Commerical method)

(iv) Pure chloroform, required in anaesthesia, is obtained by chloral hydrate with NaOH.

$CCl_3.CH(OH)_2 + NaOH \xrightarrow{\text{distil}} CHCl_3 + HCOONa + H_2O$

2. **Properties :**

(i) ***Oxidation :*** On exposure to air and sunlight, chlorofrom, a colourless heavy liquid, oxidises to **carbonyl chloride (phosgene),** a highly poisonous gas used in warfare.

$CHCl_3 + \frac{1}{2}O_2 \xrightarrow{\text{light}} \underset{\text{unstable}}{CCl_3(OH)} \longrightarrow COCl_2 + HCl$

To avoid this oxidation chlorofrom is always stored in dark coloured bottles filled to the brim to exclude any air. Further nearly 1% alcohol is also added to destroy traces of phosgene, if formed, to harmless diethyl carbonate.

$2C_2H_5OH + Cl_2C = O \longrightarrow \underset{\text{Diethyl carbonate}}{(C_2H_5O)_2C = O} + 2HCl$

(ii) ***Reduction :***

(a) $CHCl_3 + 2[H] \xrightarrow{\text{Zn / HCl}} CH_2Cl_2 + HCl$

(b) $CHCl_3 + 4[H] \xrightarrow{\text{Zn / alc. KOH}} CH_3Cl + 2HCl$

(c) $CHCl_3 + 6[H] \xrightarrow{\text{Zn / }H_2O} CH_4 + 3HCl$

(iii) ***Chlorination :***

$CHCl_3 + Cl_2 \xrightarrow{\text{sunlight}} CCl_4 + HCl$

(iv) ***Nitration :***

$CHCl_3 + HONO_2(\text{conc.}) \longrightarrow \underset{\text{Chloropicrin}}{NO_2.CCl_3}$

Chloropicrin (nitrochloroform) is a useful insecticide and lachrymatory (tear producing) substance.

(v) ***Hydrolysis :***

$CHCl_3 \xrightarrow{\text{NaOH}} CH(OH)_3 \xrightarrow{-H_2O}$

$HCOOH \xrightarrow{\text{NaOH}} \underset{\text{Sod. formate}}{HCOONa}$

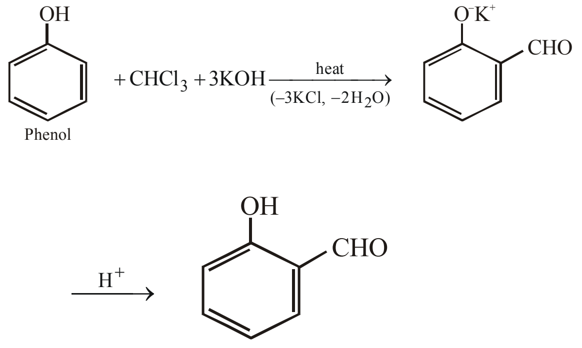
(vi) ***Carbylamine reaction :***

$\underset{\text{Any 1° amine}}{R - NH_2} + CHCl_3 + 3KOH\ (\text{alc.}) \xrightarrow{\text{heat}}$

$\underset{\text{Alkyl carbylamine}}{RN \overset{\rightarrow}{=} C} + 3KCl + 3H_2O$

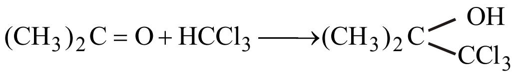
Alkyl carbylamines or alkyl isocyanides have extremely bad smell, hence this reaction is used for detecting the presence of a primary amine.

(vii) ***Reimer-Tiemann reaction :***



Salicylaldehyde

(viii) ***Condensation with Ketones :***



$(CH_3)_2C = O + HCCl_3 \longrightarrow (CH_3)_2C(OH)(CCl_3)$

Chloretone

Chloretone is used as a *hypnotic (sleep producing substance).*

(ix) ***Dehalogenation :***

$HCCl_3 + 6Ag + HCCl_3 \xrightarrow{\text{heat}} HC \equiv CH + 6AgCl$

IODOFORM :

1. **Iodoform** is prepared by heating ethanol or acetone with

NaOH or Na_2CO_3.

$$CH_3CH_2OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + 5NaI + 5HCOONa + 5H_2O$$

$$CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + 3NaI + CH_3COONa + 3H_2O$$

2. **Relative reactivity of haloforms :** $CHI_3 > CHBr_3 > CHCl_3$
   Being highly reactive,
   (a) iodoform when comes in contact with organic matter, decomposes easily to free iodine, an ***antiseptic***.
   (b) iodoform gives yellow precipitate of AgI, on heating with silver nitrate, while chloroform does not give any precipitate with $AgNO_3$ solution.
3. **Iodoform test :** Any compound containing CH_3CO- or $CH_3CH(OH)-$ group, when heated with iodine and aqueous NaOH or NaOI (sodium hypoiodite) gives yellow precipitate of iodoform, this reaction is called **iodoform reaction.**

$$CH_3.CH(OH).R \xrightarrow{I_2/NaOH} CH_3.CO.R$$

$$\xrightarrow{I_2/NaOH} I_3C.CO.R \xrightarrow{I_2/NaOH} \underset{\text{Iodoform}}{CHI_3} + RCOONa$$

Thus iodoform reaction is used for detecting CH_3CO- or $CH_3CH(OH)-$ group in an organic compound. Hence iodoform test can be used for distinguishing between

(a) $\underset{\text{Methyl alcohol}}{CH_3OH}$ and $\underset{\text{Ethyl alcohol*}}{CH_3CH_2OH}$

(b) $\underset{\text{1-Propanol}}{CH_3CH_2CH_2OH}$ and $\underset{\text{2-Propanol*}}{CH_3CHOHCH_3}$

(c) $\underset{\text{Methanal}}{HCHO}$ and $\underset{\text{Ethanal*}}{CH_3CHO}$

(d) $\underset{\text{Propanal}}{CH_3CH_2CHO}$ and $\underset{\text{Propanone*}}{CH_3.CO.CH_3}$

(e) $\underset{\text{2-Phenylethanol}}{C_6H_5CH_2CH_2OH}$ and $\underset{\text{1-Phenylethanol*}}{C_6H_5CHOHCH_3}$

(f) $\underset{\text{2-Phenylethanol}}{C_6H_5CH_2CH_2OH}$ and $\underset{\text{Acetophenone*}}{C_6H_5COCH_3}$

(g) $\underset{\text{Benzophenone}}{C_6H_5COC_6H_5}$ and $\underset{\text{Acetophenone*}}{C_6H_5COCH_3}$

(h) $\underset{\text{Pentanone-3}}{CH_3CH_2COCH_2CH_3}$ and $\underset{\text{Pentanone-2*}}{n-C_3H_7.CO.CH_3}$

Compound marked with asteristk $*$ responds iodoform test.

CARBON TETRACHLORIDE (TETRACHLORO METHANE OR PERCHLOROMETHANE) :

1. **Preparation :**

(i) $CH_4 + 4Cl_2 \xrightarrow{\text{sun light}} CCl_4 + 4HCl$

(ii) $CHCl_3 + Cl_2 \xrightarrow{hv} CCl_4 + HCl$

(iii) $CS_2 + 3Cl_2 \xrightarrow[\text{or } SbCl_5]{\text{anhy.}AlCl_3} CCl_4 + \underset{\text{Sulphur}}{S_2Cl_2}$

$$\underset{\text{monochloride}}{2S_2Cl_2} + CS_2 \longrightarrow CCl_4 + 6S$$

(iv) $CH_3CH_2CH_3 + 9Cl_2 \xrightarrow[\text{74–100 atm}]{673K} CCl_4 + C_2Cl_6 + 8HCl\uparrow$

1. When all hydrogen atoms of a hydrocarbon are replaced by corresponding number of halogens, halogen derivative is known as **perhalohydrocarbon**. Perchloroethane, C_2Cl_6 is a solid and known as artificial camphor, it is used as moth repellents.
2. **Properties :**
   (i) It is a colourless, non-inflammable, poisonous liquid, soluble in alcohol and ether.
   (ii) On heating with steam at about 773K, it undergoes ***oxidation*** forming carbonyl chloride.

$$CCl_4 + H_2O\ (\text{steam}) \xrightarrow{773K} COCl_2 + 2HCl$$

(iii) It reacts with HF in presence of $SbCl_5$ forming ***dichlorodifluoromethane;*** commonly known as ***freon-12.***

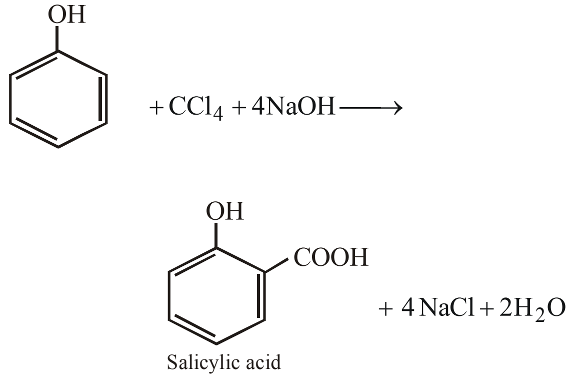
$$CCl_4 + 2HF \xrightarrow{SbCl_5} CCl_2F_2 + 2HCl$$

or

$$3CCl_4 + 2SbF_3 \longrightarrow \underset{\text{Freon-12}}{3CCl_2F_2} + 2SbCl_3$$

Freon is a widely used as refrigerant and propellant in aerosols and foams. However, freons destruct ozone layer in the atmosphere.

(iv) ***Reimer-Tiemann reaction :***



Salicylic acid

(v) ***Reduction :***

(a) $CCl_4 + 2[H] \xrightarrow{Fe/HCl} CHCl_3 + HCl$

(b) $CCl_4 + 4[H] \xrightarrow{Fe/H_2O} CH_2Cl_2 + 2HCl$

(vi) ***Hydrolysis :***

$$CCl_4 \xrightarrow{\text{KOH (aq.)}} C(OH)_4 \xrightarrow{-2H_2O} CO_2 \xrightarrow[(-H_2O)]{KOH} K_2CO_3$$

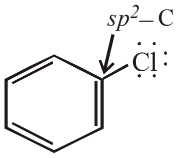
Due to non-availability of *d*-orbital in C, CCl_4 resists hydrolysis with boiling water.

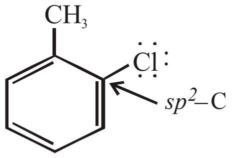
3. **Uses :** Carbon tetrachloride is used (i) as a solvent for oils, fats, resins, (ii) in dry cleaning, (iii) as a laboratory reagent, (iv) as anthelmentic (removal of worms) for hook worms and (v) as a fire extinguisher under the name of **pyrene**. Carbon tetrachloride gives dense, and incombustible vapours which cover the burning surface and thus prevents oxygen to reach the fire. After the use of pyrene, the room should be well ventilated to remove poisonous phosgene vapours formed by the oxidation of carbon tetrachloride.

UNSATURATED HALOGEN DERIVATIVES:

1. **These are of two types :**
   (a) Those in which halogen atom is attached on unsaturated carbon atoms. Since in such compounds lone pair of electrons on halogen are conjugated with the π-bond, these undergo resonance, the C-Cl bond acquires double bond character, hence it is strong and chlorine is non-reactive.

$$H_2C{=}\underset{sp^2\text{-}C}{CH}-\ddot{\underset{\cdot\cdot}{X}}:$$

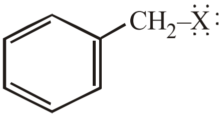




   (b) Those in which halogen is attached on the saturated carbon atom; hence resonance not possible; halogen is reactive.

$H_2C{=}CH{-}CH_2-\ddot{\underset{\cdot\cdot}{X}}:$ Allyl halide

$CH_3{-}CH{=}CH{-}CH_2-\ddot{\underset{\cdot\cdot}{X}}:$ Crotyl halide



2. **Vinyl halides :**
   (i) ***Preparation :***

(a) $HC \equiv CH + HCl \longrightarrow CH_2 = CHCl$

(b) $\underset{\text{Ethylene chloride}}{CH_2Cl.CH_2Cl} \xrightarrow{OH^-/C_2H_5OH} \underset{\text{Vinyl chloride}}{CH_2 = CHCl}$

$$CH_2Cl-CH_2Cl \xleftarrow{\bar{O}H/C_2H_5OH} \underset{\text{Ethylidene chloride.}}{CH_3-CH_2-Cl}$$

Properties :

(i) As mentioned above, halogen atom of vinyl halides is inert to nucleophilic substitution. However, like alkyl halides they undergo elimination reaction, and form Grignard reagents.

$$CH_2 = CHCl \xrightarrow{\text{alc. KOH}} CH \equiv CH;$$

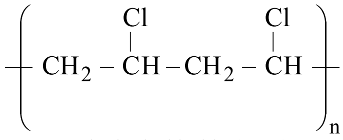
$$CH_2 = CHCl + Mg \xrightarrow{THF} CH_2 = CHMgCl$$

(ii) Like alkenes, it undergoes the usual addition reactions such as addition of H_2, X_2, HX and polymerisation.

$$\underset{anti\text{-Markownikoff product}}{BrCH_2-CH_2Cl} \xleftarrow{\text{peroxide}} \underset{\text{Vinyl chloride}}{CH_2 = CHCl + HBr}$$

$$\longrightarrow \underset{\text{Markownikoff product}}{CH_3CHBrCl}$$

$$n\ CH_2 = CHCl \xrightarrow[\text{(polymerisation)}]{\text{benzoyl peroxide}}$$



$$\left[CH_2-\overset{Cl}{\overset{|}{CH}}-CH_2-\overset{Cl}{\overset{|}{CH}} \right]_n$$

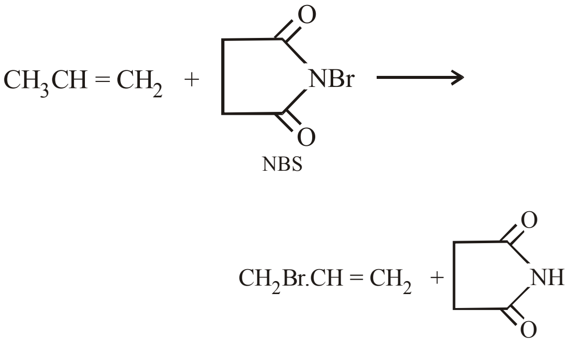
Polyvinyl chloride (PVC)

PVC is a plastic of great importance.

3. **Allyl chloride :** It can best be prepared by allylic chlorination of propene with chlorine at about 673K (*a free radical substitution*).

$$CH_3.CH = CH_2 + Cl_2 \xrightarrow{673K} ClCH_2.CH = CH_2 + HCl$$

4. **Allyl bromide:** It is best prepared by allylic bromination using N-bromosuccinimide (NBS) in presence of sunlight (***a free radical substitution***).

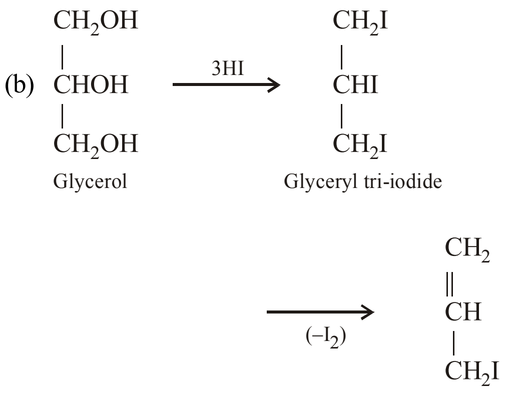


5. **Allyl iodide:** It is prepared either from allyl chloride or glycerol.

(a) $CH_2 = CHCH_2Cl + NaI \xrightarrow{\text{acetone}}$

$CH_2 = CHCH_2I + NaCl \downarrow$ (Insoluble in acetone)

(b)



$$\underset{\text{Glycerol}}{\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}} \xrightarrow{3HI} \underset{\text{Glyceryl tri-iodide}}{\begin{matrix} CH_2I \\ | \\ CHI \\ | \\ CH_2I \end{matrix}} \xrightarrow[(-I_2)]{} \underset{\text{Allyl iodide}}{\begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CH_2I \end{matrix}}$$

Allyl halides give the usual addition reactions of the double bond and also nucleophilic substitution. Allyl halides undergo nucleophilic substitutions much faster than the alkyl halides because the intermediate allyl carbocation stabilises due to resonance.

$$CH_2 = CH - \overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2 - CH = CH_2$$

6. There are two isomeric dichloroethenes, (a) 1,2-dichloroethene (acetylene dichloride) and (b) 1,1-dichloroethene (vinylidene dichloride).

(a)

$$\underset{\text{1,1,2,2-Tetrachloroethane}}{Cl_2CH - CHCl_2} + Zn \xrightarrow{CH_3OH,\ heat} \underset{\text{1,2-Dichloroethene}}{ClCH = CHCl}$$

1,2-Dichloroethene exists in two geometrical isomeric forms, *i.e. cis*- and *trans*-. It is used as a solvent.

(b) $$\underset{\text{Vinyl chloride}}{CH_2 = CHCl} \xrightarrow{Cl_2} ClCH_2 - CHCl_2$$

$$\xrightarrow[363K]{Ca(OH)_2} \underset{\text{1,1-Dichloroethene}}{CH_2 = CCl_2}$$

1,1-Dichloroethene does not show *cis, trans*- isomerism. It is used in the manufacture of *saran wrap* used for food packaging.

Types of halogens : Halogen present in organic compounds can be of three types.

(i) ***Ionic halogens*** as in benzenediazonium halides $(C_6H_5\overset{+}{N_2}X^-)$ and quaternary ammonium halides $(R_4N^+X^-)$. Aqueous solution of such halides when treated with $AgNO_3$ solution in presence of dil. HNO_3 give white or yellow precipitate ***in cold***.

(ii) ***Labile halogens*** as in alkyl halides (R – X), allyl halides $(CH_2 = CHCH_2X)$ and benzyl halides $(C_6H_5CH_2X)$. These halogens are also precipitated as silver halides but under strong conditions. Organic halide is boiled with aqueous KOH solution, cooled, acidified with dil. HNO_3 and then treated with $AgNO_3$ solution; appearance of a white or yellow precipitate indicates labile halogen.

(iii) ***Inert halogen*** as in aryl halides (ArCl) and vinyl halides $(CH_2=CHX)$. These compounds give precipitate with $AgNO_3$ solution neither in cold nor on heating.

Exercise-1 | NCERT Based Questions

Very Short/ Short Answer Questions

1. Chloroalkanes are used as industrial solvents and not bromo and iodo compounds. Explain why.

2. Arrange the following in order of increasing boiling point: C_2H_5Br, C_2H_5I, C_2H_5Cl.

3. Why are aryl halides insoluble in water but soluble in organic solvents?

4. Why a small amount of ethyl alcohol is added to chloroform bottles during storage of chloroform?

5. Ethyliodide is colourless when freshly prepared but changes to brown gradually when lying on shelf for a long time. Explain.

6. Arrange the following in order of increasing ease towards nucleophilic substitution:

2, 4, 6-Trinitrochlorobenzene, 4-Nitrochlorobenzene, Chlorobenzene, 2,4-Dinitrochlorobenzene.

7. Haloarenes and haloalkanes are polar compounds but insoluble in water. Why?

8. An organic compound ‘A’ on heating with NH_3 and cuprous oxide at high pressure gives compound ‘B’. The compound ‘B’ on treatment with ice cold solution of $NaNO_2$ and HCl gives compound ‘C’, which on heating with copper turnings and HCl gives ‘A’ again. Identify A, B, and C.

9. A compound ‘A’ contains C and H only and has molecular mass of 72. Its photochlorination gives a mixture containing only one monochloro and two dichloro hydrocarbons. Deduce the structures of starting compound, ‘A’ and chlorinated products.

10. Identify X, Y and Z in the following reactions:

(*i*) $C_6H_5NH_2 \xrightarrow{NaNO_2} X \xrightarrow[HBr]{CuBr} Y \xrightarrow[623\,K,\,Pressure]{NaOH} Z$

(*ii*) $C_6H_5CH_3 \xrightarrow{Cl_2,\,FeCl_3} X \xrightarrow{Cl_2/hv} Y \xrightarrow{aq\,KOH}$

(*iii*) $C_6H_5N_2^+Cl^- \xrightarrow[Warm]{KI} X \xrightarrow{Cu} Y$

11. A primary alkyl halide (A), C_4H_9 Br reacted with not alcoholic KOH to give compound (B). Compound (B) reacted with HBr to give (C), which is an isomer of A. When (A) was reacted with sodium metal it gave a compound (D), C_8H_{18} which was different than the compound when n-butyl bromide was reacted with sodium. Give the structural formula of (A) and write equations for all the reactions.

12. How will you prepare m-bromoiodobenzene from benzene?

13. How will you carry out the following conversions:

(*i*) 1-Iodobutane from 1-butene

(*ii*) Sec-propyl bromide from isobutyric acid

(*iii*) Fluoroethane from ethanol

14. (a) Write a chemical test to distinguish between

(i) Chlorobenzene and Benzyl chloride

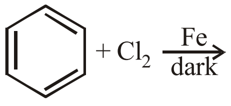
(ii) Chloroform and Carbon tetrachloride

(b) Why is methyl chloride hydrolysed more easily than chlorobenzene?

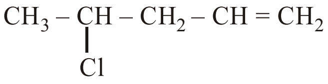
15. Predict the order of reactivity of the following compounds in S_N1 reaction:

$C_6H_5CH_2Br$, $C_6H_5C(CH_3)$, $(C_6H_5)Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$

16. Draw the structure of major monohalo product in the following reaction :



17. Write the IUPAC name of



$$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH=CH_2$$

18. Account for the following:

(a) The C – Cl bond length in chlorobenzene is shorter than that in CH_3-Cl.

(b) Chloroform is stored in closed dark brown bottles.

Multiple Choice Questions

19. Which of the following possesses highest melting point?

(a) Chlorobenzene

(b) m-dichlorobenzene

(c) o-dichlorobenzene

(d) p-dichlorobenzene

20. Which reagent cannot be used to prepare an alkyl halide from an alcohol ?

(a) $HCl + ZnCl_2$ (b) NaCl

(c) PCl_5 (d) $SOCl_2$

21. In which of the following conversions, phosphorus pentachloride is used as the reagent?

(a) $H_2C = CH_2 \longrightarrow CH_3CH_2Cl$

(b) $CH_3CH_2OH \longrightarrow CH_3CH_2Cl$

(c) $H_3C - O - CH_3 \longrightarrow CH_3Cl$

(d) $CH \equiv CH \longrightarrow CH_2 = CHCl$

22. Industrial preparation of chloroform employs acetone and

(a) phosgene
(b) calcium hypochlorite
(c) chlorine gas
(d) sodium chloride.

23. Vapour density of an organic compound is 23. It contains 52.17% of carbon and 13% of hydrogen. The compound gives iodoform test. The compound is :

(a) ethanol
(b) dimethyl ether
(c) acetone
(d) methanol

24. Alkyl halides on heating with dry Ag_2O yield :

(a) esters
(b) ethers
(c) ketones
(d) AgCl + hydrocarbon

25. Mg reacts with RBr best in

(a) $C_2H_5OC_2H_5$
(b) $C_6H_5OCH_3$
(c) $C_6H_5N(CH_3)_2$
(d) Equally in all the three

26. Which of the following is not used in Friedel-Crafts reaction?

(a) N–Phenyl acetanilide
(b) Bromobenzene
(c) Benzene
(d) Chlorobenzene

Exercise-2 | CONCEPTUAL MCQs

1. $C_3H_8 + Cl_2 \xrightarrow{\text{Light}} C_3H_7Cl + HCl$ is an example of

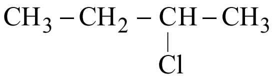
(a) substitution (b) elimination

(c) addition (d) rearrangement reaction

2. Iso-butyl bromide may be obtained from iso-butylene and HBr in the presence of

(a) peroxide (b) hydroquinone

(c) diphenylamine (d) All of these

3. 

$CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$ obtained by chlorination of *n*-butane, will be

(a) meso-form (b) racemic mixture

(c) *d*-form (d) *ℓ*-form

4. Which of the following possesses highest melting point?

(a) Chlorobenzene (b) *o*-Dichlorobenzene

(c) *m*-Dichlorobenzene (d) *p*-Dichlorobenzene

5. Which of the following will have the maximum dipole moment?

(a) CH_3F (b) CH_3Cl

(c) CH_3Br (d) CH_3I

6. Arrange the following compounds in order of increasing dipole moment :

Toluene (I)

m-dichlorobenzene (II)

o-dichlorobenzene (III)

p-dichlorobenzene (IV)

(a) $I < IV < II < III$ (b) $IV < I < II < III$

(c) $IV < I < III < II$ (d) $IV < II < I < III$

7. C – X bond is strongest in

(a) CH_3Cl (b) CH_3Br

(c) CH_3F (d) CH_3I

8. C – Cl bond of chlorobenzene in comparison to C – Cl bond in methyl chloride is

(a) longer and weaker (b) shorter and weaker

(c) shorter and stronger (d) longer and stronger

9. The reaction for preparing alkyl cyanide by reacting alkyl halide with potassium cyanide is

(a) elimination reaction (b) electrophilic reaction

(c) nucleophilic reaction (d) condensation reaction

10. Most reactive halide towards S_{N^1} reaction is

(a) *n*-Butyl chloride (b) *sec*-Butyl chloride

(c) *tert*-Butyl chloride (d) Allyl chloride

11. In S_N1 reaction, the recemization takes place. It is due to

(a) inversion of configuration

(b) retention of configuration

(c) conversion of configuration

(d) both (a) & (b)

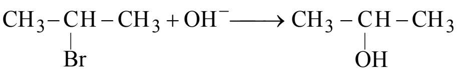
12. The order of reactivities of the following alkyl halides for a S_N2 reaction is

(a) $RF > RCl > RBr > RI$ (b) $RF > RBr > RCl > RI$

(c) $RCl > RBr > RF > RI$ (d) $RI > RBr > RCl > RF$

13. Which of the following is an example of S_N2 reaction?

(a) $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$

(b) 

$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 + OH^- \longrightarrow CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

(c) $CH_3CH_2OH \xrightarrow{-H_2O} CH_2 = CH_2$

(d) $(CH_3)_3C-Br + OH^- \longrightarrow (CH_3)_3COH + Br^-$

14. S_N2 mechanism proceeds through intervention of

(a) carbonium ion (b) transition state

(c) free radical (d) carbanion

15. Which among MeX, RCH_2X, R_2CHX and R_3CX is most reactive towards S_N2 reaction?

(a) MeX (b) RCH_2X

(c) R_2CHX (d) R_3CX

16. Isopropyl chloride undergoes hydrolysis by

(a) S_N1 mechanism

(b) S_N2 mechanism

(c) S_N1 and S_N2 mechanisms

(d) Neither S_N1 nor S_N2 mechanism

17. Butanenitrile is formed by reaction of KCN with

(a) propyl alcohol (b) butyl chloride

(c) butyl alcohol (d) propyl chloride

18. Which of the following alkyl halides is used as a methylating agent?

(a) C_2H_5Br (b) C_6H_5Cl

(c) CH_3I (d) C_2H_5Cl

19. Ethyl bromide reacts with lead-sodium alloy to form

(a) tetraethyl lead (b) tetramethyl bromide

(c) Both (a) & (b) (d) None of these

20. The rection of an alkyl halide with RCOOAg produces

(a) ester (b) ether

(c) aldehyde (d) ketone

21. A compound that will form an offensive smell when heated with chloroform and alcoholic potash is

(a) $C_2H_5NH_2$
(b) $(C_2H_5)_2NH$
(c) $(CH_3)_3N$
(d) CH_3CN

22. 1-Chlorobutane on reaction with alcoholic potash gives

(a) 1-Butene
(b) 1-Butanol
(c) 2-Butene
(d) 2-Butanol

23. 2-Bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is

(a) 2-Ethoxypentane
(b) Pentene-1
(c) *cis*-Pentene-2
(d) *trans*-Pentene-2

24. The reactivity order of halides for dehydrohalogenation is

(a) $R-F > R-Cl > R-Br > R-I$
(b) $R-I > R-Br > R-Cl > R-F$
(c) $R-I > R-Cl > R-Br > R-F$
(d) $R-F > R-I > R-Br > R-Cl$

25. The order of reactivity of alkyl halides towards elimination reaction is

(a) $3° > 2° > 1°$
(b) $2° > 1° > 3°$
(c) $3° > 1° > 2°$
(d) $1° > 2° > 3°$

26. The reaction of $C_6H_5N_2^+Cl^-$ with CuCl gives

(a) C_6H_5Cl
(b) C_6H_6
(c) $C_6H_5-C_6H_5$
(d) $C_6H_4Cl_2$

27. Bromination of toluene gives

(a) only *m*-substituted product
(b) only *p*-substituted product
(c) mixture of *ortho*- and *para*-substituted products
(d) mixture of *ortho*- and *m*-substituted products

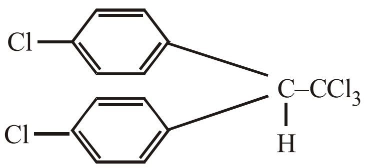
28. On sulphonation of C_6H_5Cl

(a) *m*-Chlorobenzenesulphonic acid is formed
(b) Benzenesulphonic acid is formed
(c) *o*-Chlorobenzenesulphonic acid is formed
(d) *o*- and *p*-Chlorobenzenesulphonic acid is formed

29. Which of the following is not used in Friedel-Crafts reaction?

(a) N–Phenyl acetanilide
(b) Bromobenzene
(c) Benzene
(d) Chlorobenzene

30.



The above structural formula refers to

(a) BHC
(b) DNA
(c) DDT
(d) RNA

31. The pesticide DDT slowly changes to

(a) CCl_3-CHO and chlorobenzene
(b) *p, p*′-Dichlorodiphenylethene
(c) *p, p*′-Dichlorodiphenyldichloroethane
(d) *p, p*′-Dichlorodiphenyldichloroethene

32. Chlorobenzene on heating with NH_3 under pressure in the presence of cuprous chloride gives

(a) benzamide
(b) nitrobenzene
(c) aniline
(d) *o*- and *p*-Chloroaminobenzene

33. *o*-Methoxybromobenzene is treated with sodamide and then with ammonia. The product formed is

(a) *o*-Methoxyaniline
(b) Aniline
(c) Methoxybenzene
(d) *m*-Methoxyaniline

34. Toluene on reaction with N-bromosuccinimide gives

(a) *p*-Bromomethylbenzene
(b) *o*-Bromomethylbenzene
(c) Phenyl bromomethane
(d) *m*-Bromomethylbenzene

35. Toluene when refluxed with Br_2 in the presence of light mainly gives

(a) *o*-bromotoluene
(b) *p*-bromotoluene
(c) mixture of *o*- and *p*-bromotoluene
(d) benzyl bromide

36. When chlorine is passed through propene at 400°C, which of the following is formed?

(a) PVC
(b) Allyl chloride
(c) Vinyl chloride
(d) 1,2-Dichloroethane

37. Which one of the following is most reactive towards nucleophilic substitution reaction?

(a) $CH_2=CH-Cl$
(b) C_6H_5Cl
(c) $CH_3CH=CH-Cl$
(d) $ClCH_2-CH=CH_2$

38. Freon-12 is commonly used as

(a) insecticide
(b) refrigerant
(c) a solvent
(d) a fire extinguisher

39. Which one of the following is mainly responsible for depletion of ozone layer?

(a) Methane
(b) Carbon dioxide
(c) Water
(d) Chlorofluorocarbons

40. Pure chloroform is prepared by

(a) distilling chloral hydrate with aqueous sodium hydroxide
(b) heating ethanol with bleaching powder
(c) heating acetone with bleaching powder
(d) reducing carbon tetrachloride

41. The starting substance for the preparation of iodoform is any one of the following, except

(a) $CH_3CH(OH)CH_3$
(b) CH_3CH_2OH
(c) HCH_2OH
(d) CH_3COCH_3

42. If chloroform is left open in air in the presence of sunlight, it gives

(a) carbon tetrachloride
(b) carbonyl chloride
(c) mustard gas
(d) lewisite

43. Chloroform when reacts with nitric acid gives

(a) $HCCl_3 . HNO_3$ (b) CCl_3CHOH

(c) CCl_3NO_2 (d) CCl_3NO_3

44. On warming with silver powder, chloroform is converted into

(a) acetylene

(b) hexachloroethane

(c) 1,1,2,2-tetrachloroethane

(d) ethylene

45. Iodoform on heating with KOH gives

(a) CH_3CHO (b) CH_3COOK

(c) HCOOK (d) HCHO

46. Cl_2 reacts with CS_2 in presence of I_2 to form

(a) $CHCl_3$ (b) CCl_4

(c) C_2H_5Cl (d) Cl_3C-NO_2

47. Identify Z in the following series

$$C_2H_5I \xrightarrow{\text{Alc. KOH}} X \xrightarrow{Br_2} Y \xrightarrow{KCN} Z$$

(a) CH_3CH_2CN (b) $NCCH_2–CH_2CN$

(c) $BrCH_2–CH_2CN$ (d) $BrCH=CHCN$

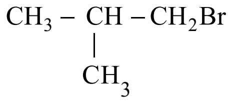
Exercise-3 | PAST COMPETITION MCQs

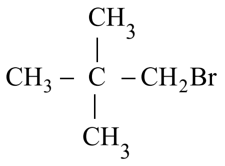
1. In a S_N2 substitution reaction of the type

$R-Br+Cl^- \xrightarrow{DMF} R-Cl+Br^-$ **[CBSE-PMT 2008]**

which one of the following has the highest relative rate ?

(a) $CH_3-CH_2-CH_2Br$

(b) 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2Br$

(c) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2Br$

(d) CH_3CH_2Br

2. Which of the following reactions is an example of nucleophilic substitution reaction? **[CBSE-PMT 2009]**

(a) $2RX+2Na \to R-R+2NaX$

(b) $RX+H_2 \to RH+HX$

(c) $RX+Mg \to RMgX$

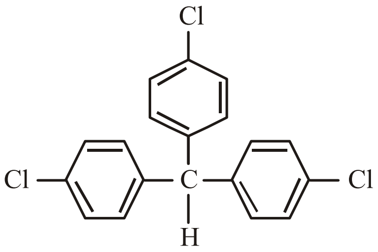
(d) $RX+KOH \to ROH+KX$

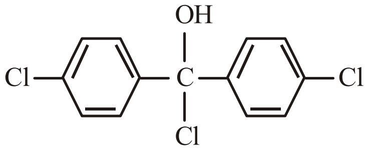
3. Benzene reacts with CH_3Cl in the presence of anhydrous $AlCl_3$ to form: **[CBSE-PMT 2009]**

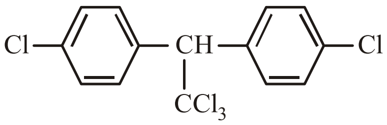
(a) chlorobenzene (b) benzylchloride

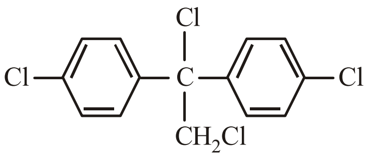
(c) xylene (d) toluene

4. Trichloroacetaldehyde, CCl_3CHO reacts with chlorobenzene in presence of sulphuric acid and produces : **[CBSE-PMT 2009]**

(a) 

(b) 

(c) 

(d) 

5. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives 'X' and reaction in presence of light gives 'Y'. Thus, 'X' and 'Y' are : **[CBSE-PMT 2010]**

(a) X = Benzal chloride, Y = *o* – Chlorotoluene

(b) X = *m* – Chlorotoluene, Y = *p* –Chlorotoluene

(c) X = o –and *p* – Chlorotoluene,
Y = Trichloromethylbenzene

(d) X = Benzyl chloride, Y = *m* – Chlorotoluene

6. Which one is most reactive towards S_N1 reaction ?

(a) $C_6H_5CH(C_6H_5)Br$ **[CBSE-PMT 2010]**

(b) $C_6H_5CH(CH_3)Br$

(c) $C_6H_5C(CH_3)(C_6H_5)Br$

(d) $C_6H_5CH_2Br$

7. Consider the reactions : **[CBSE-PMT 2011 M]**

(i) $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5OH} (CH_3)_2CH-CH_2OC_2H_5+HBr$

(ii) $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5O^-} (CH_3)_2CH-CH_2OC_2H_5+Br^-$

The mechanisms of reactions (i) and (ii) are respectively :

(a) S_N1 and S_N2 (b) S_N1 and S_N1

(c) S_N2 and S_N2 (d) S_N2 and S_N1

8. In the following sequence of reactions **[CBSE-PMT 2012]**

$CH_3-Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} B \xrightarrow[\text{ether}]{LiAlH_4} C$, the end product (C) is :

(a) acetone (b) methane

(c) acetaldehyde (d) ethyl alcohol

9. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment ? **[AIEEE 2003]**

(a) A was $C_6H_5CH_2I$

(b) B was C_6H_5I

(c) Addition of HNO_3 was unnecessary

(d) A was C_6H_5I

10. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid, is **[AIEEE 2004]**

(a) freon (b) DDT

(c) gammexene (d) hexachloroethane

11. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of **[AIEEE 2005]**

(a) steric hindrance (b) inductive effect

(c) instability (d) insolubility

12. Alkyl halides react with dialkyl copper reagents to give **[AIEEE 2005]**

(a) alkenyl halides (b) alkanes

(c) alkyl copper halides (d) alkenes

13. Which types of isomerism is shown by 2, 3-dichlorobutane? **[AIEEE 2005]**

(a) Structural (b) Geometric

(c) Optical (d) Diastereo

14. Elimination of bromine from 2-bromobutane results in the formation of – **[AIEEE 2005]**

(a) predominantly 2-butyne

(b) predominantly 1-butene

(c) predominantly 2-butene

(d) equimolar mixture of 1 and 2-butene

15. Fluorobenzene (C_6H_5F) can be synthesized in the laboratory **[AIEEE 2006]**

(a) by direct fluorination of benzene with F_2 gas

(b) by reacting bromobenzene with NaF solution

(c) by heating phenol with HF and KF

(d) from aniline by diazotisation followed by heating the diazonium salt with HBF_4

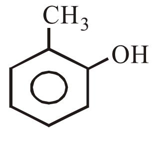
16. $CH_3Br+Nu^- \longrightarrow CH_3-Nu+Br^-$ The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is **[AIEEE 2006]**

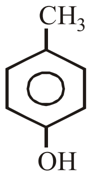
[Nu^- = (A) PhO^-, (B) AcO^-, (C) HO^-, (D) CH_3O^-]

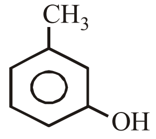
(a) A > B > C > D (b) B > D > C > A

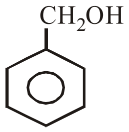
(c) D > C > A > B (d) D > C > B > A

17. The structure of the compound that gives a tribromo derivative on treatment with bromine water is **[AIEEE 2006]**

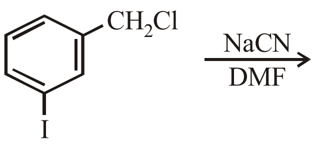
(a) 

(b) 

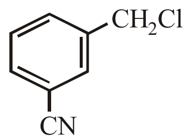
(c) 

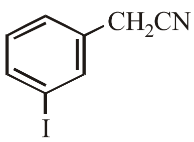
(d) 

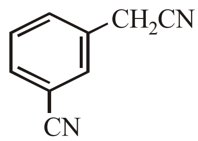
18. The structure of the major product formed in the following reaction **[AIEEE 2006]**

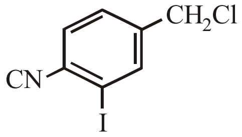


is

(a) 

(b) 

(c) 

(d) 

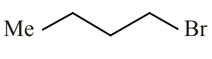
19. Which of the following is the correct order of decreasing S_N2 reactivity? **[AIEEE 2007]**

(a) $R_2CHX > R_3CX > RCH_2X$
(b) $RCHX > R_3CX > R_2CHX$
(c) $RCH_2X > R_2CHX > R_3CX$
(d) $R_3CX > R_2CHX > RCH_2X$.
(X is a halogen)

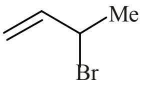
20. The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction, is **[AIEEE 2008]**

(a) $(C_2H_5)_2CHCl$ (b) $(CH_3)_3CCl$
(c) $(CH_3)_2\,CHCl$ (d) CH_3Cl

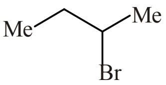
21. Consider the following bromides :



(A)



(B)



(C)

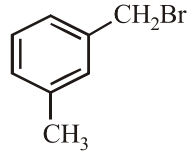
The correct order of S_N1 reactivity is **[AIEEE 2010]**

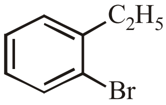
(a) B > C > A (b) B > A > C
(c) C > B > A (d) A > B > C

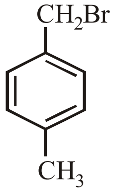
22. Iodoform can be prepared from all except : **[AIEEE 2012]**

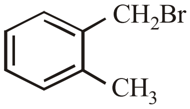
(a) Ethyl methyl ketone
(b) Isopropyl alcohol
(c) 3-Methyl 2-butanone
(d) Isobutyl alcohol

23. Compound (A), C_8H_9Br, gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A). **[JEE M 2013]**

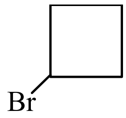
(a)


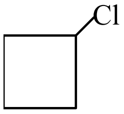
(b)


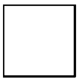
(c)


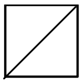
(d)


24. What would be the product formed when 1–bromo–3–chlorocyclobutane reacts with two equivalents of metallic sodium in ether? **[IIT-JEE 2005 S]**

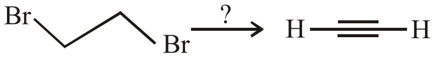
(a)


(b)


(c)


(d)


25. The reagent(s) for the following conversion,

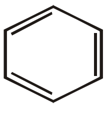


is/are **[IIT-JEE 2007]**

(a) alcoholic KOH
(b) alcoholic KOH followed by $NaNH_2$
(c) aqueous KOH followed by $NaNH_2$
(d) Zn/CH_3OH

Exercise-4 | Applied MCQs

1. Silver benzoate reacts with bromine to form

(a)


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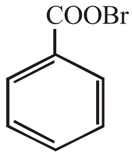
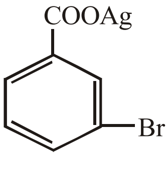


(c)


(d) C_6H_5Br

2. In the following groups :

–OAc (I) –OMe (II)
– OSO_2 Me (III) –OSO_2CF_3 (IV)

the order of leaving group ability is

(a) I > II > III > IV (b) IV > III > I > II
(c) III > II > I > IV (d) II > III > IV > I

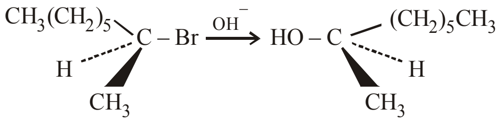
3. Arrange the following halides in the decreasing order of S_N1 reactivity :

$\underset{\text{I}}{CH_3CH_2CH_2Cl}$, $\underset{\text{II}}{CH_2 = CHCH(Cl)CH_3}$,

$\underset{\text{III}}{CH_3CH_2CH(Cl)CH_3}$

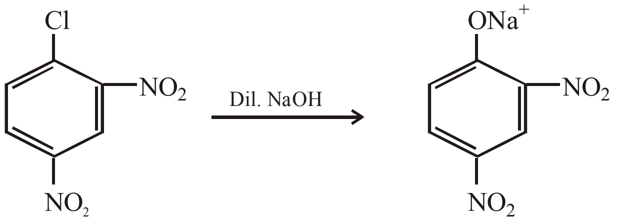
(a) I > II > III (b) II > I > III
(c) II > III > I (d) III > II > I

4. The reaction is described as



(a) $S_{E}2$ (b) $S_{N}1$
(c) $S_{N}2$ (d) $S_{N}0$

5.



The above transformation proceeds through
(a) electrophilic-addition
(b) benzyne intermediate
(c) activated nucleophilic substitution
(d) S_N1

6. Replacement of Cl of chlorobenzene to give phenol requires drastic conditions but chlorine of 2, 4-dinitrochlorobenzene is readily replaced. This is because
(a) NO_2 makes the ring electron rich at *ortho* and *para* positions
(b) NO_2 withdraws e^- from *meta*-position
(c) NO_2 donates e^- at *m*-position
(d) NO_2 withdraws e^- from *ortho/para*-positions

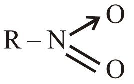
7. The decreasing order of reactivity of
m-nitrobromobenzene (I);
2,4,6-trinitrobromobenzene (II);
p-nitrobromobenzene (III); and
2,4-dinitrobromobenzene (IV)
towards OH^- ions is
(a) I > II > III > IV (b) II > IV > III > I
(c) IV > II > III > I (d) II > IV > I > III

8. The reaction of benzyl chloride with sodium cyanide followed by reduction with hydrogen in the presence of nickel gives
(a) β-Phenylethylamine (b) N-Isobutylaniline
(c) Benzylamine (d) Aniline

9. A set of compounds in which the reactivity of halogen atom in the ascending order is
(a) chlorobenzene, vinyl chloride, chloroethane
(b) chloroethane, chlorobenzene, vinyl chloride
(c) vinyl chloride, chlorobenzene, chloroethane
(d) vinyl chloride, chloroethane, chlorobenzene

10. A compound has vapour density 29. On warming with a solution of iodine in alkali, it gives a yellow precipitate, the compound is
(a) CH_3CH_2CHO (b) CH_3COCH_3
(c) $CH_3CHOHCH_3$ (d) $CH_2 = CHCH_2Br$

11. Which of the following pairs is/are correctly matched?

	Reaction	**Product**
I.	$RX + AgCN$	RNC
II.	$RX + KCN$	RCN
III.	$RX + KNO_2$	 $R-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$
IV.	$RX + AgNO_2$	R–O–N = O

(a) Only I (b) I and II
(c) III and IV (d) I, II, III and IV

12. Match list I (compound) with list II (use) and select the correct answer using the codes given below in the list :

	List I		*List II*
I.	Acetylsalicylic acid	A.	Insecticide
II.	DDT	B.	Drug
III.	Naphthalene	C.	Moth repellent
IV.	Carbon tetra-chloride	D.	Fire extinguisher
		E.	Refrigerant

(a) I-B, II-A, III-C, IV-D (b) I-E, II-C, III-D, IV-A
(c) I-B, II-C, III-D, IV-A (d) I-E, II-A, III-C, IV-D

13. Identify Z in

$$CH_3CH_2CH_2Br \xrightarrow{\text{Aq. NaOH}} X$$
$$\xrightarrow{Al_2O_3} Y \xrightarrow{Cl_2/H_2O} Z$$

(a) Mixture of $CH_3CHClCH_2Cl$ and $CH_3CHOHCH_2Cl$
(b) $CH_3CHOHCH_2Cl$
(c) $CH_3CHClCH_2OH$
(d) $CH_3CHClCH_2Cl$

14. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives
(a) *o*-Cresol (b) *p*-Cresol
(c) 2,4-Dihydroxytoluene (d) Benzoic acid

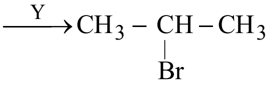
15. The compound

$$C_7H_8 \xrightarrow{3Cl_2/\Delta} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCl} C$$

The compound C is
(a) *o*-Bromotoluene
(b) *m*-Bromotoluene
(c) *p*-Bromotoluene
(d) 3-Bromo-2, 4, 6-trichlorotoluene

16. Identify the set of reagent/reaction conditions 'X' and 'Y' in the following set of transformations:

$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{Product}$



$$\xrightarrow{Y} CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$$

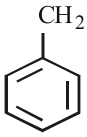
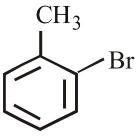
(a) X = dilute aqueous NaOH, 20°C; Y = HBr / acetic acid, 20°C

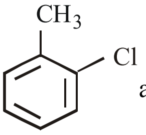
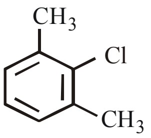
(b) X = concentrated alcoholic NaOH, 80°C; Y = HBr / acetic acid, 20°C

(c) X = dilute aqueous NaOH, 20°C; Y = Br_2 / $CHCl_3$, 0°C

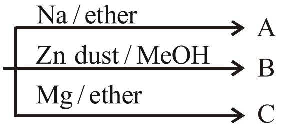
(d) X = concentrated alcoholic NaOH, 80°C; Y = Br_2 / $CHCl_3$, 0°C

17. Which compound in each of the following pairs is most reactive to the conditions indicated ?

(A)  and (B)  (KOH in CH_3OH)

(C)  and (D)  ($NaNH_2$ in NH_3)

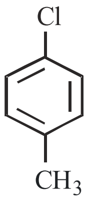
(a) A and C
(b) B and C
(c) A and D
(d) B and D

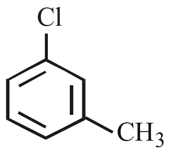
18. 1, 3 - dibromopropane 

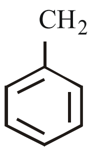
Which of the following is correct ?

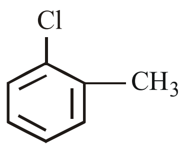
(a) A and B are same and C is different.
(b) A and C are same and B is different.
(c) A, B and C are same.
(d) B and C are same and A is different.

19. Which of the following has the weakest carbon - chlorine bond ?

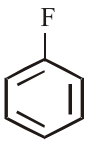
(a) 

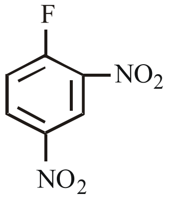
(b) 

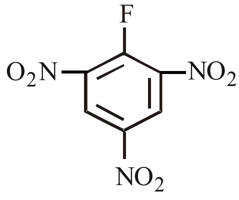
(c) 

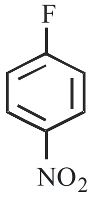
(d) 

20. Which of the following reacts at the fast rate with CH_3OK in CH_3OH?

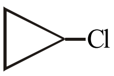
(a) 

(b) 

(c) 

(d) 

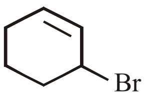
21. The compound most reactive towards S_N1 reaction

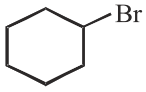
(a) Me_3COCH_2Cl
(b) $MeOCH_2Cl$
(c) $C_6H_5CH_2CH_2Cl$
(d) 

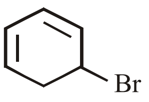
22. The correct Kinetic rate equation for the addition- elimination mechanism of nucleophilic aromatic substitution

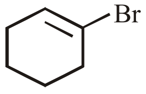
(a) rate = k [Aryl halide] [nucleophile]
(b) rate = k [Aryl halide]
(c) rate = k [Aryl halide] $[\text{nucleophile}]^2$
(d) rate = k [nucleophile]

23. Which of the following is fast de-brominated ?

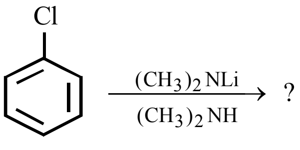
(a) 

(b) 

(c) 

(d) 

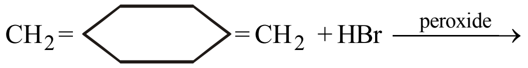
24. What is the product of the following reaction ?



(a) N, N-dimethyl aniline
(b) phenyl lithium (C_6H_5Li)
(c) para chloro-N, N-dimethyl aniline
(d) meta chloro-N, N-dimethyl aniline

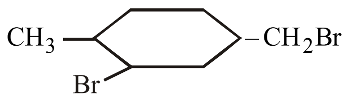
25. Which of the following reagents react readily with bromobenzene ?

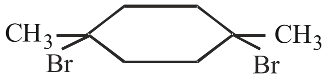
(a) $NaNH_2 / NH_3$ at −33°C
(b) $(CH_3)_2NH$ at. 25°C
(c) CH_3CH_2ONa at. 25°C
(d) NaCN / DMSO at. 25°C

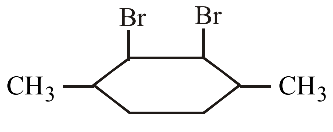
26. 

A, then

A is

(a) 

(b) 

(c) 

(d) 

27. $CH_3CHDCHBrCHMe_2$ when treated with alcoholic KOH, it gives

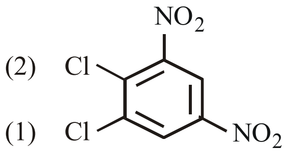
(a) an alkene containing D and show geometrical isomerism.

(b) an alkene containing D and cannot show geometrical isomerism.

(c) an alkene which contains D and cannot show optical isomerism.

(d) an alkene which does not contain D and can show geometrical isomerism.

28. Which chlorine is most susceptible to nucleophlic substitution with CH_3ONa in methanol

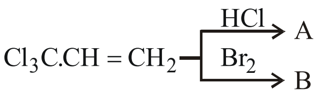


(a) 2

(b) 1

(c) both are equally susceptible

(d) substitution is not posssible

29. 
$$Cl_3C.CH=CH_2 \begin{cases} \xrightarrow{HCl} A \\ \xrightarrow{Br_2} B \end{cases}$$

Which of the following is correct ?

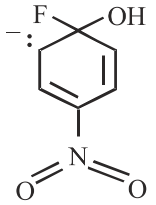
(a) A on reaction with aq. KOH gives $HOCH_2CH_2COOK$

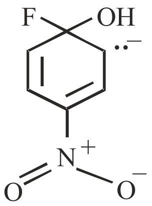
(b) B can be resolved into d– and *l*–forms

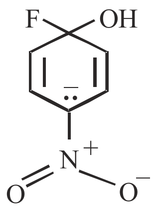
(c) Both (a) and (b)

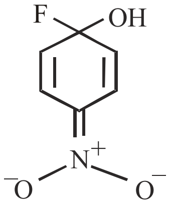
(d) Neither (a) nor (b)

30. Which resonance from is not possible in the nucleophilic addition of OH^- ion to para-fluoro nitro benzene ?

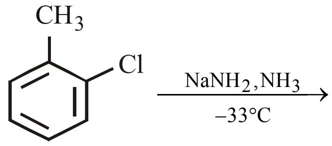
(a) 

(b) 

(c) 

(d) 

31. Identify the product of the following reaction



(a) only ortho-methyl aniline

(b) ortho-methyl aniline and meta-methyl aniline

(c) ortho-methyl aniline and para-methyl aniline

(d) meta-and para-methyl aniline

32. The correct order is

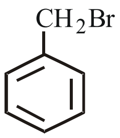
(a) RI > RBr > RCl (substitution reaction)

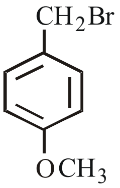
(b) $Me_3CBr > MeCH_2CHBrMe > Me_2CHCH_2Br$ (tendency for elimination)

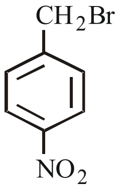
(c) Both are correct

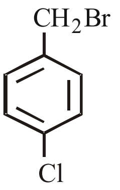
(d) None is correct

33. Which of the following halides undegoes S_N1 reaction at the fastest rate ?

(a) 

(b) 

(c) 

(d) 

34. In the following sequence of reactions, which is incorrect

$$CH_2=CH-CH=CH_2 \xrightarrow[80°C]{HBr} A \xrightarrow{HBr} B \xrightarrow{Mg} C$$

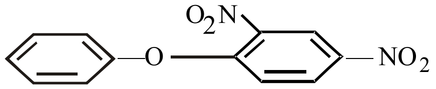
(a) A is $CH_3-CH=CH-CH_2Br$

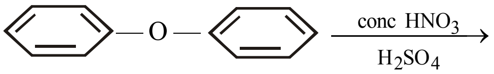
(b) B is $CH_3CHBr-CH_2-CH_2-Br$

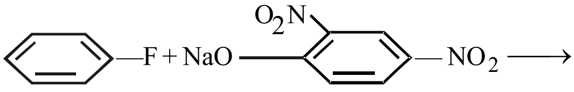
(c) C is cyclopropyl methane

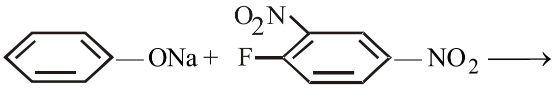
(d) B on S_N2 with aqueous NaOH gives $CH_3CHOH.CH_2CH_2Br$ and not $CH_3CHBr.CH_2CH_2OH$

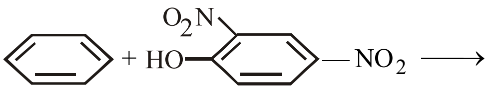
35. The following ether is best synthesised from



(a) 

(b) 

(c) 

(d) 

36. Isobutene $\xrightarrow[\text{peroxide}]{\text{HBr}}$ A $\xrightarrow{\text{KCN}}$

B $\xrightarrow{\text{dil. } H_2SO_4}$ C + inorganic salt D

C and D are

(a) $Me_2CH.CH_2COOH,\ (NH_4)_2SO_4$

(b) $Me_2CH.COOH,\ (NH_4)_2SO_4$

(c) $Me_2CH.CH_2COOK,\ NH_4OH$

(d) $Me_2CH.CH_2COOK,\ K_4SO_4$

37. A is an optically inactive alkyl chloride which on reaction with aqueous KOH gives B. B on heating with Cu at 300°C gives on alkene C, what are A and C

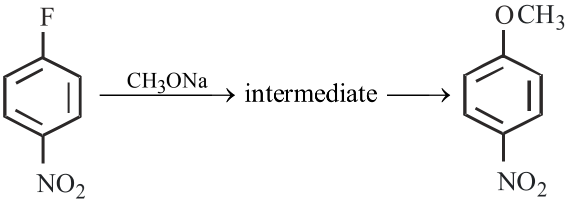
(a) $CH_3CH_2Cl,\ CH_2 = CH_2$

(b) $Me_3CCl, MeCH=CH.Me$

(c) $Me_3CCl,\ Me_2C=CH_2$

(d) $Me_2CH.CH_2Cl,\ Me_2C=CH_2$

38. Which of the following is (are) true concerning the intermediate in the addition-elimination mechanism of the following reaction ?



A = The intermediate is aromatic, B = The intermediate is a resonance stabilised anion, C = electron withdrawing groups on the benzene ring stabilises the intermediate

(a) only A	(b) only B
(c) A and C	(d) B and C

39. Which of the following order is not correct ?

(a) $MeBr > Me_2CHBr > Me_3CBr > Et_3CBr (S_N2)$

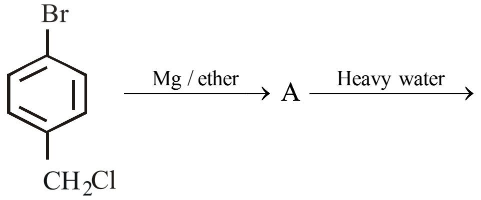
(b) $PhCH_2Br > PhCHBrMe > PhCBrMe_2 >$

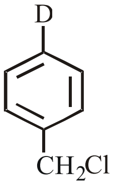
$PhCBrMePh (S_N1)$

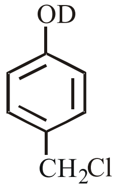
(c) $MeI > MeBr > MeCl > MeF\ (S_N2)$

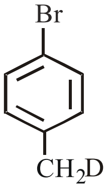
(d) All are correct

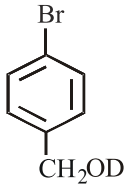
40. The final product obtained in the reaction



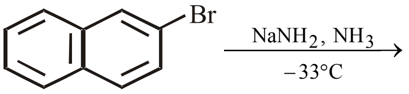
(a) 

(b) 

(c) 

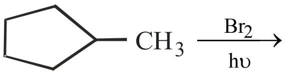
(d) 

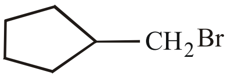
41. How many isomeric naphthylamines are expected in the following reaction ?

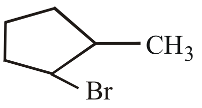


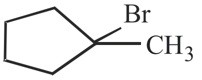
(a) two	(b) only single product
(c) four	(d) three

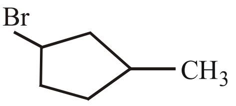
42. The major product obtained in the reaction



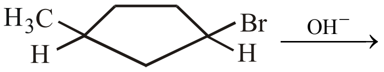
(a) 

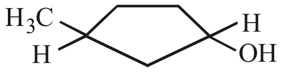
(b) 

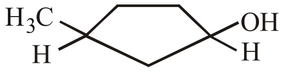
(c) 

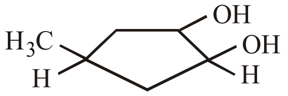
(d) 

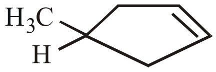
43. The correct product obtained in the reaction



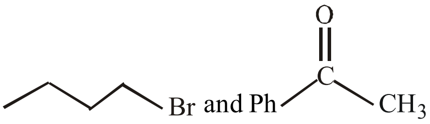
(a) 

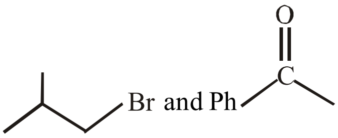
(b) 

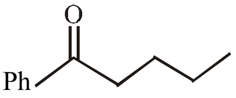
(c) 

(d) 

44. 2-phenyl-2-hexanol can be prepared by Grignard synthesis. The pair of compounds giving the desired product is

(a) 

(b) 

(c)  and PhBr

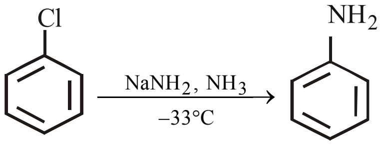
(d) None of these

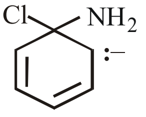
45. The following reaction proceeds through the intermediate formation of

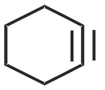
$RCOOAg + Br_2 \longrightarrow RBr + CO_2 + AgBr$

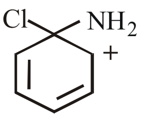
(a) $RCOO^{\bullet}$
(b) $R^{\bullet}$
(c) $Br^{\bullet}$
(d) All of these

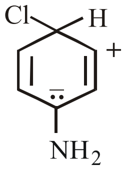
46. Which of the following is a key intermediate in the reaction shown below ?



(a) 

(b) 

(c) 

(d) 

47. Which of the following will give vinyl chloride ?

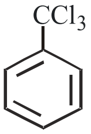
(a) $CH_2 = CH_2 + Cl_2 \xrightarrow{600°C}$

(b) $ClCH_2 - CH_2Cl \xrightarrow[\text{ethanol}]{\text{KOH}}$

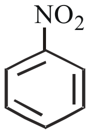
(c) $CH \equiv CH + HCl \xrightarrow{Hg^{2+}}$

(d) All of these

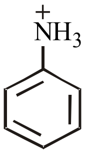
48. In which of the following NO_2^+ will attack at m-position?



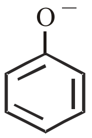
(I)



(II)

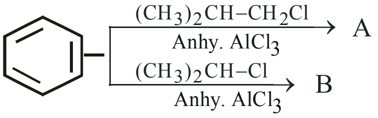


(III)



(IV)

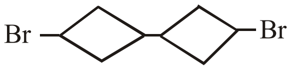
(a) I, II and III
(b) II and IV
(c) II and III only
(d) I only

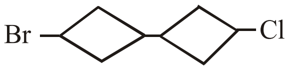
49. 

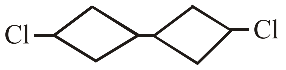
A and B are

(a) tert.-butyl benzene, n-propyl benzene
(b) iso-butyl benzene, iso-propyl benzene
(c) t-butyl benzene, isopropyl benzene
(d) iso-butyl benzene, n-propyl benzene

50. The product of 1-bromo-3-chloro cyclobutane with Na in presence of dioxane

(a) 

(b) 

(c) 

(d) None of these

Hints & Solutions

EXERCISE 1

1. Chloro compounds are most stable, most volatile and are most polar among chloro, bromo and iodo alkanes.

2. The boiling points are in the order: $C_2H_5Cl < C_2H_5Br < C_2H_5I$.

4. Ethyl alcohol converts the poisonous phosgene into non-poisonous ethyl carbonate.

6. Chlorobenzene < 4-nitrochlorobenzene < 2, 4-dinitrochlorobenzene < 2, 4, 6-trinitrochlorobenzene

7. They are unable to form hydrogen bond with water

8. 'A' is chlorobenzene, B is aniline, C is benzene diazonium chloride,

10. (*i*) $X = C_6H_5N_2^+Cl^-$; $Y = C_6H_5Br$; $Z = C_6H_5OH$.

(*ii*) $X = p\,Cl\,C_6H_4CH_3$; $Y = p\,Cl\,C_6H_4CH_2Cl$;

$Z = pCl\,C_6H_4CH_2OH$.

(*iii*) $X = C_6H_5I$, $Y = C_6H_5 - C_6H_5$.

11. (A) is iso-butyl bromide.

19. **(d)** **20.** **(b)** **21.** **(b)** **22.** **(b)** **23.** **(a)**

24. **(b)** **25.** **(a)** **26.** **(a)**

EXERCISE 2

1. **(a)**

2. **(a)** Proceed backward

$$\underset{\text{Isobutyl bromide}}{(CH_3)_2CHCH_2Br} \xleftarrow{HBr} \underset{\text{Isobutylene}}{(CH_3)_2C = CH_2}$$

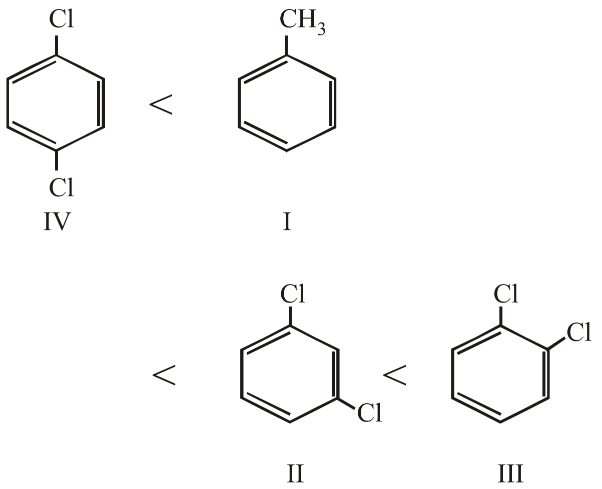
Note that, here HBr is added in anti-Markownikoff's manner, so reaction should take place in presence of peroxide. Hydroquinone and diphenylamine are not free-radical producing substances but scavangers.

3. **(b)** Chlorination of alkanes is a free-radical reaction. Since the intermediate free radical is planar (sp^2 hybridised) it can be attacked on either side of the face forming racemic mixture.

4. **(d)** Due to symmetrical structure, *p*-dichlorobenzene fits closely in the crystal lattice.

5. **(b)** CH_3Cl has higher dipole moment than CH_3F due to *much longer* C–Cl bond length than the C–F bond. The much longer bond length of the C–Cl bond outweighs the effect produced by lower electronegativity of Cl than that of F.

6. **(b)** In *p*-dichlorobenzene, the two equal dipoles are in opposite direction, hence the molecule has zero dipole moment. In *o*- and *m*- dichlorobenzenes, the two dipoles are at 60° and 120° apart respectively, and thus according to parallelogram law of forces, the dipole moment of *o*-dichlorobenzene is much higher than that of *m*-isomer. Lastly, toluene with a +I group possesses little dipole moment. Thus the overall order is



7. **(c)** Because of the small size of F, the C–F bond is strongest in CH_3F.

8. **(c)** Due to resonance in chlorobenzene.

9. **(c)** $K^+ CN^-$ is a nucleophilic reagent.

10. **(c)** More stable the carbocation, more reactive will be the parent alkyl halide towards S_N1 reaction.

3° > Benzyl > Allyl > 2° > 1° > methyl

11. **(d)** S_N1 reaction involves carbocation which are planar (sp^2 hybridised) and thus can be attacked on either face of the carbon.

12. **(d)** Weaker the C–X bond, greater is the reactivity.

13. **(a)** Only 1° alkyl halides (i.e. CH_3Br) undergo S_N2 reaction.

14. **(b)**

15. **(a)** 1° Alkyl halides (having least steric hindrance at the α-carbon atom) are most reactive towards S_N2 reaction.

16. **(c)** Isopropyl chloride, being 2° alkyl halides, can undergo S_N1 as well as S_N2 mechanism.

17. **(d)** Butanenitrile is $CH_3CH_2CH_2CN$ hence will be prepared from $CH_3CH_2CH_2Cl$ (propyl chloride) and not from butyl chloride.

18. **(c)** C_2H_5Br and C_2H_5Cl are ethylating agents, while C_6H_5Cl is inert.

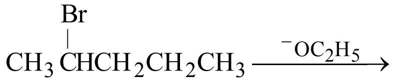
19. (a)

20. (a) $RCOOAg + XR' \longrightarrow RCOOR' + AgX$.

21. (a)

22. (a) Alkyl halides, on treatment with strong base like alc. KOH, undergo elimination reaction rather substitution reaction.

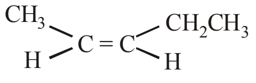
23. (d) Potassium ethoxide is a strong base, hence causes elimination reaction. The alkene formed is governed by Saytzeff rule "more substituted an alkene, higher will be its stability".

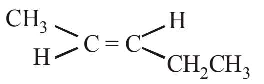


$$CH_3\overset{Br}{\overset{|}{C}}HCH_2CH_2CH_3 \xrightarrow{^{-}OC_2H_5}$$

$$\underset{\text{Pentene–1}}{CH_2 = CHCH_2CH_2CH_3} + \underset{\text{Pentene–2 (more stable)}}{CH_3CH = CHCH_2CH_3}$$

Further pentene-2 shows geometrical isomerism, *cis*- and *trans*- of which *trans*-isomer having bulkier groups away from each other is more stable than the *cis*-isomer.


cis-Pentene-2


trans-Pentene-2 (more stable)

24. (b) Order of reactivity of alkyl halides (having same value of R) towards substitution/dehydro-halogenation follows the same order, i.e. $R-I > R-Br > R-Cl > R-F$

25. (a) Elimination reactions of alkyl halides involve carbocations, hence the order of reactivity is 3° > 2° > 1° alkyl halide.

26. (a)

27. (c) $-CH_3$ group is *o, p*–directing.

28. (d) $-Cl$ is *o, p*–directing.

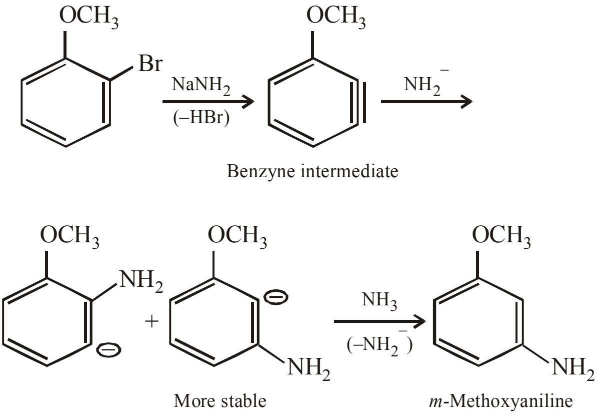
29. (a) N-Phenylacetanilide precipitates out to a complex with anhydrous $AlCl_3$.

30. (c)

31. (d)

32. (c)

33. (d)



34. (c) Allylic bromination by NBS (free-radical reaction).

35. (d) In presence of light, toluene undergoes bromination in side chain (free radical reaction).

36. (b) At high temperature, propene undergoes substitution, rather than addition, with chlorine.

37. (d) More the stability of the carbocation, higher will be the reactivity of the parent chloride.

Allyl chloride > Vinyl chloride > Chlorobenzene

38. (b)

39. (d)

40. (a) $(Cl_3CCH(OH)_2 + NaOH \longrightarrow CHCl_3 + HCOONa + H_2O$

41. (c) CH_3OH does not undergo iodoform reaction, all others do so.

42. (b)

43. (c)

44. (a)

45. (c) $CHI_3 \xrightarrow[(-3KI)]{3KOH} [CH(OH)_3] \xrightarrow[(-H_2O)]{}$

$$HCOOH \xrightarrow[(-H_2O)]{KOH} HCOOK$$

46. (b)

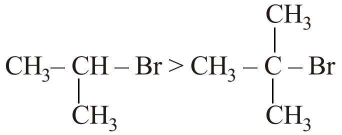
47. (b) $C_2H_5I \xrightarrow{\text{alc. KOH}} CH_2 = CH_2 \xrightarrow{Br_2}$

$$BrCH_2 - CH_2Br \xrightarrow{KCN} CNCH_2.CH_2CN$$

EXERCISE 3

1. (d) For such a reaction the rate of S_N2 substitution reaction is maximum in case of CH_3CH_2Br because S_N2 mechanism is followed in case of primary and secondary halides i.e., S_N2 reaction is favoured by small groups on the carbon atom attached to halogens so order of S_N2 substitution reaction will be

$CH_3\,CH_2\,Br > CH_3\,CH_2\,CH_2\,Br >$

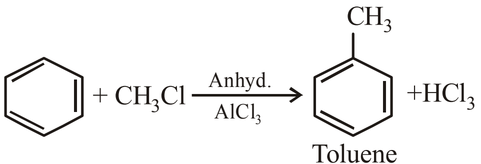


$$CH_3-\underset{CH_3}{\underset{|}{C}}H-Br > CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-Br$$

i.e. option (d) is correct.

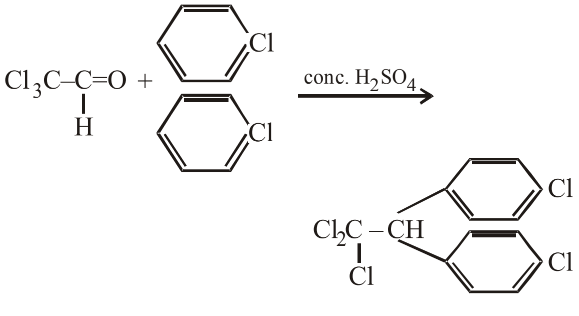
2. (d) It is a nucleophilic substitution reaction as here stronger nucleophile OH^- is replacing weaker nucleophile X^-

3. (d)



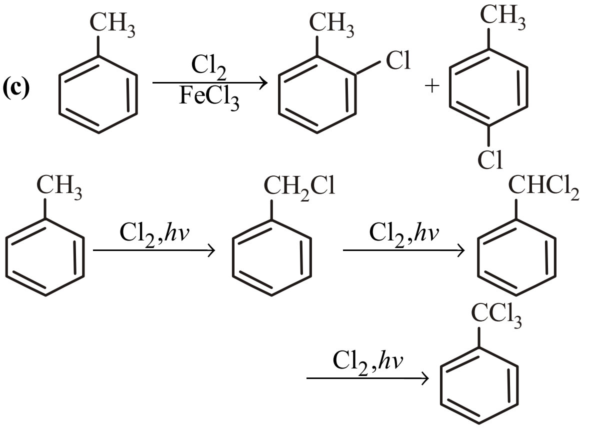
Friedel Craft's reaction.

4. (c)



DDT

5. (c)



6. (c) S_N1 reactions involve the formation of carbocations, order of stability of carbocation is 3° > 2° > 1° hence higher the stability of carbocation, more will be the reactivity of the parent alkyl halide. Moreover the tertiary carbocation formed from (c) is stabilized by two phenyl groups.

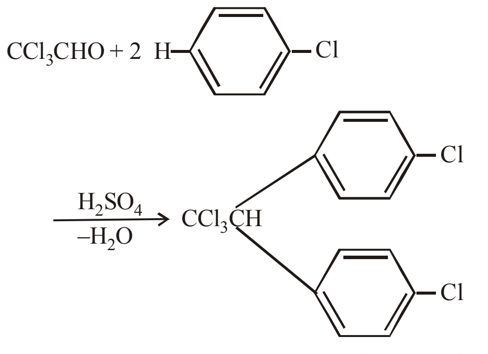
7. (a) A strong nucleophile favours the S_N2 reaction and a weak nucleophile favours the S_N1 reaction.
First reaction is S_N1 reaction because C_2H_5OH is used as solvent which is a weak nucleophile.
Second reaction is S_N2 reaction because $C_2H_5O^-$ is strong nucleophile.

8. (d) $CH_3-Br \xrightarrow{KCN} \underset{(A)}{CH_3-CN} \xrightarrow{H_3O^+}$

$$\underset{(B)}{CH_3-COOH} \xrightarrow{LiAlH_4} \underset{\text{Ethyl alcohol}}{\underset{(C)}{CH_3-CH_2-OH}}$$

9. (d) C_6H_5I will not respond to silver nitrate test because C-I bond has a partial double bond character.

10. (b) DDT is prepared by heating chlorbenzene and chloral with concentrated sulphuric acid



1,1,1-trichloro–2,2 bis (p-chlorophenyl) ethane
or
DDT

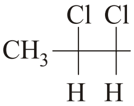
11. (b) Due to steric hindrance tertiary alkyl halide do not react by S_N2 mechanism they react by S_N1 mechanism. S_N2 mechanisam is followed in case of primary and secondary alkyl halides of

$$CH_3-X > CH_3-CH_2X > (CH_3)_2-CH.X > (CH_3)_3-C-X$$

12. (b) Corey House alkane, synthesis

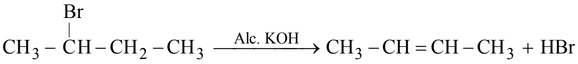
$$R'X + LiR_2Cu \longrightarrow R'-R + RCu + LiX$$

13. (c)



$CH_3-\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{Cl}{C}}-CH_3$. 2, 3-dichloro butane will exhibit optical isomerism due to the presence of two asymmetric carbon atom.

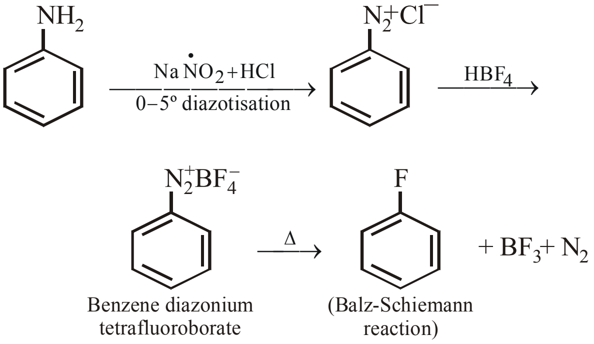
14. (c)



$CH_3-\overset{Br}{\overset{|}{C}}H-CH_2-CH_3 \xrightarrow{\text{Alc. KOH}} CH_3-CH=CH-CH_3 + HBr$

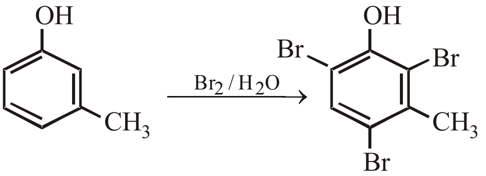
The formation of 2-butene is in accordance to Saytzeff's rule. The more substituted alkene is formed.

15. (d)

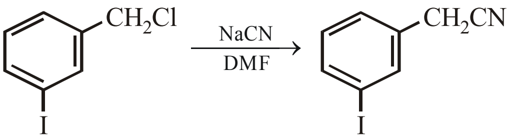


16. (c) The acid character follows the order :
$CH_3COOH > C_6H_5OH > H_2O > CH_3OH$
The basic character will follow the order
$CH_3COO^- < C_6H_5O^- < O^-H < CH_3O^-$
The stronger the acid, the weaker the conjugate base formed.

17. (c) OH group activates the benzene nucleus and



18. (b)



Nuclear substitution will not take place.

19. (c) In S_N2 mechanism transition state is pentavalent. Thus bulky alkyl group will be sterically hindered and smaller alkyl group will favour the S_N2 mechanism. So the decreasing order of reactivity of alkyl halides is
$RCH_2X > R_2CHX > R_3CX$

20. (d) S_N2 reaction is favoured by small groups on the carbon atom attached to halogen.
So, the order of reactivity is

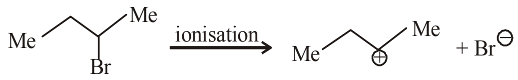
$$CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl > (C_2H_5)_2CHCl$$

S_N2 reaction is shown to maximum extent by primary halides. The only primary halides given is CH_3Cl so the correct answer is (d).

21. (a)

(A)

(B)

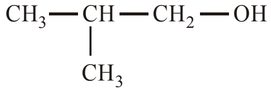


(C)

Since S_N1 reactions involve the formation of carbocation as intermediate in the rate determining step, more is the stability of carbocation higher will be the reactivity of alkyl halides towards S_N1 route. Now we know that stability of carbocations follows the order : 3° > 2° > 1°, so S_N1 reactivity should also follow the same order.

3° > 2° > 1° > Methyl **(S_N1 reactivity)**

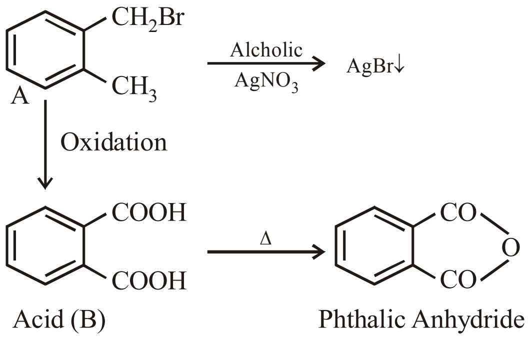
22. (d) Iodoform test is given by methyl ketones, acetaldehyde and methyl secondary alcohols.



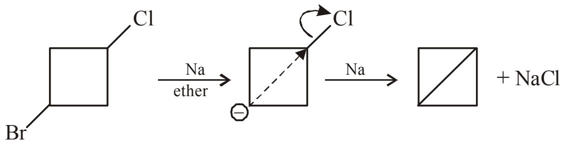
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$$

Isobutyl alcohol is a primary alcohol hence does'nt give positive iodoform test.

23. (d)



24. (d) It is an example of intramolecular Wurtz reaction.



Br^- is a better leaving group than chloride. In this reaction alkali metal (Na) is electron donor.

25. (b) $BrCH_2-CH_2Br \xrightarrow[-HBr]{\text{Alc. KOH}} CH_2=CHBr$

$$\xrightarrow[-HBr]{NaNH_2} CH\equiv CH$$

Elimination of HBr from $CH_2=CHBr$ requires a stronger base because here, Br acquires partial double bond character due to resonance.

EXERCISE 4

1. (d) $C_6H_5COOAg + Br_2 \xrightarrow{\text{Hunsdiecker reaction}}$

$$C_6H_5Br + CO_2 + AgBr$$

2. (b) Weaker the base, better the leaving group. Hence

$$\xrightarrow{\text{Decreasing order of basicity}}$$

$$\underset{(II)}{OMe}\quad \underset{(I)}{OAc}\quad \underset{(III)}{OSO_2Me}\quad \underset{(IV)}{OSO_2CF_3}$$

$$\xleftarrow[\text{Decreasing order of leaving group}]{}$$

3. (c) Stability of the three corresponding carbocations

$$\underset{\text{Allyl Carbocation}}{CH_2=CH\overset{+}{C}HCH_3} > \underset{\text{2° Carbocation}}{CH_3CH_2\overset{+}{C}HCH_3} > \underset{\text{1° Carbocation}}{CH_3CH_2\overset{+}{C}H_2}$$

4. (c) Inversion in configuration occurs in S_N2 reactions.

5. (c)

6. (d) $-NO_2$ group withdraws electrons from *o*- and *p*-positions and hence activates the –Cl present on that position towards nucleophilic substitution.

7. (b) Reactivity decreases as the number of $-NO_2$ group w.r.t. –Br decreases. *m*-Nitrobromobenzene is, however, less reactive than the *p*-nitrobromobenzene since the $-NO_2$ group at the *m*-position cannot stabilize the intermediate carbanion by resonance.

8. (a) $\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow{NaCN} C_6H_5CH_2CN \xrightarrow{H_2/Ni}$

$$\underset{\beta-\text{Phenylethylamine}}{C_6H_5CH_2CH_2NH_2}$$

9. (a) $CH_3CH_2Cl > CH_2=CHCl > C_6H_5Cl$

10. (b) Only CH_3COCH_3 has 58 as molecular weight.

11. (b)

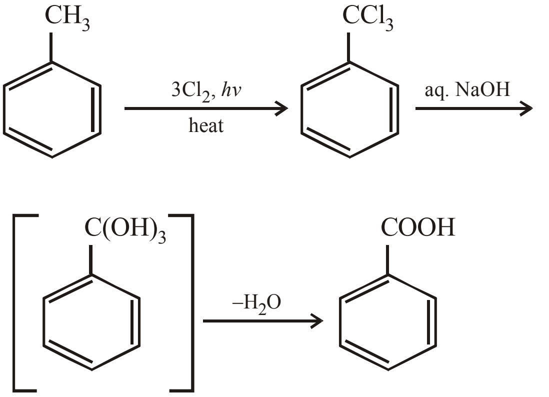
12. (a)

13. (b)

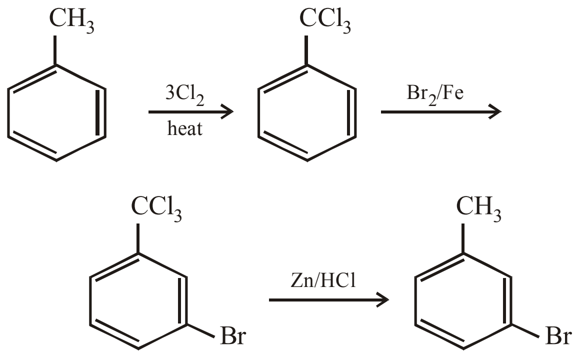
$$CH_3CH_2CH_2Br \xrightarrow{\text{aq. KOH}} CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{Al_2O_3}$$

$$CH_3CH=CH_2 \xrightarrow{Cl_2/H_2O} CH_3.CHOH.CH_2Cl$$

14. (d)



15. (b)



16. (b) $CH_3CH_2CH_2Br \xrightarrow[80°C]{\text{conc. alc. NaOH}}$

$CH_3CH = CH_2 \xrightarrow[20°C]{HBr/CH_3COOH} CH_3.CHBr.CH_3$

17. (a) In the first case the reaction gives side chain substitution product which is easier in A. In the second case the reaction will proceed by benzyne mechanism for which ortho position w. r. to Cl must have H-atoms.

18. (c)

19. (c) Nuclear substituted halogen has double bond character due to resonance.

20. (c) The electron withdrawing nitro groups weaken the C – F bond by inductive effect and resonance.

21. (b) $MeOCH_2Cl \xrightarrow{Slow} \underset{(i)}{Me\ddot{\underset{\cdot\cdot}{O}}\overset{\oplus}{C}H_2} + Cl^-$

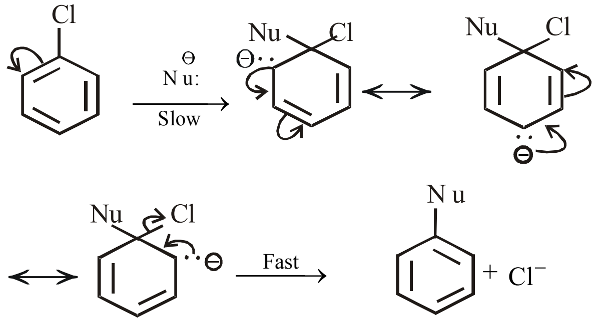
$\updownarrow$

$Me-\underset{\cdot\cdot}{\overset{\oplus}{O}}=CH_2$

(ii)

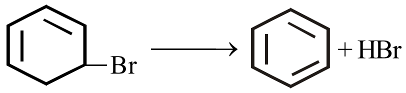
Though (ii) contains +ve charge on oxygen. Since octet around each atom is complete the structure II is more stable than I.

22. (a)



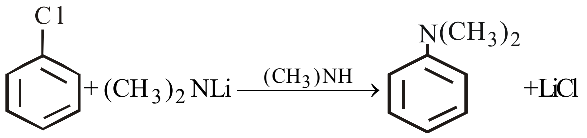
Rate $\propto$ $[C_6H_5Cl]\,[Nu^-:] = k[\text{Aryl halide}]$ [nucleophile]

23. (c)

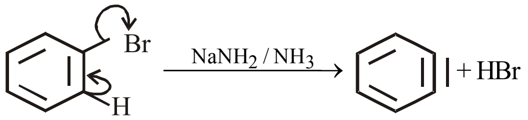


It results in formation of more stable aromatic compound which is benzene.

24. (a)



25. (a)



26. (d) Addition product is formed by anti-Markownikoff's rule.

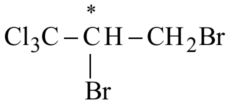
27. (b) The product formed is $CH_3CHD.CH = C(Me)_2$ which cannot exhibit geometrical isomerism due to presence of similar Me groups on alkylenic carbon atom.

28. (a) The nitro groups withdraw electrons from ortho and para positions and make Cl atom (2) more ionic in nature and easy to replace by nucleophile.

29. (c) The compound A is

$Cl_3C.CH_2.CH_2Cl \xrightarrow{aq.KOH} (OH)_3C.CH_2CH_2OH$

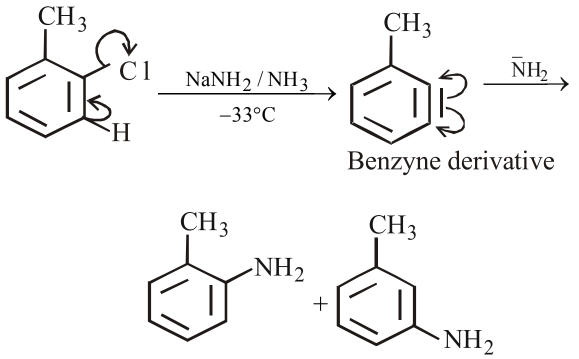
$\xrightarrow{-2H_2O} HO\ CH_2.CH_2COOK.$



The compounds B is $Cl_3C-\underset{\underset{Br}{|}}{\overset{*}{C}}H-CH_2Br$ has chiral centre and can be resolved into d and *l* form.

30. (a) The resonating structure (a) is not possible.

31. (b)



32. (c) Bond energy of $\geqslant C-X$ bond is

$\geqslant C-F > \geqslant C-Cl > \geqslant C-Br > \geqslant C-I$

Hence ease of substitution is

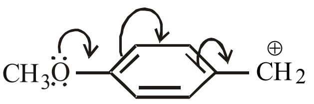
RI > RBr > RCl.

The stability of carbonium ion is 3° > 2° > 1° > methyl.

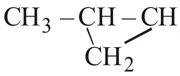
Hence ease of elimination is

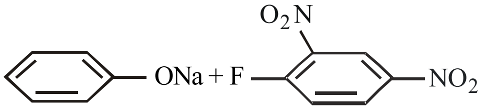
$Me_3CBr > MeCH_2CHBrMe > Me_2CHCH_2Br$

33. (b) Resonance stabilisation of

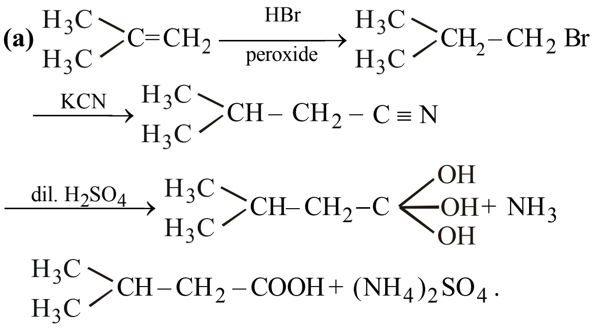


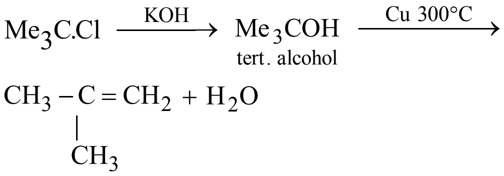
intermediate is more due to + M effect of $CH_3\ddot{\underset{\cdot\cdot}{O}}$ – group.

34. (d) A is 1, 4-addition product due to conjugation B is obtained by further addition of HBr. $(CH_3CHBr.CH_2.CH_2Br)$. B gives C by cyclisation  $CH_3-CH-CH_2$ (CH_2). If B reacts by S_N2 mechanism, Br on 1° carbon must be replaced by OH^- to give $CH_3CHBr-CH_2-CH_2OH$.

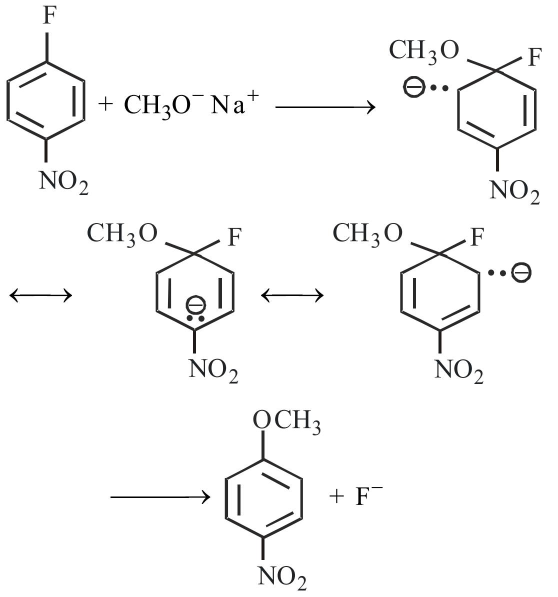
35. (c) 

The C – F bond is more ionic due to inductive effect and – M effect of NO_2 groups.

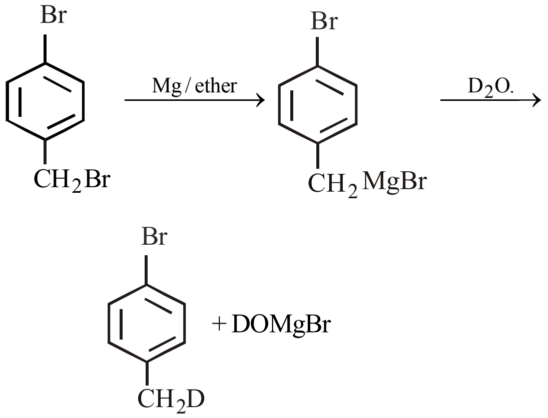
36. (a) 

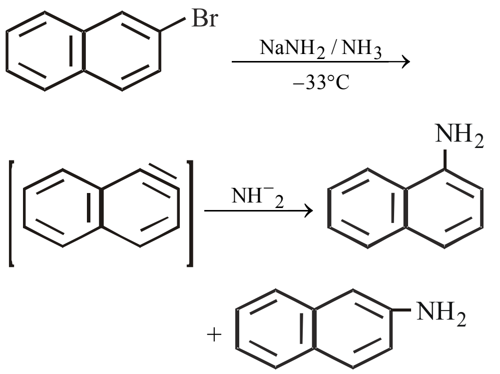
37. (c) 

$Me_3C.Cl \xrightarrow{KOH} Me_3COH$ (tert. alcohol) $\xrightarrow{Cu\ 300°C} CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2+H_2O$

38. (d) 

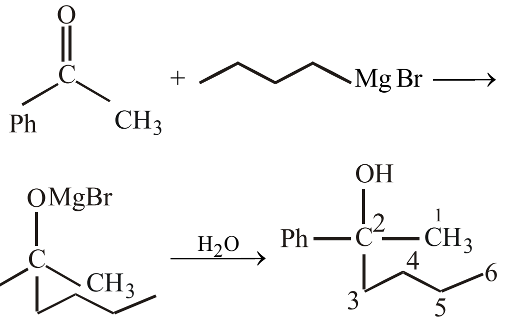
39. (b) The more is the stability of intermediate carbonium ion, the more is the chance of S_N1 mechanism. The intermediates obtained will be $Ph\overset{+}{C}H_2$ (i), $Ph\overset{+}{C}H-Me$ (ii), $Ph\overset{+}{C}-Me_2$ (iii), $Ph\overset{+}{C}MePh$ (iv). The stabilty is of the order iv > iii > ii > i.

40. (c) 

41. (a) 

42. (c) The ease of replacement of H-atoms is 3° > 2° > 1°.

43. (a) In 2° halides of this type the product formed has inverted configuration (S_N2 mechanism).

44. (a) 

2 – phenyl -2-hexanol

45. (d) Mechanism of Hunsdiecker's reaction is

$$R-COO^-\overset{+}{Ag}\xrightarrow[-Ag\,Br]{Br_2}RCOOBr\longrightarrow$$

$$RCO\dot{O}+\dot{Br}\longrightarrow R^{\bullet}+CO_2;$$

$$R^{\bullet}+RCOO\,Br\longrightarrow R-Br+RCO\dot{O}$$

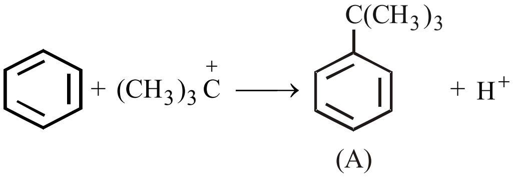
46. (b) The benzyne is intermediate of this type of reaction.

47. (d) All given reactions give the vinyl chloride by substitution (a), by dehydrohalogen atom (b) and by addition (c)

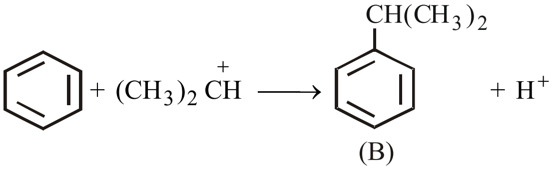
48. (a) $-CCl_3, -NO_2$ and $-\overset{+}{N}H_3$ are meta directing in nature

49. (c) $(CH_3)_2CH-CH_2Cl \xrightarrow[\text{anhy.}]{AlCl_3} (CH_3)_2CH-\overset{\oplus}{C}H_2$

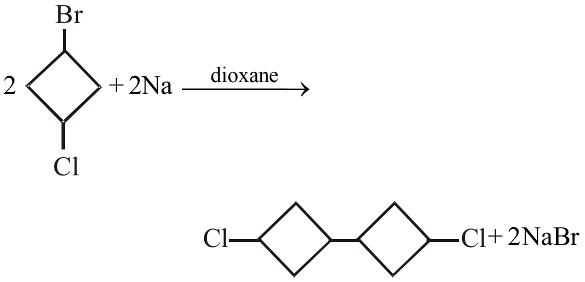
$\xrightarrow{\text{Rearrangement}} (CH_3)\underset{3^\circ}{\overset{+}{C}}$



$(CH_3)_2CH-Cl \xrightarrow[\text{anhy.}]{AlCl_3} (CH_3)_2\underset{2^\circ}{\overset{+}{CH}}$



50. (c) Bond strength follows the order
$C-F > C-Cl > C-Br > C-I$



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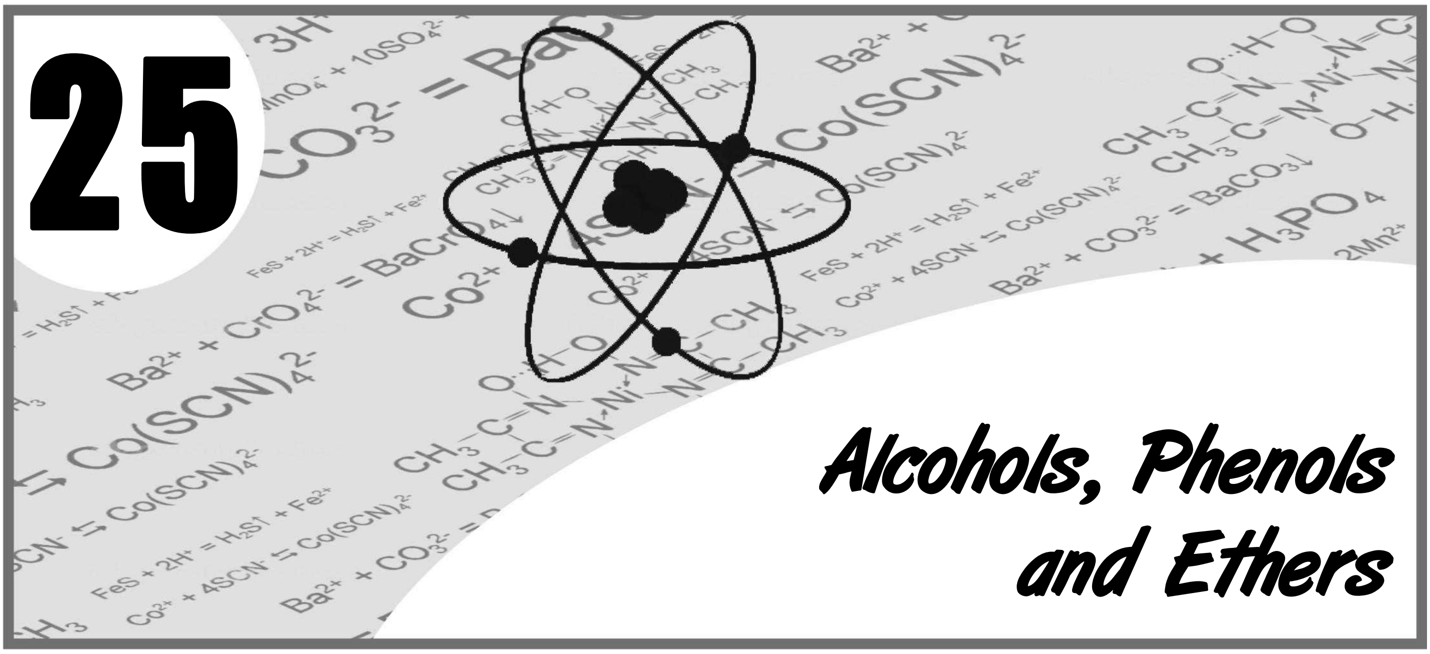
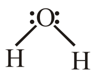
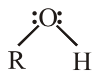


25

Alcohols, Phenols and Ethers

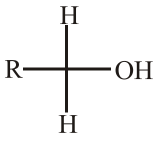
Alcohols are organic compounds containing hydroxyl (OH) group and can be considered analogues of water



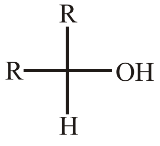


CLASSIFICATION :

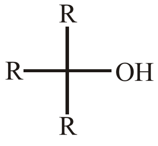
Alcohols are usually classified as **primary**, **secondary** and **tertiary**



Primary



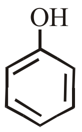
Secondary



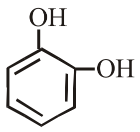
Tertiary

Further they may be monohydric - containing one OH group
dihydric - containing two OH groups
trihydric - containing three OH groups

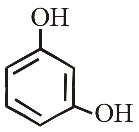
Phenols: Compounds with hydroxyl group bound directly to an aromatic (benzene) ring are called phenols



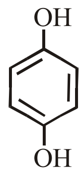
Phenol



Catechol



Resorcinol



Quinol

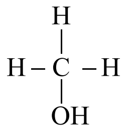
NOMENCLATURE OF ALCOHOLS :

There are three systems of nomenclature

(a) ***The common system:*** According to this system alcohols are named as Alkyl alcohols eg.

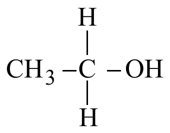
H_3C-OH Methyl alcohol; $H_3C.CH_2OH$ Ethyl alcohol

(b) ***Carbinol system:*** In this system the alcohols are regarded as dervivatives of methyl alcohol which is expressed as ***"carbinol"***.



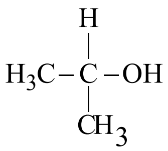
H_3C-OH

Carbinol (methyl alcohol)



CH_3-CH_2-OH

Methyl carbinol
Ethyl alcohol

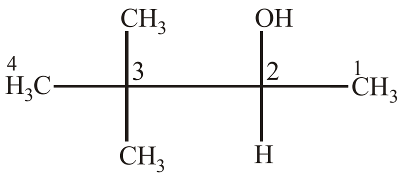


$H_3C-CH(OH)-CH_3$

Dimethyl carbinol

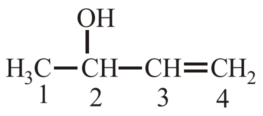
(c) ***IUPAC system:***

(i) Drop the last -e from the alkane name and add -ol to obtain the root name.
(ii) Number the longest chain starting at the end nearest the –OH group
(iii) Name the remaining substituents and their numbers as for alkanes and alkenes.



$\overset{4}{H_3C}-\overset{3}{C}(CH_3)_2-\overset{2}{CH}(OH)-\overset{1}{CH_3}$

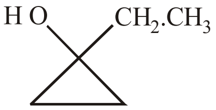
3, 3 - Dimethyl - 2 - butanol



$\underset{1}{H_3C}-\underset{2}{CH}(OH)-\underset{3}{CH}=\underset{4}{CH_2}$

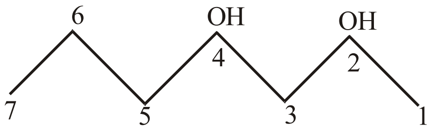
3-Buten-2-ol

(iv) Cyclic alcohols have the prefix cyclo, and the hydroxyl group is deemed to be on C-1



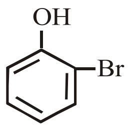
1-Ethyl cyclopropanol

The compounds with two hydroxyl groups are known as diols

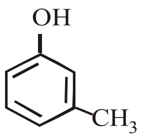


2, 4 - Heptandiol

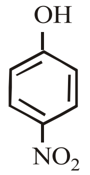
In case of phenols the position of substituents are represented by numbers (the terms ortho, meta and para are non (IUPAC)



2-Bromo phenol
(orthobromo phenol)



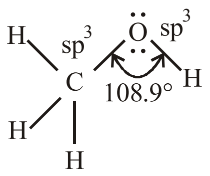
3-Methylphenol
meta-methylpenol



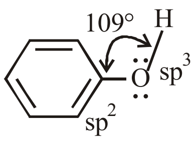
4-Nitrophenol
para-nitrophenol

STRUCTURE :

The oxygen atom in alcohols and phenols is sp^3 hybridised and they have tetrahedral disposition of hybrid atomic orbitals. The two hybrid atomic orbitals have lone pair of electrons and remaining two are involved in bond formation.



C–O bond 142 pm



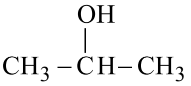
C–O bond 136 pm
(due to resonance)

The value of $\angle ROH$ bond angle depends upon the bulk of R group and repulsion between lone pair of electrons on oxygen.

ISOMERISM :

The alcohols exhibit

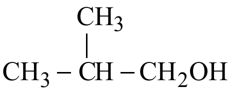
(i) Position isomerism: eg. $CH_3-CH_2-CH_2-OH$
1 – Propanol



$$CH_3-\underset{}{\overset{OH}{\overset{|}{C}}}H-CH_3$$

2-Propanol

(ii) Chain isomerism: eg. $CH_3-CH_2-CH_2-CH_2OH$
1 – Butanol



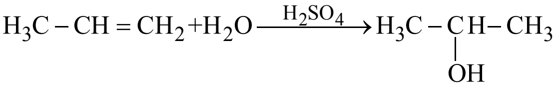
$$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2OH$$

2 – Methyl – 1 – propanol

GENERAL METHODS OF PREPARATION :

(1) From alkenes

(i) Acid catalysed hydration of alkenes: Addition of water to an unsymmetrical alkene follows Markowni Kov's rule



$$H_3C-CH=CH_2+H_2O\xrightarrow{H_2SO_4}H_3C-\underset{OH}{\underset{|}{C}}H-CH_3$$

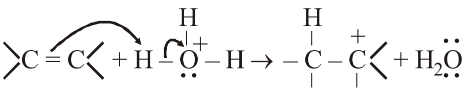
Isopropyl Alcohol

The method is suitable for the preparation of secondary and tertiary alcohols only.

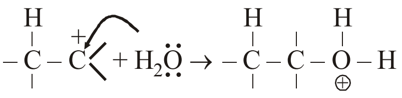
Mechanism :

(i) Protonation of alkene :

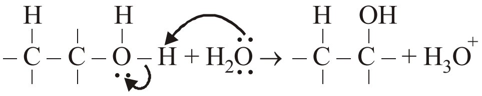
$$H_2O+H^+\rightarrow H_3O^+$$



(ii) Nucleophilic attack of $H_2\ddot{O}$

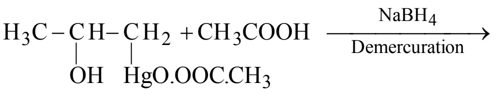


(iii) Deprotonation

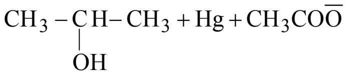


(ii) Oxymecuration-demercuration: The overall process is the addition of water molecule to unsymmetrical alkene according to Markovnikov's rule

$$CH_3-CH=CH_2+Hg(OOC.CH_3)_2+H_2O\xrightarrow[\text{Oxymercuration}]{\text{THF}}$$



$$H_3C-\underset{OH}{\underset{|}{C}}H-\underset{HgO.OOC.CH_3}{\underset{|}{C}}H_2+CH_3COOH\xrightarrow[\text{Demercuration}]{NaBH_4}$$



$$CH_3-\underset{OH}{\underset{|}{C}}H-CH_3+Hg+CH_3CO\overline{O}$$

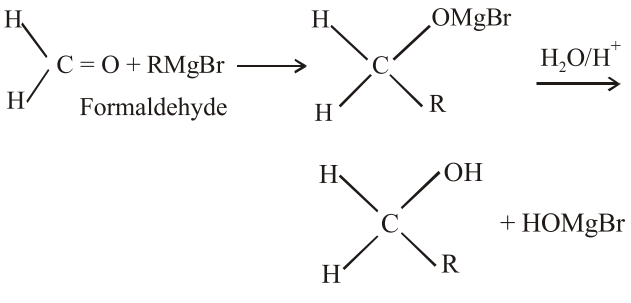
(iii) ***Hydroboration:*** oxidation of alkenes. The overall process is the addition of water molecule to unsymmetrical alkene follow Kharasch's effect

$$3CH_3-CH=CH_2+BH_3 \rightarrow (CH_3-CH_2-CH_2)_3B$$

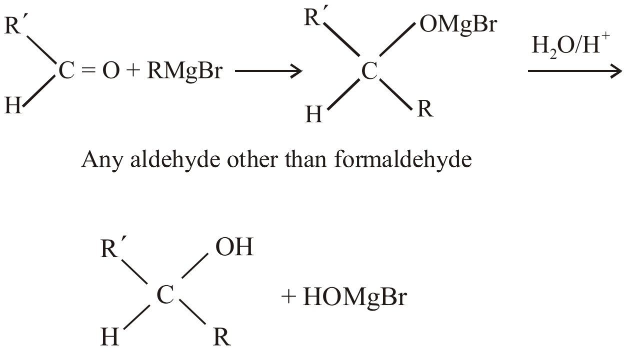
$$\xrightarrow[H_2O_2]{\overline{OH}} CH_3-CH_2CH_2OH+H_3BO_3$$

(2) From carbonyl compounds:

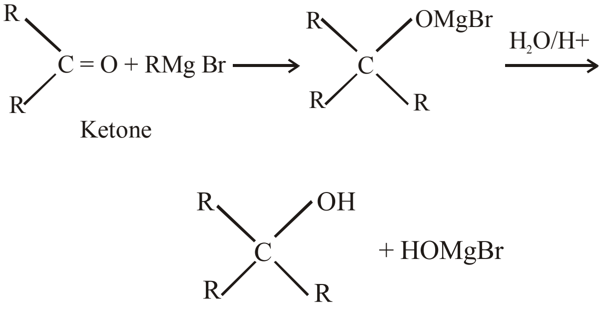
(i) using Grignard's reagent.



Primary alcohol



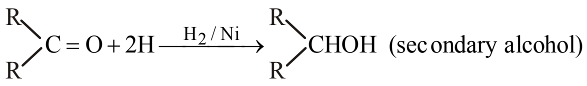
Secondary alcohol



Tertiary alcohol

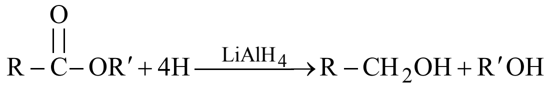
(ii) ***By reduction:*** Catalytic hydrogenation. The reducing agents used are H_2/Ni, $LiAlH_4$, $NaBH_4$ or Na/C_9H_5OH

$$RCHO+2H \xrightarrow{H_2/Ni} RCH_2OH. \text{ (primary alcohol)}$$



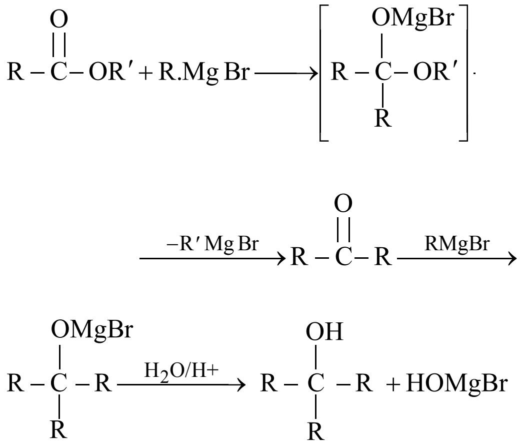
(3) From esters:

(i) By reduction with $LiAlH_4$ or Na/C_2H_5OH (Bouveault-Blanc reduction)



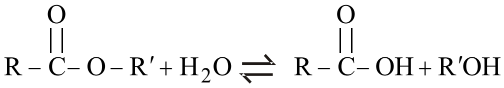
$$R-\overset{\overset{O}{||}}{C}-OR'+4H \xrightarrow{LiAlH_4} R-CH_2OH+R'OH$$

(ii) By using Grignard's reagent.



Tertiary alcohol

(iii) By hydrolysis of esters:



$$R-\overset{\overset{O}{||}}{C}-O-R'+H_2O \rightleftharpoons R-\overset{\overset{O}{||}}{C}-OH+R'OH$$

(4) Hydrolysis of alkyl halides:

$$R-X+NaOH \xrightarrow{Water} ROH+NaX$$

To avoid dehydrohalogenation of RX, mild alkalis like moist silver oxide or aqueous potassium carbonate is used

Ease of hydrolysis of alkyl halides RI > RBr > RCl and t > s > p

(5) By reduction of Acids and their derivatives:

$$RCOOH \xrightarrow{LiAlH_4} RCH_2OH$$

$$RCOCl+2H_2 \xrightarrow{Ni} R.CH_2OH+HCl$$

(6) By hydrolysis of ethers:

$$R-\ddot{O}-R+H_2O \xrightarrow{H_2SO_4} 2ROH$$

(7) From primary amines: By treatment with nitrous acid.

$$RNH_2+HONO \xrightarrow{NaNO_2+HCl} ROH+N_2+H_2O$$

Note: Methylamine does not give methyl alcohol when treated with HNO_2. It gives CH_3OCH_3 and CH_3ONO

GENERAL PROPERTIES :

Alcohols are neutral substances and do not effect litmus. Lower alcohols are colourless toxic liquids, C_4– C_{11} members are oily liquids and higher alcohols are waxy solids.

Solubility :

The hydroxyl groups in alcohols can form hydrogen bonds with water and many low molecular weight alcohols are miscible with water. The hydroxyl group is said to be ***hydrophilic*** (water loving) and alkyl (hydrocarbon) end is ***hydrophobic*** (water hating). The solubility decreases with increase in molecular mass. The hydrophobic effect of alkyl group predominates the hydrophilic effect of –OH group. Among isomeric alcohols, the branched chain alcohols are more soluble due to less surface area of hydrophobic part.

Acidity of Alcohols :

Just like water the hydroxyl groups in alcohols are weakly acidic - strong bases can generate alkoxide ions

$$R-O-H+B:^{-} \longrightarrow R-O^{\ominus}+B-H$$

The acidities of alcohols vary greatly depending on the substituents.

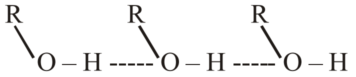
Alcohol	*pka*	
Methanol	CH_3OH	15.5
Ethanol C_2H_5OH		15.9
t-Butyl alcohol	$(CH_3)_3$ C–OH	19.0
2-Chloro ethanol	ClC_2H_4OH	14.3
2, 2, 2-Chloro ethanol	$Cl_3.CCH_2OH$	12.4
Cyclohexanol	$C_6H_{11}OH$	18.0
Phenol	$C_6H_5.OH$	10.0
Water	HOH	15.7

(The lower the p_{ka}, the stronger the acid)

Electrons withdrawing groups on an alcohol increase the acidity by stabilising the alkoxide formed.

Boiling points :

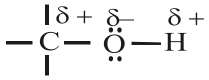
Due to intermolecular hydrogen bonding the alcohols have higher value for boiling points.



For isomeric alcohols the boiling points follow the order ***primary alcohol*** > ***secondary alcohol*** > ***tertiary alcohol***

CHEMICAL PROPERTIES :

The alcohols contain ionic C–O and O–H bonds



$$-\overset{|}{\underset{|}{C}}^{\delta+}-\ddot{\underset{\cdot\cdot}{O}}^{\delta-}-H^{\delta+}$$

Hence three types of reactions are shown by alcohols.

(1) Reactions involving rupture of – O – H bond

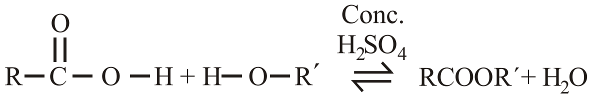
(a) Acidic character of alcohols

$$2ROH+2Na \longrightarrow 2R\bar{O}Na^{+}+H_2$$

The acid strength follows the order

Methyl alcohol > Primary alcohol > Secondary alcohol > Tertiary alcohol

(b) Ester formation: Alcohols react with acids to give esters in presence of Conc H_2SO_4 ***(Fischer Esterification)***



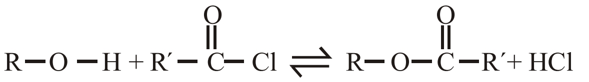
$$R-\overset{\overset{O}{||}}{C}-O-H+H-O-R' \underset{}{\overset{\text{Conc. } H_2SO_4}{\rightleftharpoons}} RCOOR'+H_2O$$

The order of ease of formation of ester

Primary alcohol > Secondary alcohol > Tertiary alcohol

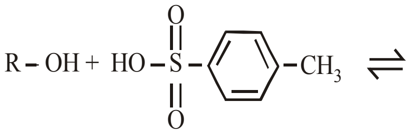
$HCOOH > CH_3COOH > (CH_3)_2CH.COOH > (CH_3)_3C.COOH$

Acid chlorides also produce esters

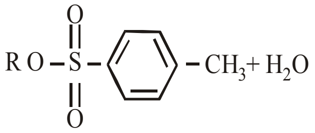


$$R-O-H+R'-\overset{\overset{O}{||}}{C}-Cl \rightleftharpoons R-O-\overset{\overset{O}{||}}{C}-R'+HCl$$

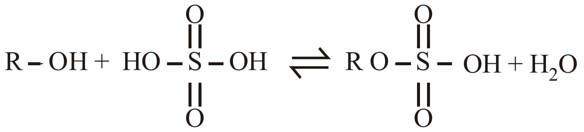
Esters of Inorganic acids: Alcohols also form esters with inorganic acids



p-Toluene sulphonic acid

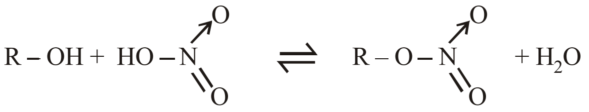


p-Toluene sulphonate ester



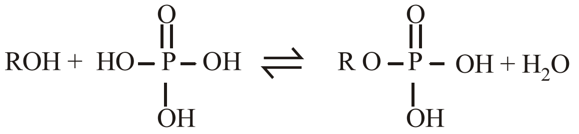
$$R-OH+HO-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}}-OH \rightleftharpoons RO-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}}-OH+H_2O$$

Sulphuric acid Alkyl sulphate



$$R-OH+HO-N\overset{\nearrow O}{\underset{\searrow O}{}} \rightleftharpoons R-O-N\overset{\nearrow O}{\underset{\searrow O}{}}+H_2O$$

Nitric acid Alkyl nitrate ester



$$ROH+HO-\overset{\overset{O}{||}}{\underset{\underset{OH}{|}}{P}}-OH \rightleftharpoons RO-\overset{\overset{O}{||}}{\underset{\underset{OH}{|}}{P}}-OH+H_2O$$

Phosphoric acid Alkyl phosphate ester

Phosphate esters are important in nature since they link the nucleotide bases together in DNA.

(c) Reaction with Grignard reagent: Hydrocarbons are formed

$$ROH+R'MgX \longrightarrow R'H+ROMgX$$

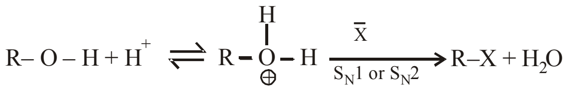
(d) Reaction with metal hydrides or metal amides:

$$ROH+\overset{+}{Na}\overset{-}{H} \longrightarrow R\overset{-}{O}\overset{+}{Na}+H_2$$

$$ROH+\overset{+}{Na}\overset{-}{NH_2} \longrightarrow R\overset{-}{O}\overset{+}{Na}+NH_3$$

(2) Reactions involving rupture of –C–O bond:

(a) Reaction with HX: Alkyl halides are formed. The OH group is a poor leaving group, but $-\overset{+}{O}H_2$ is an excellent leaving group. In acidic medium, the alcohol is in equilibrium with protonated form



$$R-O-H+\overset{+}{H} \rightleftharpoons R-\underset{\oplus}{\overset{H}{\overset{|}{O}}}-H \xrightarrow[S_N1 \text{ or } S_N2]{\bar{X}} R\text{–}X+H_2O$$

If R is primary alkyl → S_N2

If R is bulky tertiary alkyl → S_N1

The order of reactivity of hydrogen halides

HI > HBr > HCl

The order of reactivity of alcohols

tertiary > secondary > primary

In case of HCl, $ZnCl_2$ (Lewis acid) is added to help compensate for the lower nucleophilicity of chloride ion.

The mixture of conc. HCl and $ZnCl_2$ is called the **Lucas Reagent**, secondary and tertiary alcohols react via S_N1 mechanism

Limitations of use of HX

(i) Carbocations can lead to rearranged products

(ii) Reaction can proceed with elimination reaction

(iii) It works better for HCl and HBr.

(iv) Yield is poor in case of primary and secondary alcohols.

(b) Reaction with phosphorous halides: Phosphorous halides convert alcohols to alkyl halides

$$ROH+PCl_5 \rightarrow RCl+POCl_3+HCl$$

$$3ROH+PBr_3 \xrightarrow{P/Br_2} 3RBr+H_3PO_3$$

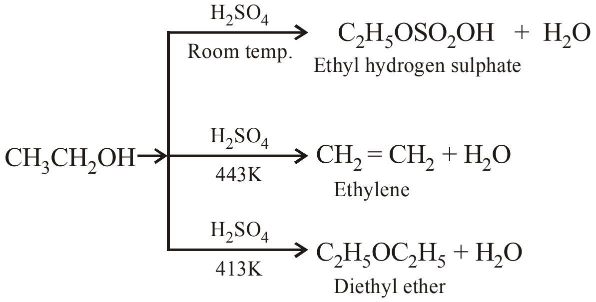
$$3ROH+PI_3 \xrightarrow{P/I_2} 3RI+H_3PO_3$$

(c) Reaction with thionyl chloride: Alkyl chlorides are obtained

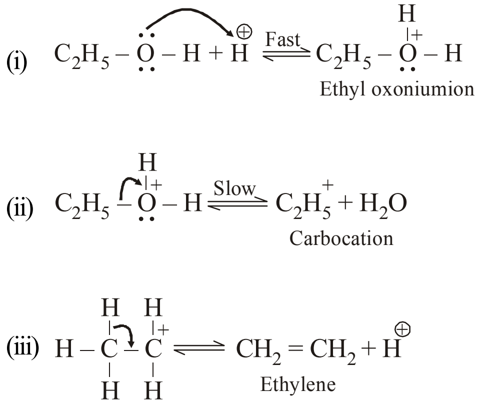
$$ROH+SOCl_2 \longrightarrow RCl+SO_2\uparrow+HCl\uparrow$$

(d) Dehydration of alcohols: It requires acidic catalyst and the reaction proceeds via intermediate formation of carbonium ion. Acidic catalyst convert hydroxyl group into a good leaving group.

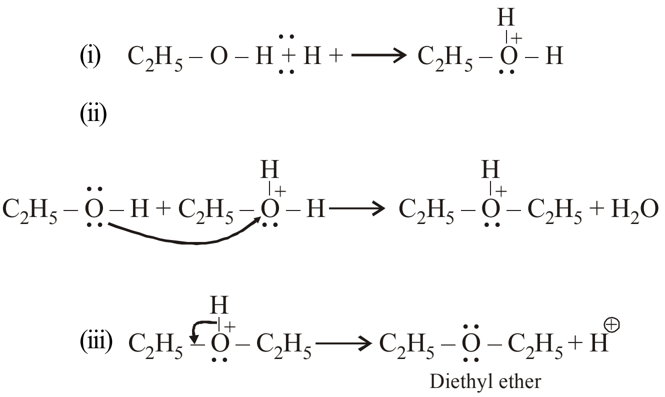
- Since the rate determining step is the formation of carbocation the ease of dehydration is
  3° > 2° > 1°
- The free carbocation undergo rearrangement
- Dehydration proceeds by Saytzeff's rule i.e. more substituted alkene is formed or hydrogen is removed from the C-atom containing lesser number of hydrogen atoms.
- The reaction of ethyl alcohol with H_2SO_4 is very sensitive to reaction conditions



Mechanism



The formation of ether is S_N2 reaction (nucleophilic bimolecular)



(e) Reaction with ammonia: A mixture of amines is obtained in presence of a catalyst like anhydrous alumina

$$ROH+NH_3 \xrightarrow{\text{anh } Al_2O_3} RNH_2+H_2O$$

$$ROH+RNH_2 \xrightarrow{\text{anh } Al_2O_3} R_2NH+H_2O$$

$$ROH+R_2NH \xrightarrow{\text{anh } Al_2O_3} R_3N+H_2O$$

Miscellaneous reactions:

1. ***Oxidation:*** Primary and secondary alcohols are easily oxidised by a variety of reagents eg. acidified potassium dichromate, acidified or alkaline potassium permangnate or dit. nitric acid.

$$\underset{\substack{\text{Ethyl alcohol}\\\text{(2C atoms)}}}{CH_3CH_2OH} \xrightarrow{[O]} \underset{\substack{\text{Acetaldehyde}\\\text{(2C atoms)}}}{CH_3CHO} \xrightarrow{[O]} \underset{\substack{\text{Acetic acid}\\\text{(2C atoms)}}}{CH_3COOH}$$

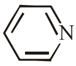
$$\underset{\substack{\text{Isopropyl alcohol}\\\text{(3C atoms)}}}{CH_3CHOHCH_3} \longrightarrow \underset{\substack{\text{Acetone}\\\text{(3C atoms)}}}{CH_3COCH_3} \longrightarrow \underset{\substack{\text{Acetic acid}\\\text{(2C atoms)}}}{CH_3COOH}$$

$$\underset{\text{tert. butyl alcohol (4C)}}{(CH_3)_3COH} \xrightarrow{[O]} \underset{\text{Acetone (3C)}}{CH_3.CO.CH_3} \xrightarrow{[O]} \underset{\text{Acetic acid (2C)}}{CH_3COOH}$$

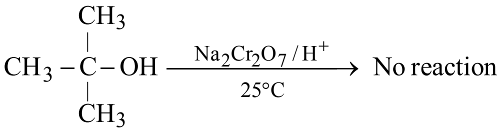
- Chromic acid is produced in situ

$$Na_2Cr_2O_7 + H_2O + 2H_2SO_4 \longrightarrow 2H_2CrO_4 + 2NaHSO_4$$

- A common reagent that selectively oxidizes a primary alcohol to an aldehyde (and no further) is pyridinium chloro chromate PCC
- Chromate PCC


N: CrO_3. HCl eg. $RCH_2OH \xrightarrow{PCC} RCHO$

- Tertiary alcohols having no hydrogen atoms attached to the oxygen bearing carbon (carbinol carbon) resist oxidation.



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH \xrightarrow[25°C]{Na_2Cr_2O_7/H^+} \text{No reaction}$$

Hence drastic condition is required.

- By oxidation, distinction are made between 1°, 2° and 3° alcohols

2. ***Dehydrogenation:*** When vapours of 1°, 2° and 3° alcohols are passed over hot reduced copper at 300°C, they give different products.

$$\underset{1° \text{ alcohol}}{RCH_2OH} \xrightarrow[\text{Dehydrogenation}]{Cu/300°C} \underset{\text{Aldehyde}}{RCHO} + H_2 \uparrow$$

$$\underset{2° \text{ alcohol}}{RCHOH-R} \xrightarrow[\text{Dehydrogen ation}]{Cu/300°C} \underset{\text{Ketone}}{R.CO.R} + H_2 \uparrow$$

$$\underset{3° \text{ alcohol}}{(CH_3)_3COH} \xrightarrow[\text{Dehydration}]{Cu/300°C} \underset{\text{Alkene (Isobutylene)}}{\overset{CH_3}{\underset{CH_3}{}}\!\!>C=CH_2} + H_2O$$

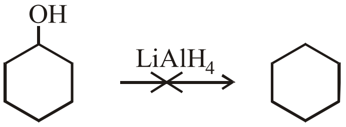
This property is also utilised for distinction between 1°, 2° and 3° alcohols

3. ***Reaction with halogens:*** The reaction with halogens is oxidation and halogenation

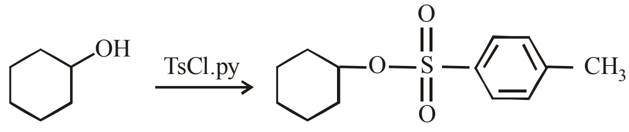
$$CH_3CH_2OH + Cl_2 \longrightarrow CH_3CHO + 2HCl \quad \text{(oxidation)}$$

$$CH_3CHO + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl \quad \text{(halogenation)}$$

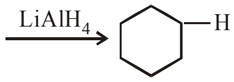
4. ***Reduction of alcohols:*** Normally an alcohol cannot be directly reduced to an alkane in one step



The –OH group is a poor leaving group. It is converted into other superior leaving groups e.g. tosylate group



Cyclohexyl tosylate



Tosylate groups undergo a variety of S_N2 reactions, the common are

$R-OTs: \rightarrow \quad \bar{O}H \longrightarrow ROH$

$\bar{C} \equiv N \longrightarrow RCN$

$\bar{Br} \longrightarrow RBr$

$:NH_3 \longrightarrow RNH_2$

$R'O^- \longrightarrow ROR'$

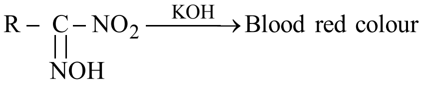
$LiAlH_4 \longrightarrow R-H$

DISTINCTION BETWEEN 1°, 2° AND 3° ALCOHOLS:

A distinction between them can be made by any of the following methods

1. **By oxidation products**] **See properties**
2. **By dehydrogenation products**]
3. ***Lucas test:*** Lucas reagent is [Conc. HCl + anhydrous $ZnCl_2$]
   3° alcohol + Lucas reagent – immediate turbidity
   2° alcohol + Lucas reagent – turbidity after 5 minutes
   1° alcohol + Lucas reagent – turbidity after 30 minutes
   In fact alkyl chloride is formed which being insoluble in the medium form cloudiness (turbidity). Hence different alcohols react with Lucas reagent in the following order
   3° alcohol > 2° alcohol > 1° alcohol
4. ***Victor Meyer's test:*** The various steps involved are

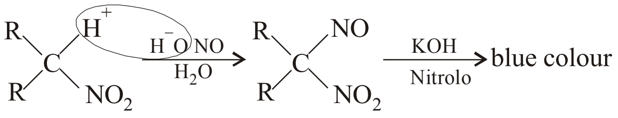
(i) $RCH_2OH \xrightarrow{HI} RCH_2I \xrightarrow{AgNO_2} RCH_2NO_2 \xrightarrow{HNO_2}$



$$R-\underset{\substack{||\\NOH}}{C}-NO_2 \xrightarrow{KOH} \text{Blood red colour}$$

Nitrolic acid

(ii) $\text{RCHOHR} \xrightarrow{\text{HI}} \begin{matrix}\text{R}\\ \text{R}\end{matrix}\!>\text{CHI} \xrightarrow{\text{AgNO}_2} \begin{matrix}\text{R}\\ \text{R}\end{matrix}\!>\text{CHNO}_2$



(iii) $\text{R}_3\text{COH} \xrightarrow{\text{HI}} \text{R}_3\text{CI} \xrightarrow{\text{AgNO}_2} \text{R}_3\text{CNO}_2$

$$\xrightarrow{\text{HNO}_2} \text{No reaction} \xrightarrow{\text{KOH}} \text{Colourless}$$

Tests for alcohols:

1. Sodium metal test

$$\text{ROH} + \text{Na} \longrightarrow \text{RONa} + \frac{1}{2}\text{H}_2 \text{ brisk}$$

2. Phosphorous pentachloride test

$$\text{ROH} + \text{PCl}_5 \longrightarrow \text{RCl} + \text{POCl}_3 + \text{HCl}\uparrow$$

Solution becomes warm with evolution of hydrogen chloride.

3. Acylation

$$\text{ROH} + \text{R}'\text{COCl} \longrightarrow \text{RO.COR}' + \text{HCl}$$

Evolution of hydrogen chloride

METHYL ALCOHOL (Carbinol or wood spirit) :

Manufacture :

1. ***From water gas : (Patart process)***

$$\underset{\text{steam}}{\text{C} + \text{H}_2\text{O}} \xrightarrow{1300°\text{C}} \text{CO} + \text{H}_2$$

$$(\text{CO} + \text{H}_2) + \text{H}_2 \xrightarrow[300°\text{C}]{\text{ZnO+Cr}_2\text{O}_3\text{+CuO}} \text{CH}_3\text{OH}$$

2. ***From natural gas :*** $2\text{CH}_4 + \text{O}_2 \xrightarrow[260°\text{C}]{\text{Cu}} 2\text{CH}_3\text{OH}$

9 : 1

3. ***From pyroligneous acid:*** The pyroligneous acid is obtained by destructive distillation of wood and contains

Acetic acid 9-10%
methyl alcohol 2-2.50%
acetone 0.5%

$$\text{Pyroligenous acid} \xrightarrow[\text{lime}]{\text{milk of}} (\text{CH}_3\text{COO})_2\text{Ca}\downarrow + \text{CH}_3\text{OH} + \text{CH}_3\text{COCH}_3$$

$$\xrightarrow{\text{fractional distillation}} \begin{matrix}\text{Ist fraction (acetone bpt 56°C)}\\ \text{IInd fraction (methyl alcohol 65°C)}\end{matrix}$$

Properties: Colourless liquid, extremely poisonous, inflamable

Uses :

(i) It is used as solvent for oils, paints andcvarnishes
(ii) Manufacture of formaldehyde
(iii) As an antifreez
(iv) To denature ethyl alcohol. (rectified spirit).

ETHYL ALCOHOL (GRAIN ALCOHOL) :

Manufacture:

(1) ***From ethylene***

$$\text{C}_2\text{H}_4 + \text{H}_2\text{SO}_4 \xrightarrow{75–80°\text{C}} \text{C}_2\text{H}_5.\text{HSO}_4$$

$$\text{C}_2\text{H}_5.\text{HSO}_4 + \text{H}_2\text{O} \xrightarrow{\Delta} \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{SO}_4$$

(2) $\text{C}_2\text{H}_4 + \text{H}_2\text{O} \xrightarrow[300°\text{C, 68 atm}]{\text{H}_3\text{PO}_4} \text{C}_2\text{H}_5\text{OH}$

(3) Fermentation of carbohydrates. From molasses

$$\underset{\text{Sucrose}}{\text{C}_{12}\text{H}_{22}\text{O}_{11}} + \text{H}_2\text{O} \xrightarrow{\text{Invertase}} \underbrace{\text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6}_{\text{Invert Sugar (Glucose+Fructose)}}$$

$$\text{C}_6\text{H}_{12}\text{O}_6 \xrightarrow{\text{Zymase}} 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2$$

$$\text{or } \underset{\text{Starch}}{2(\text{C}_6\text{H}_{10}\text{O}_5)_n} + n\text{H}_2\text{O} \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{n\text{C}_{12}\text{H}_{22}\text{O}_{11}}$$

$$\underset{\text{Maltose}}{\text{C}_{12}\text{H}_{22}\text{O}_{11}} + \text{H}_2\text{O} \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2\text{C}_6\text{H}_{12}\text{O}_6}$$

$$\underset{\text{Glucose}}{\text{C}_6\text{H}_{12}\text{O}_6} \xrightarrow{\text{Zymase}} 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2$$

Properties:

Colourless liquid, burns with blue flame, b.pt. 78.1°C, Sp. gr. 0.789. It can not be dried over anhydrous calcium chloride due to formation of addition product. $\text{CaCl}_2.4\text{C}_2\text{H}_5\text{OH}$. It gives iodofarm test.

Uses :

(1) As a solvent for paints, oils, varnishes etc (2) In the manufacture of alcohlic beverages (3) Manufacture of acetic acid, chloroform, iodoform etc (4) As an antifreez (5) With saturated calcium acetate solution forms a solid gel which burns like alcohol.

SOME COMMERCIALLY IMPORTANT ALCOHOLS:

(1) **Rectified spirit:** It contains 95.5% ethyl alcohol and 4.50% water. It is an azeotrope (Constant boiling mixture) and boils at 74°C.

(2) **Absolute alcohol:** Alcohol containing no water i.e. 100% $\text{C}_2\text{H}_5\text{OH}$ is known as absolute alcohol. It is prepared as follows.

1. **Quick lime process :**

$$(\text{Rectified spirit} + \text{CaO}) \xrightarrow[\text{days}]{4-5} \text{C}_2\text{H}_5\text{OH} + \text{Ca(OH)}_2$$

$$\xrightarrow{\text{distill}} \text{Absolute alcohol}$$

Final traces of water are removed by adding anhydrous CuSO_4 or metallic magnesium and again distillation, Mg forms Mg(OH)_2.

2. **Azeotropic method:** Rectified spirit + Excess of benzene → a temporary azeotrope is formed which is subjected to fractional distillation

   Ist fraction distills at 64.8ºC consisting water 7.49%, alcohol 18.5%, benzene 74.1%

   IInd fraction distills at 68.2ºC, consisting of alcohol 32.4%, benzene 67.6%

   IIIrd fraction distills at 78.2ºC and give absolute alcohol

3. **Methylated spirit:** The rectified spirit rendered poisonous by addition of 4-5% methyl alcohol, traces of pyridine and some copper sulphate is known as methylated spirit or denatured alcohol.
4. **Power alcohol:** Alcohol mixed with petrol and used in internal combustion engines is known as power alcohol. Mixing is done in presence of 1% benzene, or 1% ether or 1% tetralin.
5. **Alcoholic Beverages:** The liquors used for drinking purposes containing alcohol as the main intoxicating agent are known as the alcoholic beverages. They are

   (a) Undistilled: Prepared from fruit juices or grains

Name	*Source*	*% alcohol*
Beer	Barley	2-6
Cidar	Apples	3-6
Wine	Grapes	8-10
Port and Sherry	Grapes	14-20

   (b) Distilled: Prepared by distillation of fermented liquids

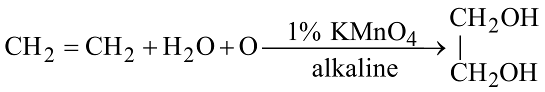
Name	*Source*	*% alcohol*
Whisky	Barley	40-50
Brandy	Peeches, apples	40-50
Rum	Molasses	35-40
Gin	Maize	40-45

6. **Proof-spirit:** An aqueous solution of alcohol containing 57.1% alcohol by volume or 49.3% alcohol by weight is called proof spirit.
7. **Over proof:** A sample containing more percentage of alcohol than proof spirit is known as over proof. 20 O.P. means that 100 ml of this sample contains alcohol equivalent to 120 ml of proof spirit.
8. **Under proof:** A sample containing lower percentage of alcohol than proof spirit is known as under proof. Thus 20 U.P. means that 100 ml of this sample contains alcohol equivalent to 80 ml of proof spirit.
9. **Alcoholmetry:** The determination of the percentage of alcohol is known as alcoholometry. We simply determine the sp. gr. of the sample by means of hydrometer and find the exact percentage of alcohol by referring reference tables.

POLYHYDROXY ALCOHOLS :

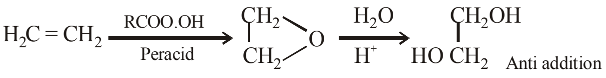
1. **Ethylene glycol (Eth 1, 2-diol)**

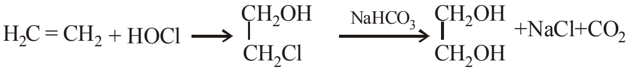
Preparation: (1) *Hydroxylation of ethylene*



$$CH_2=CH_2+H_2O+O\xrightarrow[\text{alkaline}]{1\%\ KMnO_4}\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}$$

Cis addition

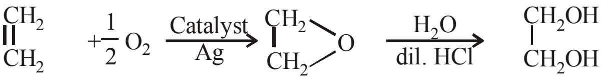




$$H_2C=CH_2+HOCl\longrightarrow\begin{array}{l}CH_2OH\\|\\CH_2Cl\end{array}\xrightarrow{NaHCO_3}\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}+NaCl+CO_2$$

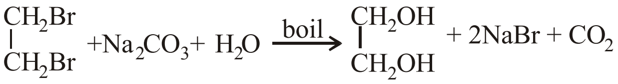
Ethylene chlorhydrin

Industrial method



Ethylene oxide

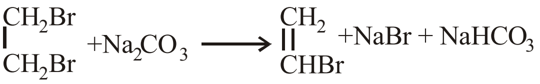
2. ***From ethylene bromide***



$$\begin{array}{l}CH_2Br\\|\\CH_2Br\end{array}+Na_2CO_3+H_2O\xrightarrow{boil}\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}+2NaBr+CO_2$$

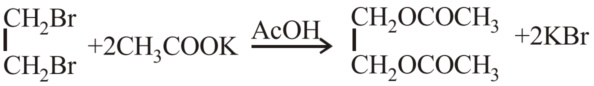
50% yield

Some vinyl bromide is also formed

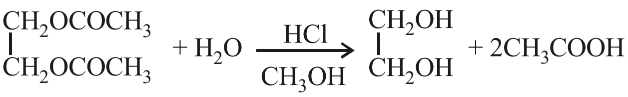


$$\begin{array}{l}CH_2Br\\|\\CH_2Br\end{array}+Na_2CO_3\longrightarrow\begin{array}{l}CH_2\\||\\CHBr\end{array}+NaBr+NaHCO_3$$

To get better yield ethylene bromide is heated with potassium acetate



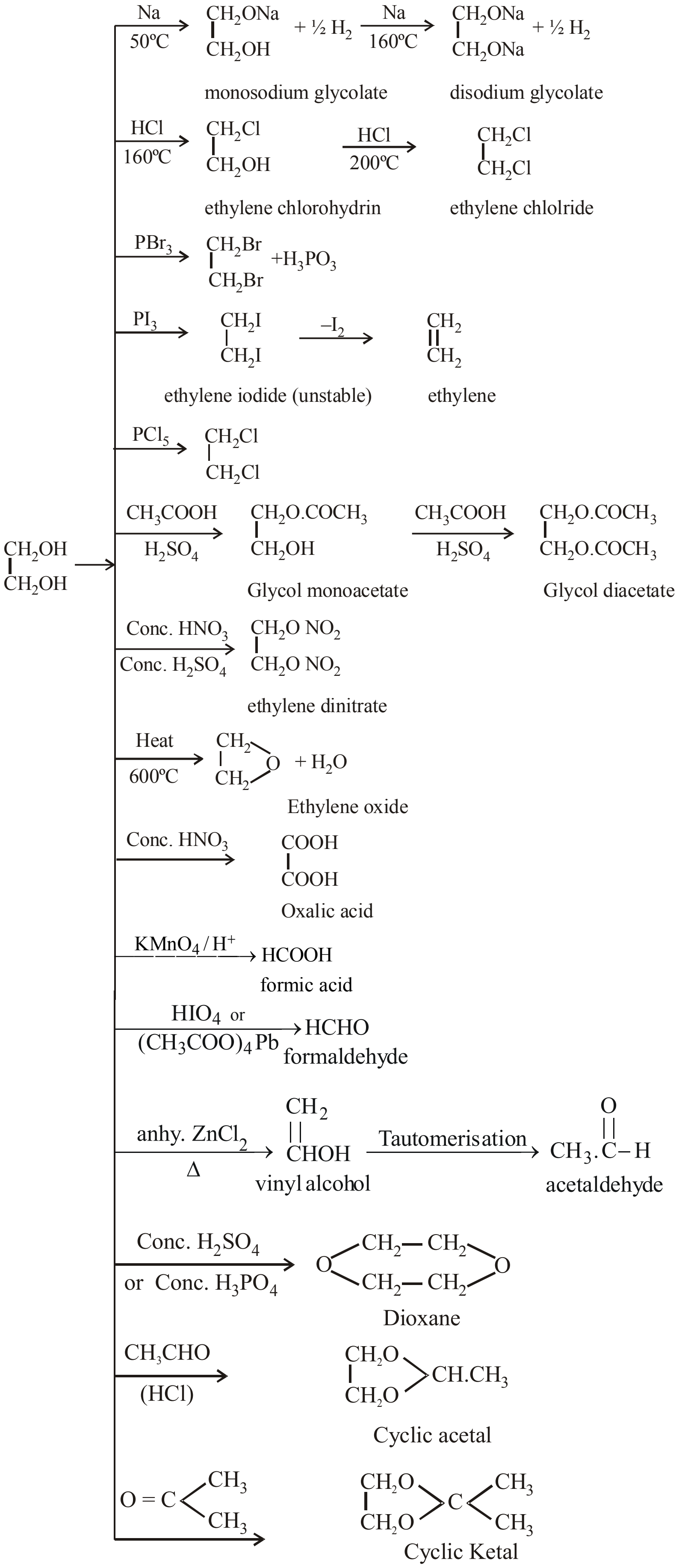
$$\begin{array}{l}CH_2Br\\|\\CH_2Br\end{array}+2CH_3COOK\xrightarrow{AcOH}\begin{array}{l}CH_2OCOCH_3\\|\\CH_2OCOCH_3\end{array}+2KBr$$



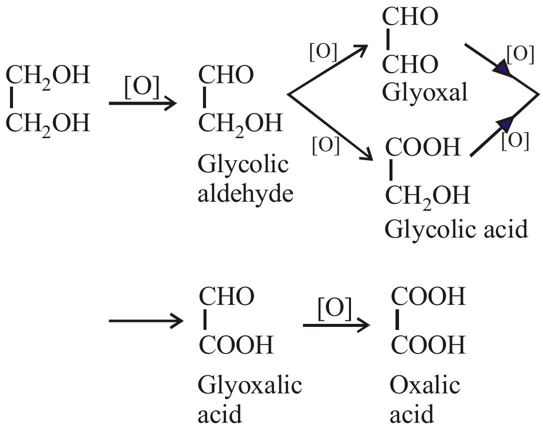
$$\begin{array}{l}CH_2OCOCH_3\\|\\CH_2OCOCH_3\end{array}+H_2O\xrightarrow[CH_3OH]{HCl}\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}+2CH_3COOH$$

Properties: It is colourless viscous liquid bpt 197ºC mpt – 11.5º, miscible with water in all proportions ***due to intermolecular hydrogen bonding.***

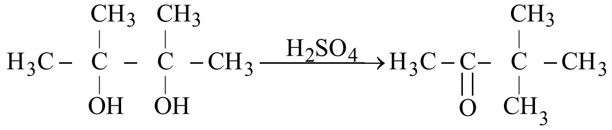
Chemical properties: These can be summarised as follows



Oxidation products obtained from ethylene glycol



Pincol Rearrangement: Reaction of Diols



$$H_3C-\underset{OH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\underset{OH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 \xrightarrow{H_2SO_4} H_3C-\underset{O}{\underset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$$

Pinacol Pinacolone

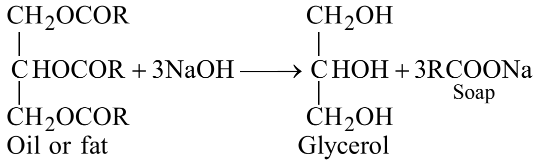
Uses of ethylene glycol

- (i) As an antifreez in car radiators
- (ii) In the manufacture of rayon
- (iii) as cooling agent.

GLYCEROL OR GLYCERINE (PROPAN - 1, 2, 3 - TRIOL) :

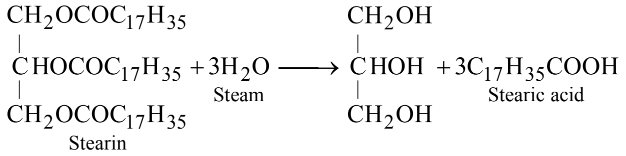
Manufacture :

It is obtained as by product by hydrolysis of oils and fats in soap and candle industry



$$\underset{\text{Oil or fat}}{\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array}} + 3NaOH \longrightarrow \underset{\text{Glycerol}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + \underset{\text{Soap}}{3RCOONa}$$

After salting out of soap by adding saturated solution of NaCl, the filtrate obtained is known as ***spentlye*** which is worked up for glycerol.



$$\underset{\text{Stearin}}{\begin{array}{l} CH_2OCOC_{17}H_{35} \\ | \\ CHOCOC_{17}H_{35} \\ | \\ CH_2OCOC_{17}H_{35} \end{array}} + \underset{\text{Steam}}{3H_2O} \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \underset{\text{Stearic acid}}{3C_{17}H_{35}COOH}$$

Stearic acid is removed by filtration. The filtrate, known as ***sweet lye,*** is worked up for glycerol.

Stearic acid is used for the manufacture of candles.

2. ***From propene***

$$\underset{\text{Prapene}}{CH_3-CH=CH_2} \xrightarrow[500^\circ C]{Cl_2} \underset{\text{Allyl Chloride}}{ClCH_2-CH=CH_2}$$

$$ClCH_2-CH=CH_2 \xrightarrow[150^\circ C,\ 12\ Atm]{aq.\ Na_2CO_3} \underset{\text{Allyl alcohol}}{HO-CH_2-CH=CH_2}$$

$$\xrightarrow{HOCl} \underset{\text{Glycerol }\beta-\text{monochlorohydrin}}{HO.CH_2CHCl.CH_2OH} \xrightarrow{NaOH}$$

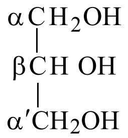
$$\underset{\text{Glycerol}}{CH_2OH.CHOH.CH_2OH}$$

3. ***By fermentation of sugars:***

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[Na_2SO_3]{Yeast} \underset{\text{Glycerol}}{C_3H_8O_3} + \underset{\text{acetaldehyde}}{CH_3CHO} + CO_2$$

Properties: It is colourless, odourless thick viscous liquid miscible with water in all proportions bpt 290°C but at this temperature it is decomposed. Hence it is purified by distillation under reduced pressure. It shows intensive hydrogen bonding.

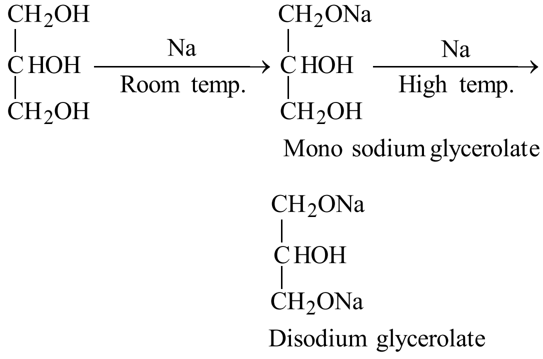
Chemical properties: It contains two primary and one secondary alcoholic group



$$\begin{array}{l} \alpha CH_2OH \\ \ \ | \\ \beta CH\ OH \\ \ \ | \\ \alpha' CH_2OH \end{array}$$

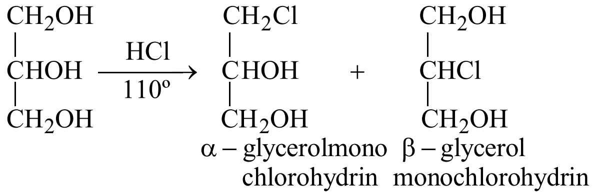
The primary alcoholic groups are more reactive than secondary alcoholic group.

(i) Reaction with sodium:

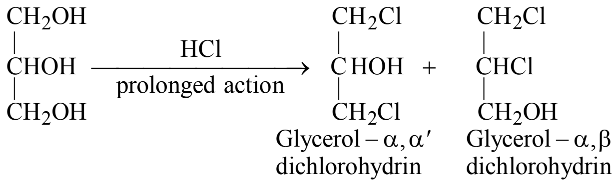


$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[\text{Room temp.}]{Na} \underset{\text{Mono sodium glycerolate}}{\begin{array}{l} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} \xrightarrow[\text{High temp.}]{Na} \underset{\text{Disodium glycerolate}}{\begin{array}{l} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2ONa \end{array}}$$

(ii) Reaction with HCl

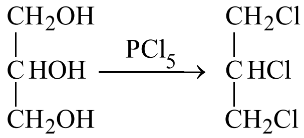


$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[110^\circ]{HCl} \underset{\alpha-\text{glycerolmono chlorohydrin}}{\begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + \underset{\beta-\text{glycerol monochlorohydrin}}{\begin{array}{l} CH_2OH \\ | \\ CHCl \\ | \\ CH_2OH \end{array}}$$



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[\text{prolonged action}]{HCl} \underset{\text{Glycerol}-\alpha,\alpha' \text{ dichlorohydrin}}{\begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2Cl \end{array}} + \underset{\text{Glycerol}-\alpha,\beta \text{ dichlorohydrin}}{\begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2OH \end{array}}$$

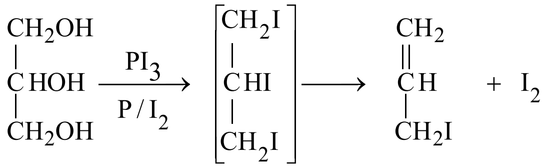
(iii) Reaction with PCl_5



$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}\xrightarrow{PCl_5}\begin{array}{l}CH_2Cl\\|\\CHCl\\|\\CH_2Cl\end{array}$$

Glyceryl trichloride

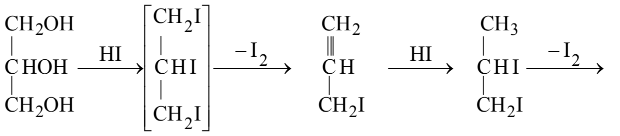
(iv) Reaction with PI_3



$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}\xrightarrow[P/I_2]{PI_3}\left[\begin{array}{l}CH_2I\\|\\CHI\\|\\CH_2I\end{array}\right]\longrightarrow\begin{array}{l}CH_2\\\|\\CH\\|\\CH_2I\end{array}+I_2$$

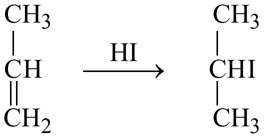
unstable Allyl iodide

(v) Reaction with HI:



$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}\xrightarrow{HI}\left[\begin{array}{l}CH_2I\\|\\CHI\\|\\CH_2I\end{array}\right]\xrightarrow{-I_2}\begin{array}{l}CH_2\\\|\\CH\\|\\CH_2I\end{array}\xrightarrow{HI}\begin{array}{l}CH_3\\|\\CHI\\|\\CH_2I\end{array}\xrightarrow{-I_2}$$

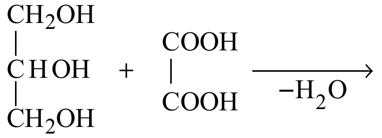
unstable Allyl iodide 1,2 – diiodoprop ane



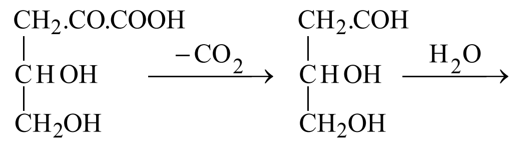
$$\begin{array}{l}CH_3\\|\\CH\\\|\\CH_2\end{array}\xrightarrow{HI}\begin{array}{l}CH_3\\|\\CHI\\|\\CH_3\end{array}$$

Propene isopropyl iodide

(vi) (a) Reaction with oxalic acid at 100°C: Lab method for the preparation of formic acid

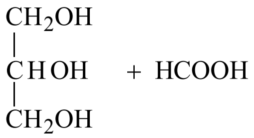


$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}+\begin{array}{l}COOH\\|\\COOH\end{array}\xrightarrow[-H_2O]{}$$



$$\begin{array}{l}CH_2.CO.COOH\\|\\CHOH\\|\\CH_2OH\end{array}\xrightarrow{-CO_2}\begin{array}{l}CH_2.COH\\|\\CHOH\\|\\CH_2OH\end{array}\xrightarrow{H_2O}$$

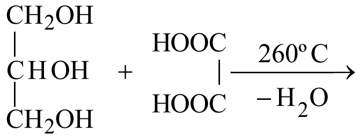
Glycerol mono – oxalate Glycerol monoformate



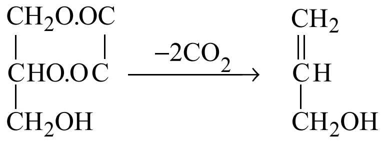
$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}+HCOOH$$

Glycerol Formic acid

(b) At 260°C allyl alcohol is the product



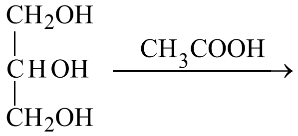
$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}+\begin{array}{l}HOOC\\|\\HOOC\end{array}\xrightarrow[-H_2O]{260^\circ C}$$



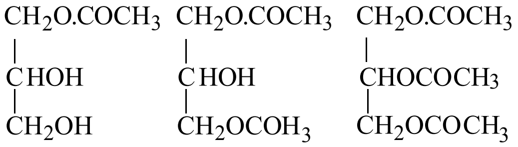
$$\begin{array}{l}CH_2O.OC\\|\quad\;\;|\\CHO.OC\\|\\CH_2OH\end{array}\xrightarrow{-2CO_2}\begin{array}{l}CH_2\\\|\\CH\\|\\CH_2OH\end{array}$$

Glycerol dioxalate Allyl alcohol

(vii) Reaction with acetic acid, acetic anhydride or acetyl chloride



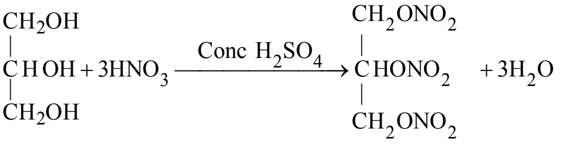
$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}\xrightarrow{CH_3COOH}$$



$$\begin{array}{l}CH_2O.COCH_3\\|\\CHOH\\|\\CH_2OH\end{array}\quad\begin{array}{l}CH_2O.COCH_3\\|\\CHOH\\|\\CH_2OCOH_3\end{array}\quad\begin{array}{l}CH_2O.COCH_3\\|\\CHOCOCH_3\\|\\CH_2OCOCH_3\end{array}$$

Monoester diester triester

(viii) Reaction with nitric acid



$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}+3HNO_3\xrightarrow{Conc\ H_2SO_4}\begin{array}{l}CH_2ONO_2\\|\\CHONO_2\\|\\CH_2ONO_2\end{array}+3H_2O$$

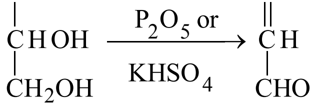
Glyceryl trinitrate (TNG)

It is also known as Nobel oil after the name of its discoverer ***Alfred Nobel.*** It is dark coloured oily liquid, highly poisonous, explodes violently when heated giving huge volume of gases

$$4C_3H_5(ONO_2)_3\longrightarrow 12CO_2+6N_2+O_2+10H_2O$$

Uses: (1) As an explosive (a) Dynamite - Starch + NH_4NO_3 or $NaNO_3$ + nitroglycerine (b) Blasting gelatin - nitroglycerine + gun cotton (cellulose nitrate) (c) Cordite-nitroglycerine + gun cotton + vaseline. It is smokeless explosive (2) As medicine. In treatment of heart disease and asthma.

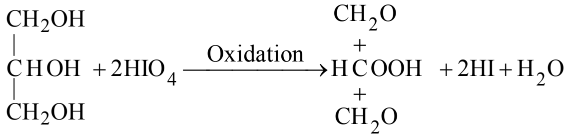
(ix) Dehydration: It can be achieved by heating alone, with $KHSO_4$ or P_2O_5 or Conc H_2SO_4



$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}\xrightarrow[KHSO_4]{P_2O_5\text{ or}}\begin{array}{l}CH_2\\\|\\CH\\|\\CHO\end{array}$$

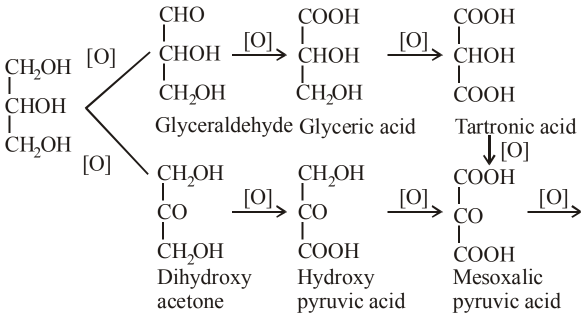
Acraldehyde or Acrolein

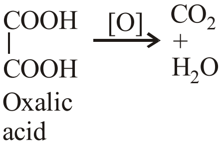
(x) Oxidation with periodic acid (HIO_4)



$$\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} + 2HIO_4 \xrightarrow{\text{Oxidation}} \begin{array}{c}CH_2O\\ +\\ HCOOH\\ +\\ CH_2O\end{array} + 2HI + H_2O$$

(xi) Oxidation: Glycerol can be oxidised to give different oxidation products under different conditions. The main products are





$$\begin{array}{l}COOH\\ |\\ COOH\end{array} \xrightarrow{[O]} \begin{array}{c}CO_2\\ +\\ H_2O\end{array}$$

Oxalic acid

Glycerose: It is a mixture of glyceraldehyde and dihydroxy acetone and is obtained by oxidation of glycerol with Fenton's reagent (H_2O_2 + Fe SO_4)

Dilute nitric acid gives glyceric acid as main product

Conc. nitric acid gives glyceric acid + tartronic acid

Bismuth nitrate gives mesoxalic acid

Uses: (i) In the manufacture of explosives (ii) In cosmatics (iii) For preserving tobacco (iv) As an antifreez (v) As lubricant in watches.

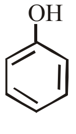
AROMATIC HYDROXY COMPOUNDS (PHENOLS) :

Aromatic hydroxy compounds are of two types

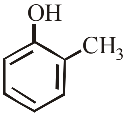
1. **Phenols:** In phenols the hydroxyl group is directly attached to aromatic nucleus.
2. **Aromatic alcohols:** In aromatic alcohols the hydroxyl group is present in the side chain e.g. $C_6H_5.CH_2OH$ benzyl alcohol.

Phenols are classified as

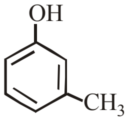
(i) Monohydric phenols:



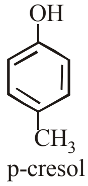
Phenol



o-cresol

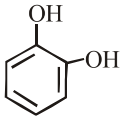


m-cresol

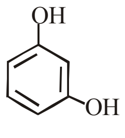


p-cresol

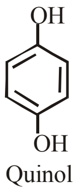
(ii) Dihydric phenols:



Catechol

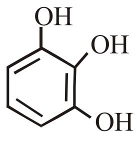


Resorcinol

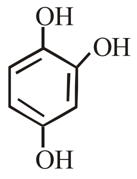


Quinol (Hydroquinone)

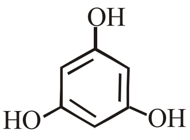
(iii) Trihydric phenols:



Pyrogallol

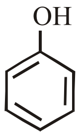


Hydroxyl quinol



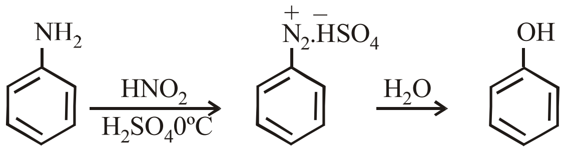
Phloroglucinol

Phenol (Carbolic acid)



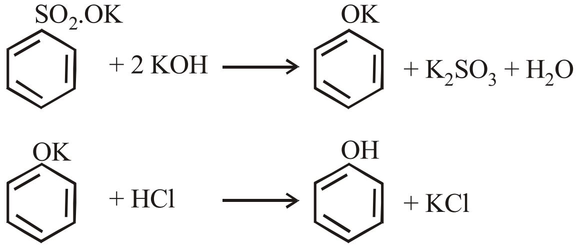
General methods of preparation of phenols

(i) ***Hydrolysis*** of diazonium salts - particularly sulphates

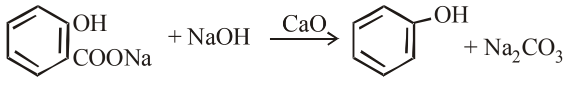


aniline diazonium hydrogen sulphate phenol

(ii) From Sulphonic acids: Alkali Salts of aryl sulphonic acids are fused with caustic alkalies to get phenates, which are decomposed by acids

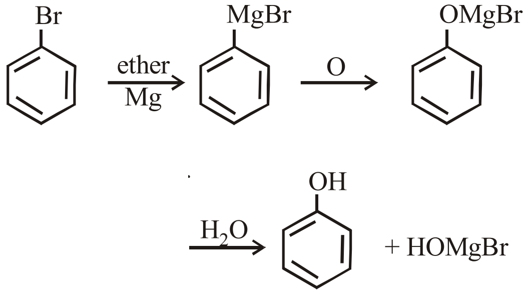


(iii) From phenolic acids: Sodium salts of phenolic acids distilled with soda lime

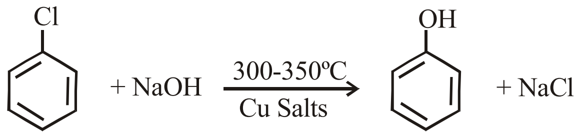


Sod. Salicylate

(iv) From Grignard's reagents:



(v) From aryl halides



Manufacture of phenol :

1. **From middle oil fraction of coaltar**. The middle oil and heavy oil fraction contain phenols and naphthalene. On cooling naphthalene separates out and removed by filter pressing. The oil left is treated with aqueous NaOH when phenols form phenoxides. To liberate phenols CO_2 is then passed

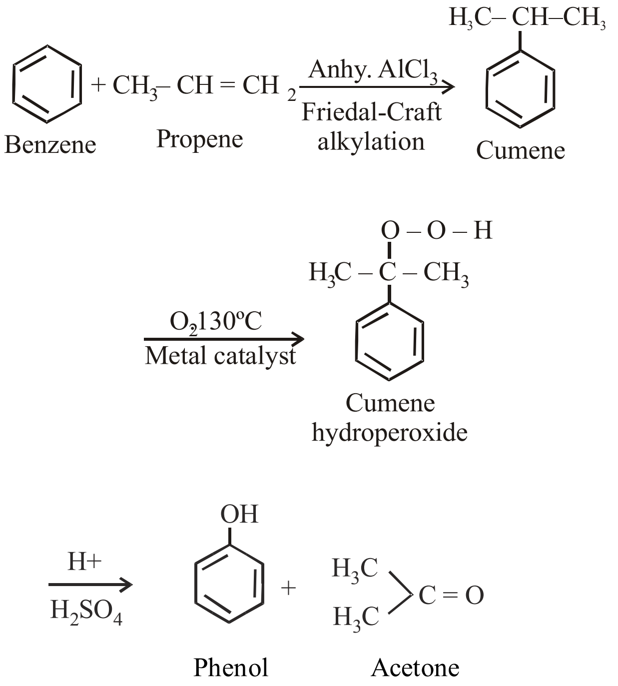
$$ArOH + NaOH \rightarrow Ar\overset{-}{O}\overset{+}{N}a + H_2O$$

$$2Ar\overset{-}{O}\overset{+}{N}a + CO_2 + H_2O \rightarrow 2ArOH + Na_2CO_3$$

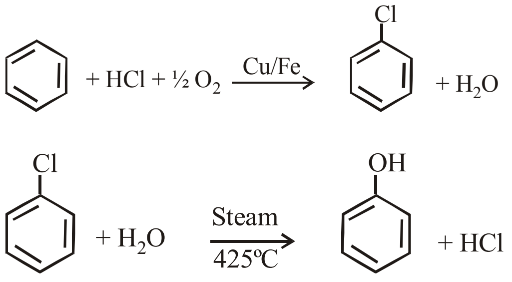
Phenols separate out as oily layer and separated from aqueous layer containing Na_2CO_3 and fractionally dislilled.

(a) Fraction distilling at 180ºC – phenol
(b) Fraction distilling at 190-203ºC– cresols (*o*, *m* and *p*)
(c) Fraction distilling at 211-225ºC–xylenols

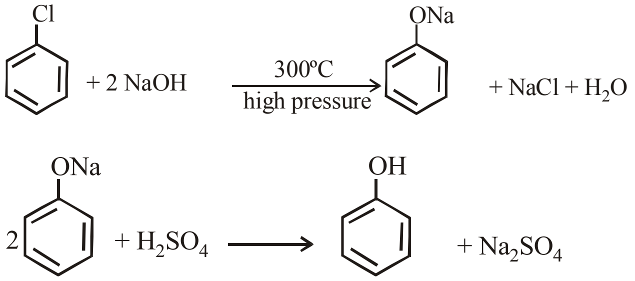
2. **Cumene mehtod:** Recent and best method



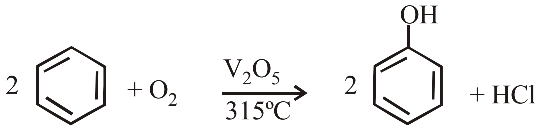
3. **Raschig's process:** Developed in Germany



4. **From Chlorobenzene "Dowprocess":**



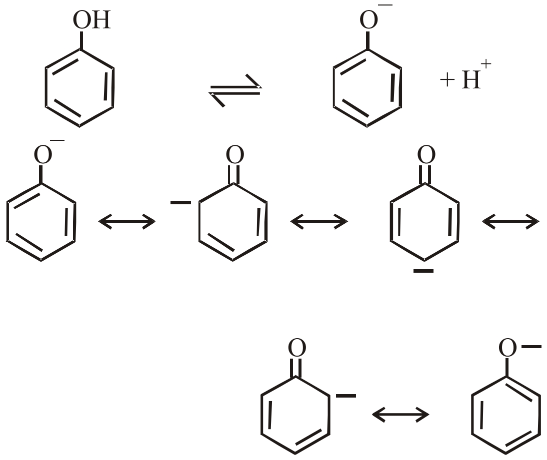
5. **Oxidation of benzene:**



Properties: Phenol is a colourless crystalline solid mpt. 42ºC and bpt 183ºC. It is deliquescent, becomes pinkish on exposure to air due to oxidation, sparingly soluble in cold water.

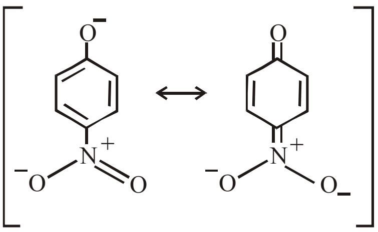
Chemical properties:

1. ***Acidic nature:*** Phenol is acidic in nature due to greater resonance stabilisation of phenoxide ion than phenol itself



The presence of electrons withdrawing groups in the nucleus increase the acidity. This is due to inductive effect and mesomeric effect.The latter effect is operative when the group is in the o- or p- but not in m-position. The resultant anion is more stabilised through delocalisation of electrons.

Compound	pk_a
C_6H_5OH	9.95
$o-O_2N.C_6H_4OH$	7.23
$m-O_2NC_6H_4OH$	8.35
$p-O_2NC_6H_4OH$	7.14
$2,4-(O_2N)_2C_6H_3OH$	4.01
$2,4,6-(O_2N)_3C_6H_2OH$	1.02

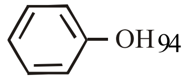
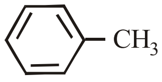


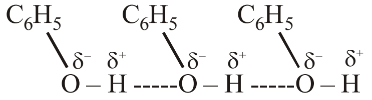
The presence of electron donating groups in the nucleus decreases the acid character of phenol though the effect is small

Compound	pk$_a$
C_6H_5OH	9.95
$MeOC_6H_4OH$	10.28
$m\,MeC_6H_4OH$	10.08
$p\,MeC_6H_4OH$	10.19

The smaller the value of pk$_a$ the more is the acid character.

2. ***Melting and boiling points*** - Phenols form the intermolecular hydrogen bonding and their mpts and bpts are much higher than hydrocarbons of comparable molecular weights

		mol wt.	*mpt.*	*bpt.*
phenol		94	42ºC	183ºC
Toluene		92	–95ºC	111ºC

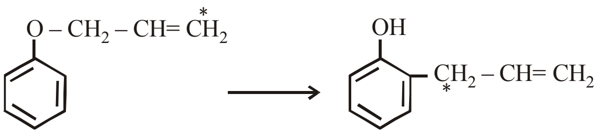


Reactions of phenols resembling alcohols:

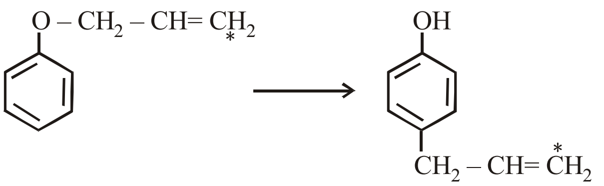
1. *Action of Na metal* – $2C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2$
2. *Formation of ethers* –

   $C_6H_5ONa + BrCH_3 \rightarrow C_6H_5OCH_3 + NaBr$

   ***Claisen's rearrangment**:* When o-allyl ether of phenols are heated to 100-250ºC without solvent or catalyst, the allyl group migrates to ortho position with inversion of configuration



If both the ortho positions are occupied the allyl group migrates to para position without inversion of configuration

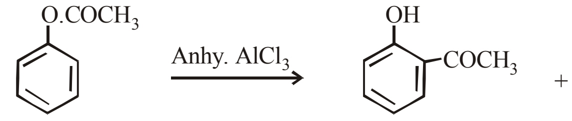


3. ***Acylation:*** with acid chloride or acid anhydride

   $C_6H_5OH + CH_3COCl \rightarrow C_6H_5O.COCH_3 + HCl$

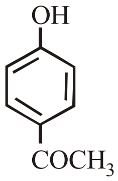
   $C_6H_5OH + (CH_3CO)_2O \rightarrow C_6H_5O.COCH_3 + CH_3COOH$

4. ***Fries rearrangement:*** The phenyl ester when heated with anhy. $AlCl_3$ or $ZnCl_2$ the acetyl group migrates to ortho and para positions to form hydroxy ketones



Phenyl acetate

o-hydroxy accetophenone



p-hydroxy accetophenone
(low temperature)

4. ***Bucherer reaction:***

$$C_6H_5OH \xrightarrow[150^\circ C]{(NH_4)_2SO_3/NH_3} C_6H_5NH_2$$

5. ***Action of PCl_5:***

$$C_6H_5OH + PCl_5 \longrightarrow C_6H_5Cl + POCl_3 + HCl$$

6. ***Action of P_2S_5:***

$$5C_6H_5OH + P_2S_5 \longrightarrow 5C_6H_5SH + P_2O_5$$

Reactions given by phenols only:

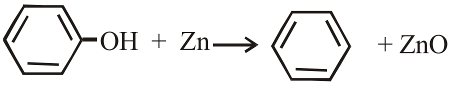
1. ***Action of NaOH:***

   $C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$

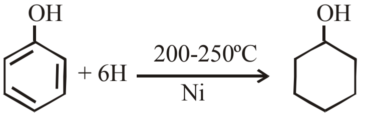
2. ***Action of aqueous $FeCl_3$:*** A violet coloured coordination complex is formed

   $3C_6H_5OH + FeCl_3 \longrightarrow [Fe(OC_6H_5)_3] + 3HCl + Fe$

3. ***Distillation with Zn dust:***

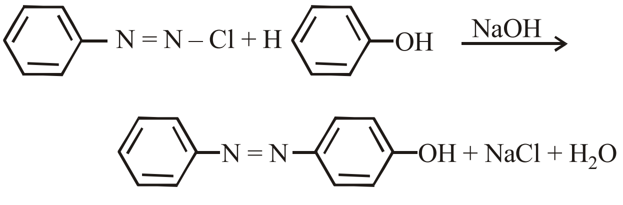


4. ***Reduction with H_2/Ni:***



Cyclohexanol (used as solvent)

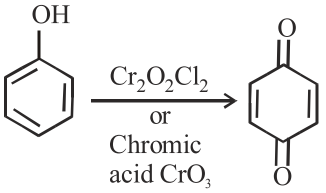
5. ***Coupling reaction:*** with diazonium salts



p-Hydroxy azobenzene

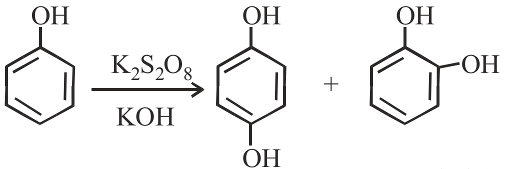
6. ***Oxidation:*** Different products are obtained under different conditions.

i. *With* $Cr_2O_2Cl_2$



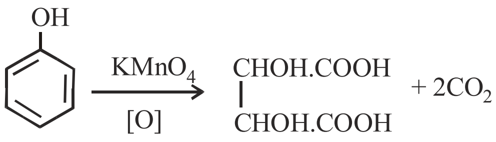
p-benzoquinone

ii. ***Elbs persulphate oxidation:***



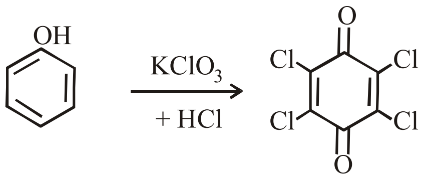
Hydroquenone or Quinol (major) Catechol (minor)

iii. ***With potassium permanganate:*** Mesotartaric acid is obtained



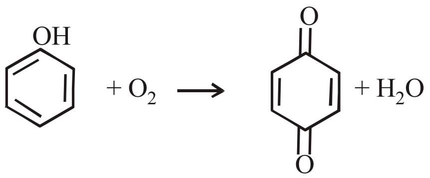
Mesotartaric acid

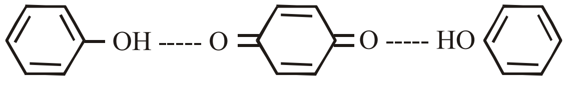
iv. ***With a mixture of $KClO_3$ and Conc. HCl:*** Chloranil called tetrachloroquinone is obtained



Chloranil

v. ***Atmospheric oxidation:*** It turns pink when exposed to air and light due to slow oxidation to quinone. Quinone forms a brilliant red addition product with phenol known as phenoquinone, through hydrogen bonding.



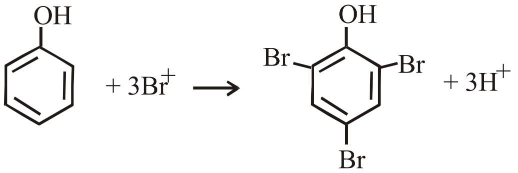


Phenoquinone (Red colour)

7. ***Electrophilic substitution reactions:*** The OH group is o, p-directing in nature with activation of benzene nucleus

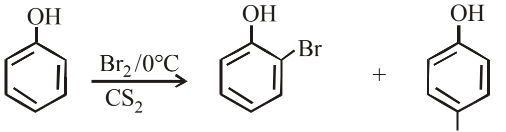
(a) ***Halogenation:*** with exces of bromine solution it gives 2, 4, 6 - tribromophenol (curdy precipitate)

$$Br_2 + Br_2 \rightleftharpoons \overset{+}{Br} + \overset{-}{Br_3}$$



2, 4, 6 - tribromophenol

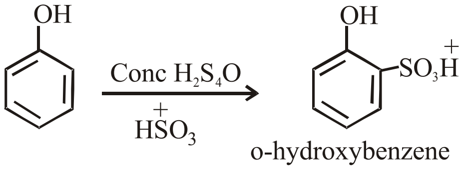
With calculated amount of Br_2 in CS_2 or $CHCl_3$ gives ortho and para product



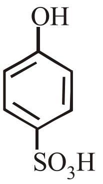
o-Bromophenol Br p-Bromophenol

(b) ***Sulphonation:*** with Conc H_2SO_4

$$2H_2SO_4 \rightleftharpoons H_3O + SO_3 + HS\overset{-}{O}_4$$



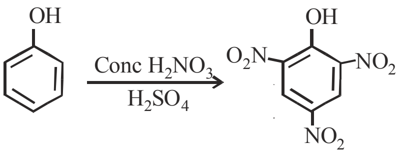
o-hydroxybenzene sulphonic acid



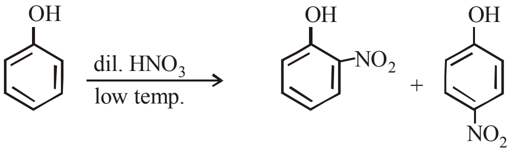
p-hydroxy benzene sulphonic acid

(c) ***Nitration:*** with Conc HNO_3 + Conc H_2SO_4

$$HNO_3 + 2H_2SO_4 \rightarrow H_3\overset{+}{O} + \overset{+}{N}O_2 + 2HS\overset{-}{O}_4$$

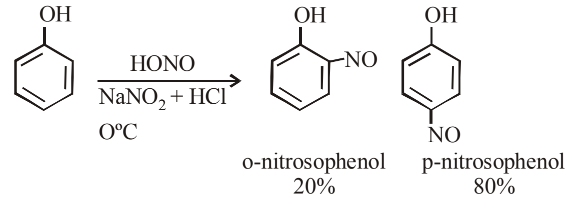


2, 4, 6 - trinitrophenol (picric acid)

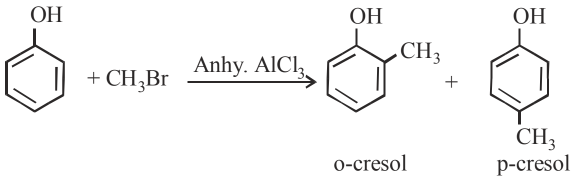


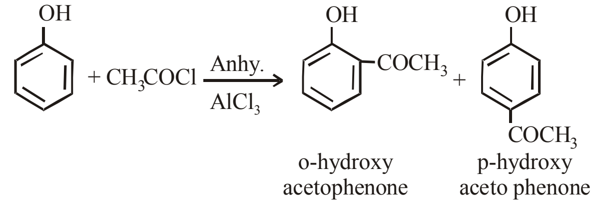
o-nitrophenol p-nitrophenol

(d) ***Nitrosation***:

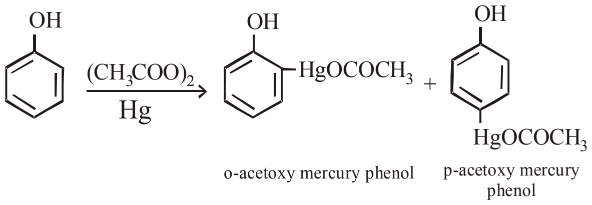


(e) ***Friedel-crafts alkylation and acylation***:



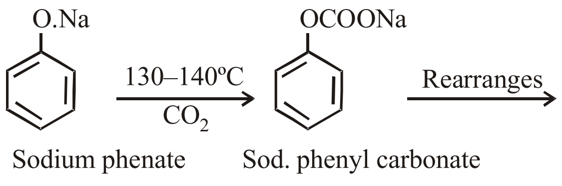


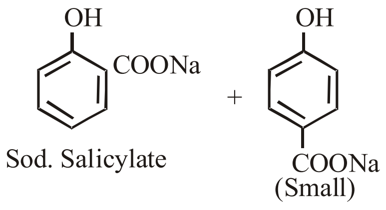
(f) ***Mercuration***: Phenol undergoes electrophilic substitution when refluxed with mercuric acetate



Miscellaneous reactions:

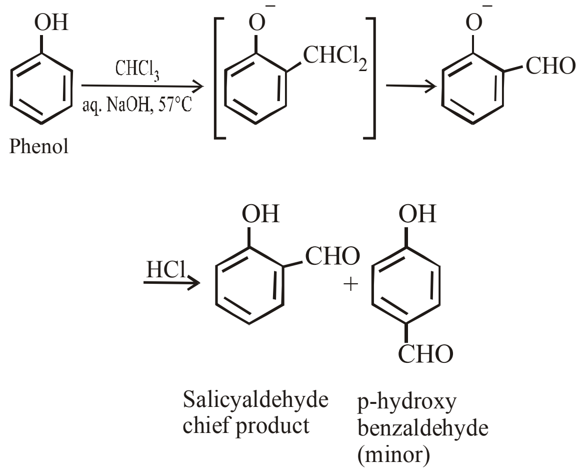
(i) Kolbe's reaction or Kolbes Schmidt reaction





The p-isomer is the main product if temperature rises above 160°C or when potassium phenate is used in place of sodium salt.

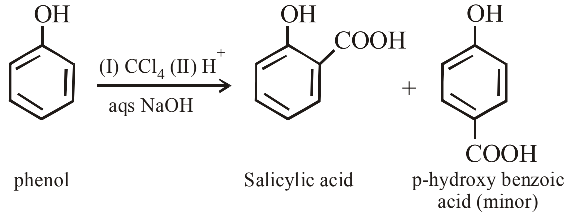
(ii) Reimer-Tiemann Reaction :



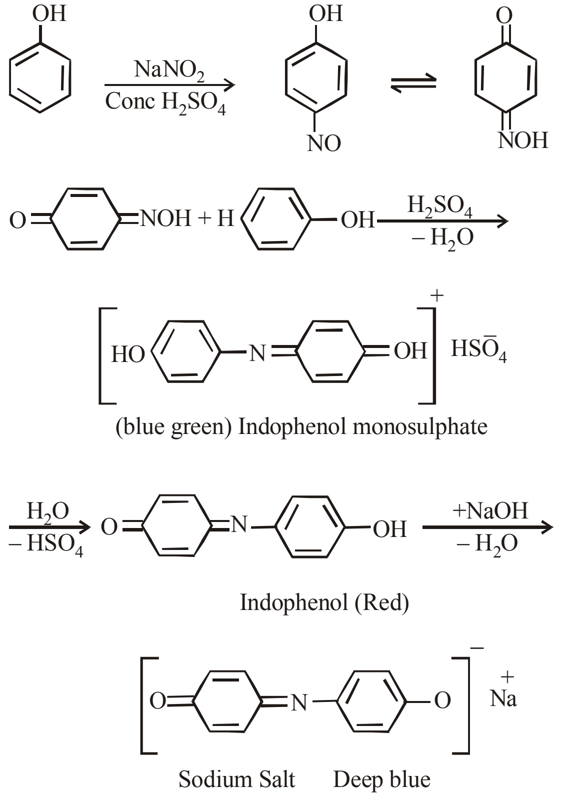
$$\overset{-}{O}H + CHCl_3 \rightleftharpoons H_2O + :\overset{-}{C}Cl_3 \longrightarrow \overset{-}{Cl} + :CCl_2$$

Dichloro carbene

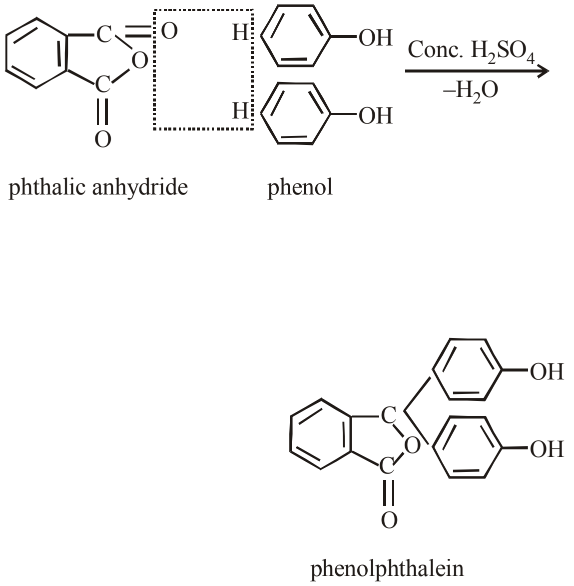
Reimer-Tiemann reaction is electrophilic substitution reaction and electrophile is dichloro carbene. Similarly with carbon tetrachloride and alkali o - and p-hydroxy benzoic acid are obtained



(iii) Liebermann's Nitroso Reaction:

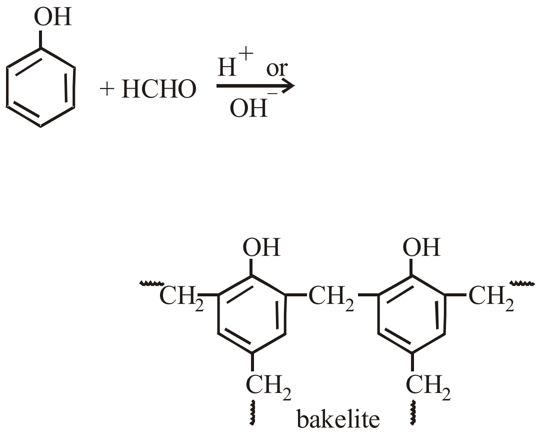


(iv) Formation of phenolphthalein

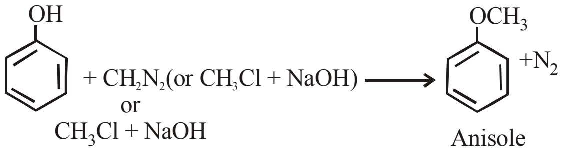


It is used as an internal indicator in acid base titration. It gives pink colour in alkaline medium and colourless in acid medium. Its pH range is 8-9.8.

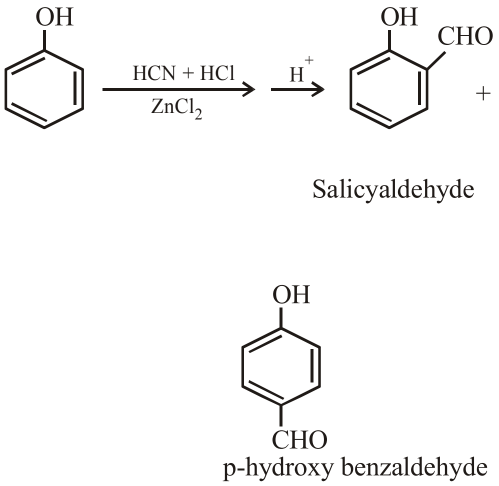
(v) Condensation: with HCHO **(Lederer-Manasse reaction)**



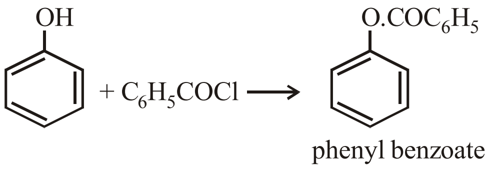
(vi) ***With diazomethane (CH_2N_2) :***



(vii) ***Gatterman Reaction :***



(viii) ***Schotten Baumann Reaction :***



Test :

(i) **Ferric chloride test:** phenol + 1% $FeCl_3$ solution - violet colour

(ii) **Bromine water:** phenol + bromine water - curdy precipitate

(iii) **Phenolphthalein test :** (phenol + phthalic anhydride + conc. H_2SO_4) + NaOH heat → pink colour

(iv) It gives **libermann's nitroso reaction**

Uses: (i) As an antiseptic (ii) Manufacture of bakelite (iii) Manufacture of salol, aspirin, phenacetin etc.

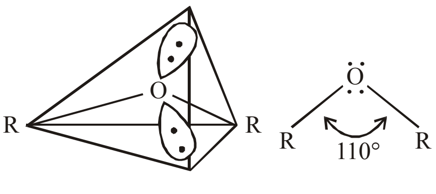
ETHERS :

The compounds having the general formula R–O–R are known as ethers

Simple ethers : when alkyl or aryl groups are the same. R–O–R

Mixed ethers : when alkyl or aryl groups are different R–O–R'

Structure: The hybridisation of O atom in ethers is sp^3 (tetrahedral) and shape is V.



Nomenclature:

(i) ***Common System:*** They are named as dialkyl ether when the two alkyl groups are the same eg.

$C_2H_5-O-C_2H_5$ diethyl ether

CH_3-O-CH_3 dimethyl ether

If alkyl groups are different, they are named alphabetically e.g. $C_2H_5-O-CH_3$ ethyl methyl ether

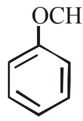
(ii) ***IUPAC System:*** They are named as Alkoxy alkane. The smaller group is made alkoxy and larger the alkane e.g.

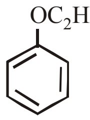
CH_3-O-CH_3 Methoxymethane

$CH_3-O-C_2H_5$ Methoxyethane

$CH_3-O-CH_2-CH_2-CH_3$

1-methoxy propane


Methoxy benzene (Anisole)


Ethoxy benzene (phenetole)

Isomerism: Ethers exhibit two types of isomerism

(i) ***Functional Isomerism:*** They are isomeric with momohydric alcohols e.g.

CH_3-O-CH_3 methoxy methane

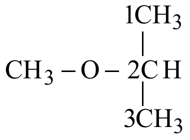
$CH_3.CH_2OH$ ethyl alcohol

(ii) ***Metamerism:*** $C_2H_5-O-C_2H_5$

ethoxy ethane

$CH_3-O-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_3$

1-methoxy propane



$CH_3-O-\overset{1CH_3}{\underset{3CH_3}{2CH}}$

2-methoxy propane

General methods of preparation:

(i) **By Dehydration of alcohols**

$$ROH + HOR \xrightarrow[140°C]{\text{Conc. } H_2SO_4} R-O-R + H_2O$$

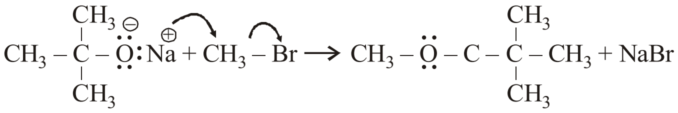
(ii) **Catalytic dehydration of alcohols**

$$2ROH \xrightarrow[250°C]{Al_2O_3} R-O-R + H_2O$$

(iii) ***Williamson's Synthesis:***

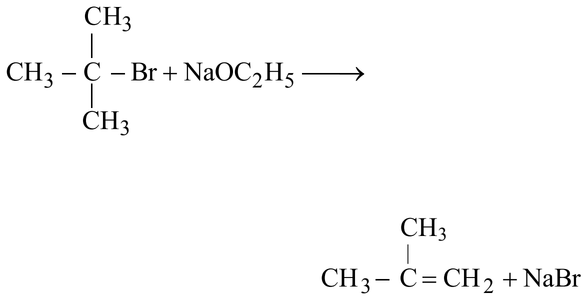
$$\underset{\text{Alkylhalide}}{R-X} + \underset{\text{Sod alkoxide}}{NaOR'} \xrightarrow{\text{ether}} \underset{\text{ether}}{R-O-R'} + NaX$$

The reaction involves S_N2 attack of an alkoxide ion on primary alkyl halide



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\ddot{\underset{\cdot\cdot}{O}}^{\ominus}\!:\overset{\oplus}{Na} + CH_3-Br \rightarrow CH_3-\ddot{\underset{\cdot\cdot}{O}}-C-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 + NaBr$$

The alkyl halide should be primary. The secondary and tertiary alkyl halides undergo elemination reaction to give alkenes.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br + NaOC_2H_5 \longrightarrow CH_3-\overset{CH_3}{C}=CH_2 + NaBr$$

(iv) ***Heating alkyl halide*** with silver oxide

$$C_2H_5Cl + Ag_2O + ClC_2H_5 \xrightarrow{\Delta} C_2H_5OC_2H_5 + 2AgCl.$$

(v) ***From alcohol*** by the action of diazomethane

$$ROH + CH_2N_2 \xrightarrow{HBF_4} ROCH_3 + N_2$$

(vi) ***From Phenol***

(vii) ***From Grignard's reagant:*** Synthesis of higher ether

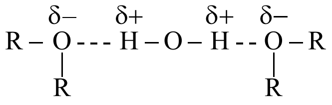
$$ROCH_2X + R'MgX \xrightarrow[\text{ether}]{\text{dry}} R-O-CH_2R' + MgX_2$$

(viii) ***Vinyl ethers:***

$$\underset{\text{Alcohol}}{ROH} + \underset{\text{ethyne}}{HC\equiv CH} \longrightarrow \underset{\text{vinyl ether}}{R-O-CH=CH_2}$$

Properties :

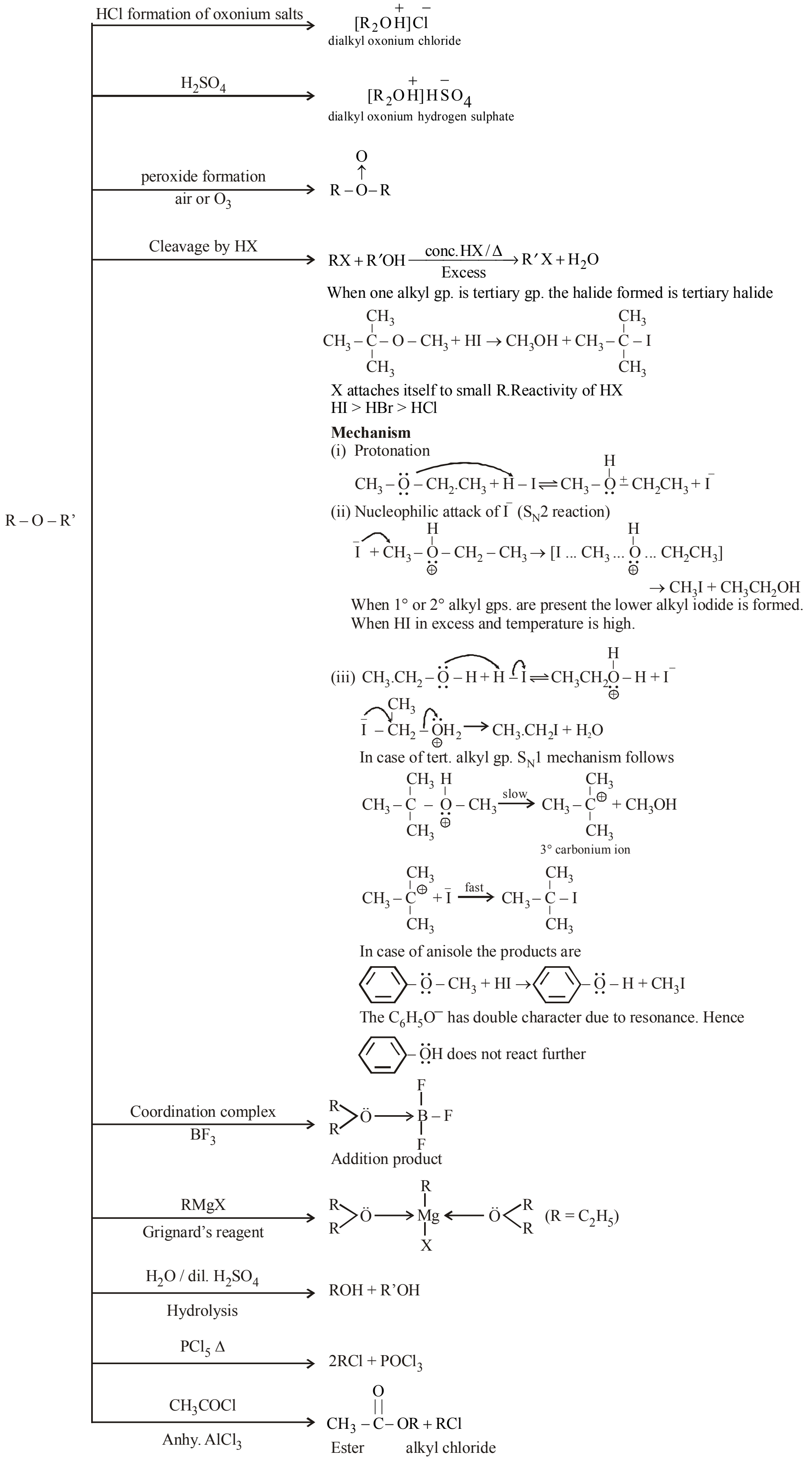
Dimethyl ether and ethyl methyl ether are gases. Others are highly volatile, inflammable liquids. Slightly soluble in water due ot H-bond formation.



$$R-\underset{R}{\overset{\delta-}{O}}\text{---}\overset{\delta+}{H}-O-\overset{\delta+}{H}\text{--}\underset{R}{\overset{\delta-}{O}}-R$$

They are polar in nature the value of dipole moment is 1.18D.

Chemical properties:



R – O – R'

HCl formation of oxonium salts → $[R_2\overset{+}{O}H]\overset{-}{Cl}$

dialkyl oxonium chloride

H_2SO_4 → $[R_2\overset{+}{O}H]\overset{-}{HSO_4}$

dialkyl oxonium hydrogen sulphate

peroxide formation, air or O_3 → $R-\overset{\overset{O}{\uparrow}}{O}-R$

Cleavage by HX → $RX + R'OH \xrightarrow[\text{Excess}]{\text{conc. HX}/\Delta} R'X + H_2O$

When one alkyl gp. is tertiary gp. the halide formed is tertiary halide

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3 + HI \rightarrow CH_3OH + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I$$

X attaches itself to small R.Reactivity of HX

HI > HBr > HCl

Mechanism

(i) Protonation

$$CH_3-\ddot{O}-CH_2.CH_3 + H-I \rightleftharpoons CH_3-\overset{H}{\ddot{O}}{}^{\pm}CH_2CH_3 + \bar{I}$$

(ii) Nucleophilic attack of $\bar{I}$ (S_N2 reaction)

$$\bar{I} + CH_3-\underset{\oplus}{\overset{H}{\ddot{O}}}-CH_2-CH_3 \rightarrow [I \ldots CH_3 \ldots \underset{\oplus}{\overset{H}{\ddot{O}}} \ldots CH_2CH_3]$$

$$\rightarrow CH_3I + CH_3CH_2OH$$

When 1° or 2° alkyl gps. are present the lower alkyl iodide is formed.

When HI in excess and temperature is high.

$$\text{(iii)}\ CH_3.CH_2-\ddot{O}-H + H-I \rightleftharpoons CH_3CH_2\underset{\oplus}{\overset{H}{O}}-H + \bar{I}$$

$$\bar{I} - \overset{CH_3}{CH_2} - \underset{\oplus}{\ddot{O}}H_2 \longrightarrow CH_3.CH_2I + H_2O$$

In case of tert. alkyl gp. S_N1 mechanism follows

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}} - \underset{\oplus}{\overset{H}{\ddot{O}}} - CH_3 \xrightarrow{\text{slow}} CH_3-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} + CH_3OH$$

3° carbonium ion

$$CH_3-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} + \bar{I} \xrightarrow{\text{fast}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I$$

In case of anisole the products are

$-\ddot{O}-CH_3 + HI \rightarrow$ $-\ddot{O}-H + CH_3I$

The $C_6H_5O^-$ has double character due to resonance. Hence

$-\ddot{O}H$ does not react further

Coordination complex, BF_3 → $\overset{R}{\underset{R}{>}}\ddot{O} \longrightarrow \underset{F}{\overset{F}{B}}-F$

Addition product

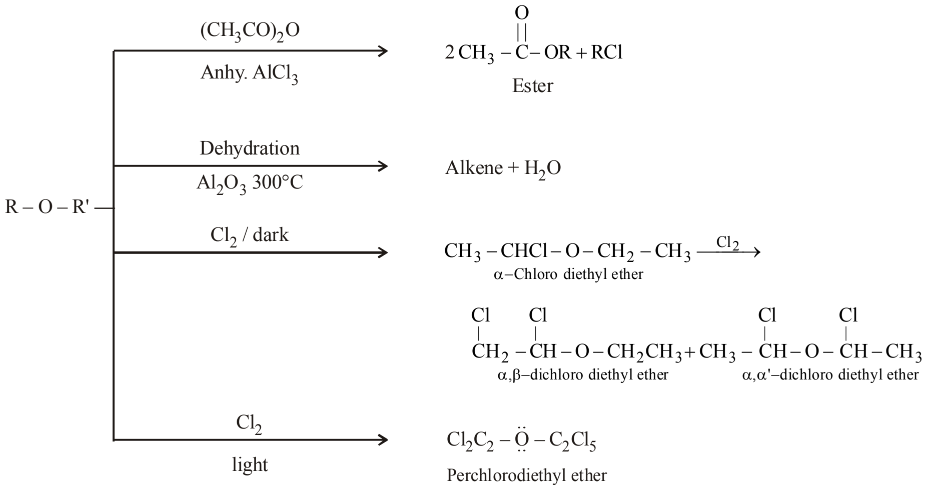
RMgX, Grignard's reagent → $\overset{R}{\underset{R}{>}}\ddot{O} \longrightarrow \underset{X}{\overset{R}{Mg}} \longleftarrow \ddot{O}\overset{R}{\underset{R}{<}}$ ($R = C_2H_5$)

H_2O / dil. H_2SO_4, Hydrolysis → ROH + R'OH

PCl_5 Δ → $2RCl + POCl_3$

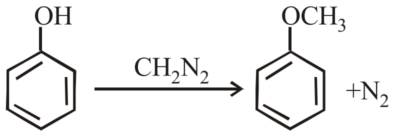
CH_3COCl, Anhy. $AlCl_3$ → $CH_3-\overset{\overset{O}{||}}{C}-OR + RCl$

Ester alkyl chloride

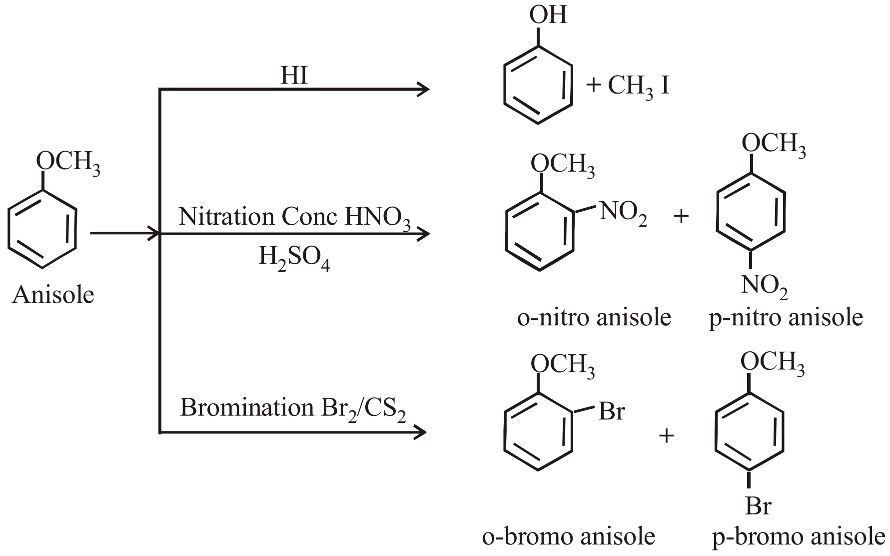


Aromatic ether: Anisole

Preparation:

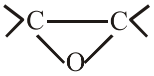


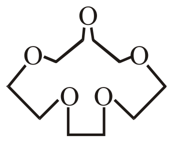
Properties



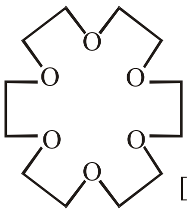
- ***Detection of peroxides in ether:*** Ether + aqueous solution of ferrous ammonium sulphate or potassium thiocyanate - Red colour.
- ***Diisopropyl ether*** is used in petrol as anti knock compound.
- ***Zeisel method:*** $C_2H_5OC_2H_5 + 2HI \rightarrow 2C_2H_5I$

  $C_2H_5I + AgNO_3\,(alc) \rightarrow AgI \downarrow$ ppt.

  AgI is estimated, therefore alkoxy group is estimated.
- ***Petrol*** mixes with alcohol in 1% diethyl ether.
- ***Mixture*** of chloroform and ether is general anaesthetic.
- ***Epoxides:*** Epoxides are cyclic ethers. Ethereal oxygen forms a part of three membered ring 
- ***Crown ethers:*** They are cyclic poly ethers



[15] CROWN-5



[18] CROWN-6

The first number indicates ring size and second number indicates the number of oxygen atoms

- ***Thio ethers*** : R–S–R - in place of –O– there is –S– linkage. Also known as sulphides.

Exercise-1 | NCERT BASED QUESTIONS

Very Short/ Short Answer Questions

1. What happens when glycerol is treated with periodic acid?

2. Phenol is acidic but does not decompose $NaHCO_3$ solution while acids like CH_3COOH decompose $NaHCO_3$ solution. Why?

3. How many sigma bonds are present in 3-methyl phenol?

4. Which of the following can be used to distinguish between phenol and cyclohexanol: Na_2CO_3, NaOH, CH_3COCl?

5. What is usually added to ethyl alcohol to make it unfit for drinking purposes?

6. Of the two hydroxy organic compound ROH and R′OH the first one is basic and the other is acidic in behaviour. How is R different from R′?

7. Write reactions for what happens when

- (*i*) glycerol reacts with excess of HI.
- (*ii*) ethylene is treated with an alkaline solution of potassium permanganate.
- (*iii*) phenol is treated with benzene diazonium chloride in presence of NaOH.

8. An organic compound (A) having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$ solution. (A) on treatment with CO_2 and NaOH at 400 K under pressure gives (B) which on acidification gives a compound (C). The compound (C) reacts with acetyl chloride to give (D) which is a popular pain killer. Deduce the structure of (A), (B), (C) and (D).

9. An aromatic compound (A) having molecular formula C_6H_6O on treatment with $CHCl_3$ and KOH gives a mixture of two isomers B and C. Both of B and C give some product D when distilled with zinc dust. Oxidation of D gives E of formula $C_7H_6O_2$. The sodium salt of E on heating with soda-lime gives F which may also be obtained by distillating A with zinc dust. Identify the compounds A to F giving sequence of reactions.

10. How will you convert

- (*a*) ethylalcohol to n-propyl alcohol,
- (*b*) phenol to benzoic acid, and
- (*c*) n-propyl alcohol to n-hexane.

11. What happens when:

- (*a*) ethyl alcohol vapours are passed over heated alumina?
- (*b*) monochlorodimethyl ether is treated with methyl magnesium bromide?

12. Anhydrous $CaCl_2$ is not recommended as a drying agent for alcohols and amines.

13. Explain the fact that in aryl alkyl ethers

- (*i*) the alkoxy group activates the benzene ring towards electrophilic substitution, and
- (*ii*) it directs the incoming substituents to ortho and para postions in benzene ring.

14. Account for the following:

- (i) Propanol has higher boiling point than butane.
- (ii) Ortho-nitrophenol is more acidic than ortho-methoxyphenol
- (iii) Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method.

15. Draw the structure and name the product formed if the following alcohols are oxidized. Assume that an excess of oxidizing agent is used.

- (i) $CH_3CH_2CH_2CH_2OH$
- (ii) 2-butenol
- (iii) 2-methyl-1-propanol

16. Explain the following behaviours:

- (i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.
- (ii) Ortho-nitophenol is more acidic than ortho-methoxyphenol.

17. How will you convert:

- (i) Propene of Propan-2-ol?
- (ii) Phenol to 2, 4, 6 - trinitrophenol?

18. Write the equations involved in the following reactions:

- (a) Reimer - Tiemann reaction
- (b) Williamson's ether synthesis

Multiple Choice Questions

19. Diethyl ether reacts, inspite of its usual inert nature, with :

- (a) Dilute suphuric acid
- (b) Dilute sodium hydroxide
- (c) Boron trifluoride
- (d) Metallic sodium

20. Formation of diethyl ether from ethanol is based on a :

- (a) Dehydrogenation reaction
- (b) Hydrogenation reaction
- (c) Dehydration reaction
- (d) Heterolytic fission reaction

21. When vapours of an alcohol are passed over hot reduced copper, alcohol is converted into alkene, the alcohol is

- (a) Primary
- (b) Secondary
- (c) Tertiary
- (d) None of above

22. Ethylene reacts with Baeyer's reagent to give

- (a) ethane
- (b) ethyl alcohol
- (c) ethylene glycol
- (d) None of these

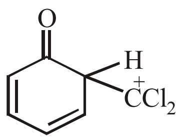
23. Alcohols of low molecular weight are

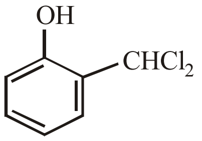
- (a) Soluble in water
- (b) Soluble in water on heating
- (c) Insoluble in water
- (d) Insoluble in all solvents

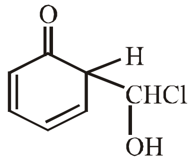
24. When ethyl alcohol reacts with acetic acid, the products formed are

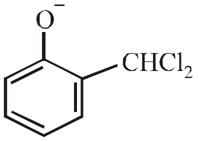
(a) Sodium ethoxide + hydrogen
(b) Ethyl acetate + water
(c) Ethyl acetate + soap
(d) Ethyl alcohol + water

25. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicyladehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediate?

(a) 

(b) 

(c) 

(d) 

26. Which statement is not correct about alcohol?

(a) Molecular weight of alcohol is higher than water.
(b) Alcohol of less no. of carbon atoms is less soluble in water than alcohol of more no. of carbon atoms
(c) Alcohol evaporates quickly.
(d) All of these

Exercise-2 | CONCEPTUAL MCQs

1. Vinyl carbinol is

(a) $HO-CH_2-CH=CH_2$
(b) $CH_3C(OH)=CH_2$
(c) $CH_3-CH=CH-OH$
(d) $CH_3-C(CH_2OH)=CH_2$

2. Epichlorohydrin is

(a) 3-Chloropropane
(b) 3-Chloropropan-1-ol
(c) 3-Chloro-1, 2-epoxypropane
(d) None of these

3. Number of metamers represented by molecular formula $C_4H_{10}O$ is

(a) 4 (b) 3 (c) 2 (d) 1

4. How many isomers of $C_5H_{11}OH$ will be primary alcohols?

(a) 5 (b) 4 (c) 2 (d) 3

5. Which of the following compounds can exist in optically active form?

(a) 1-Butanol (b) 2-Butanol
(c) 3-Pentanol (d) 4-Heptanol

6. How many optically active stereoisomers are possible for butane-2, 3-diol?

(a) 1 (b) 2 (c) 3 (d) 4

7. Isopropyl alcohol is obtained by reacting which of the following alkenes with concentrated H_2SO_4 followed by boiling with H_2O?

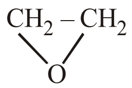
(a) Ethylene (b) Propylene
(c) 2-Methylpropene (d) Isoprene

8. Benzylamine reacts with nitrous acid to form

(a) azobenzene (b) benzene
(c) benzyl alcohol (d) phenol

9. The reaction of Grignard reagent with formaldehyde followed by acidification gives

(a) an aldehyde (b) a primary alcohol
(c) a carboxylic acid (d) a ketone

10. The reaction  CH_2-CH_2 (with O bridging, $\underset{O}{\diagdown\!\diagup}$) with RMgX leads to the formation of

(a) RCHOHR (b) $RCHOHCH_3$
(c) R_2CHCH_2OH (d) RCH_2CH_2OH

11. The reaction of CH_3MgBr with acetone and hydrolysis of the resulting product gives

(a) $CH_3CH_2CH_2OH$ (b) $CH_3CH_2CH_2CH_2OH$
(c) $(CH_3)_2CHOH$ (d) $(CH_3)_3COH$

12. To prepare 3-ethylpentan-3-ol, the reagents needed are

(a) $CH_3CH_2MgBr + CH_3COCH_2CH_3$
(b) $CH_3MgBr + CH_3CH_2CH_2COCH_2CH_3$
(c) $CH_3CH_2MgBr + CH_3CH_2COCH_2CH_3$
(d) $CH_3CH_2CH_2MgBr + CH_3COCH_2CH_3$

13. Ethyl acetate reacts with CH_3MgBr to form

(a) secondary alcohol
(b) tertiary alcohol
(c) primary alcohol and an acid
(d) an acid

14. 1-Phenylethanol can be prepared by the reaction of benzaldehyde with

(a) methyl bromide

(b) ethyl iodide and magnesium

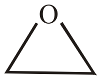
(c) methyl iodide and magnesium

(d) methyl bromide and aluminium bromide

15. 2-Phenylethanol may be prepared by the reaction of phenylmagnesium bromide with

(a) HCHO (b) CH_3CHO

(c) CH_3COCH_3 (d)



16. The compound obtained by the reaction of ethene with diborane followed by hydrolysis with alkaline hydrogen peroxide is

(a) ethanol (b) propanol

(c) ethanal (d) triethyl boride

17. Conversion of cyclohexene to cyclohexanol can be conveniently achieved by

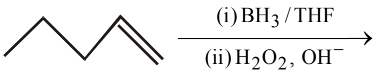
(a) $NaOH - H_2O$

(b) $Br_2 - H_2O$

(c) hydroboration–oxidation

(d) hydroboration–hydrolysis

18. The product of the following reaction is



(a) 1-Pentanol (b) 2-Pentanol

(c) Pentane (d) 1,2-Pentanediol

19. The most appropriate reagent to convert

$$RCOOEt \longrightarrow RCH_2OH \text{ is}$$

(a) $LiAlH_4$ (b) $NaBH_4$

(c) H_2/Pd-C (d) Li/NH_3 (liq)

20. The alcohol manufactured from water gas is

(a) butanol (b) ethanol

(c) methanol (d) isobutanol

21. Rectified spirit is a mixture of

(a) 95% ethyl alcohol + 5% water

(b) 94% ethyl alcohol + 4.53 water

(c) 94.4% ethyl alcohol + 5.43% water

(d) 95.87% ethyl alcohol + 4.13% water

22. Which of the following is the most suitable method for removing the traces of water from ethanol?

(a) Heating with Na metal

(b) Passing dry HCl gas through it

(c) Distilling it

(d) Reaction with Mg

23. Absolute alcohol (100% alcohol) is prepared by distilling rectified spirit over

(a) Na (b) $CaCl_2$

(c) Mg (d) $Mg(OC_2H_5)_2$

24. Which of the following has lowest solubility in water?

(a) MeOH (b) C_2H_5OH

(c) $(CH_3)_2CHOH$ (d) $(CH_3)_3COH$

25. The correct order of boiling points for primary (1°), secondary (2°) and tertiary alcohol (3°) is

(a) $1° > 2° > 3°$ (b) $3° > 2° > 1°$

(c) $2° > 1° > 3°$ (d) $2° > 3° > 1°$

26. Zerevitinov's determination of active hydrogen in a compound is based upon its reaction with

(a) Na (b) CH_3Mgl

(c) Zn (d) Al

27. On reaction with sodium, 1 mol of a compound X gives 1 mol of H_2. Which one of the following compounds might be X?

(a) $CH_3CH_2CH=CH_2$

(b) $CH_3COOCH_2CH_3$

(c) $CH_3CH_2CH_2OH$

(d) $CH_2OHCH_2CH_2CH_2OH$

28. Ethyl alcohol exhibits acidic character on reacting it with

(a) acetic acid (b) sodium metal

(c) hydrogen chloride (d) acidic $K_2Cr_2O_7$

29. Among the following compounds, strongest acid is

(a) $HC \equiv CH$ (b) C_6H_6

(c) C_2H_6 (d) CH_3OH

30. For the reaction,

$$C_2H_5OH + HX \xrightarrow{ZnCl_2} C_2H_5X + H_2O$$

the order of reactivity is

(a) $HBr > HI > HCl$ (b) $HI > HCl > HBr$

(c) $HI > HBr > HCl$ (d) $HCl > HBr > HI$

31. The compound which reacts fastest with Lucas reagent at room temperature is

(a) Butan-1-ol (b) Butan-2-ol

(c) 2-Methylpropan-1-ol (d) 2-Methylpropan-2-ol

32. In the following reaction,

$$C_2H_5OH \xrightarrow[443\,K]{Conc.\ H_2SO_4} Z \text{ identify Z:}$$

(a) $CH_2=CH_2$ (b) $CH_3CH_2OCH_2CH_3$

(c) CH_3CH_2–HSO_4 (d) $(CH_3CH_2)_2SO_4$

33. Which one of the following cannot be obtained from a mixture of ethanol and concentrated sulphuric acid, if the composition of the mixture and the reaction conditions are suitably adjusted?

(a) C_2H_4 (b) CH_3CHO

(c) $CH_3CH_2OCH_2CH_3$ (d) $CH_3CH_2HSO_4$

34. Order of esterification of alcohols is

(a) $3° > 2° > 1°$ (b) $2° > 3° > 1°$

(c) $1° > 2° > 3°$ (d) None of these

35. Conversion of ethyl alcohol to acetaldehyde is an example of
(a) reduction
(b) molecular rearrangement
(c) hydrolysis
(d) oxidation

36. Which one of the following on oxidation gives a ketone?
(a) Primary alcohol (b) Secondary alcohol
(c) Tertiary alcohol (d) All of these

37. When wine is put in air, it becomes sour due to
(a) bacteria
(b) oxidation of C_2H_5OH to CH_3COOH
(c) virus
(d) formic acid formation

38. When the vapours of ethyl alcohol are passed over red hot copper (300ºC), then product formed is
(a) ethylene (b) acetaldehyde
(c) acetic acid (d) None of these

39. The reagent used for dehydration of an alcohol is
(a) phosphorus pentachloride
(b) calcium chloride
(c) aluminium oxide
(d) sodium chloride

40. The alcohol which does not give a stable compound on dehydration is
(a) ethyl alcohol (b) methyl alcohol
(c) n-Propyl alcohol (d) n-Butyl alcohol

41. Which of the following is not true in case of reaction with heated copper at 300ºC?
(a) Phenol $\longrightarrow$ Benzyl alcohol
(b) Primary alcohol $\longrightarrow$ Aldehyde
(c) Secondary alcohol $\longrightarrow$ Ketone
(d) Tertiary alcohol $\longrightarrow$ Olefin

42. In presence of alkali, C_2H_5OH reacts with Cl_2 to give
(a) ethane (b) ethyl chloride
(c) chloroform (d) pyridine

43. Which of the following gives positive iodoform test?
(a) CH_3OH (b) $(CH_3)_2CHOH$
(c) $(CH_3)_3COH$ (d) $n–C_3H_7OH$

44. Haloform reaction does not take place with
(a) Acetone (b) 2-Chloropropane
(c) Ethanol (d) Methanol

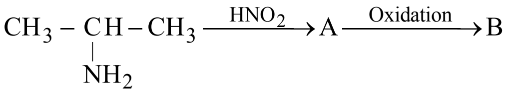
45. Which of the following will not give iodoform test?
(a) Ethanol (b) Ethanal
(c) Isopropyl alcohol (d) Benzyl alcohol

46. Victor Meyer's test is not given by
(a) $(CH_3)_3COH$ (b) C_2H_5OH
(c) $(CH_3)_2CHOH$ (d) $CH_3CH_2CH_2OH$

47. 1-Propanol and 2-propanol can be distinguished by
(a) oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution
(b) oxidation with acidic dichromate followed by reaction with Fehling solution
(c) oxidation by heating with copper followed by reaction with Fehling solution
(d) oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution

48. *n*-propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent
(a) PCl_5
(b) reduction
(c) oxidation with potassium dichromate
(d) ozonolysis

49. In the following sequence of reactions,



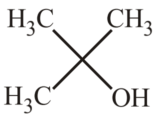
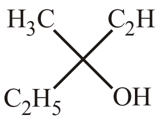
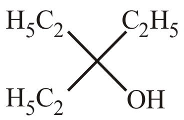
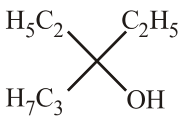
$$CH_3-\underset{NH_2}{\underset{|}{C}}H-CH_3 \xrightarrow{HNO_2} A \xrightarrow{\text{Oxidation}} B$$

$$B \xrightarrow[\text{ii) } H_3O^+]{\text{i) } CH_3MgI} C$$

the compound C formed will be
(a) Butanol-1 (b) Butanol-2
(c) 2-Methylpropanol-1 (d) 2-Methyl-2-propanol

50. Ethyl ester

$\xrightarrow[\text{excess}]{CH_3MgBr}$ P. The product P will be

(a) 
(b) 
(c) 
(d) 

51. A compound of the formula $C_4H_{10}O$ reacts with sodium and undergoes oxidation to give a carbonyl compound which does not reduce Tollen's reagent, the original compound is
(a) Diethyl ether (b) *n*-Butyl alcohol
(c) Isobutyl alcohol (d) *sec*-Butyl alcohol

52. Which of the following is correct?
(a) Reduction of an aldehyde gives secondary alcohol
(b) Reaction of vegetable oil with H_2SO_4 gives glycerine
(c) Alcoholic iodine with NaOH gives iodoform
(d) Sucrose on reaction with NaCl gives invert sugar

53. An organic compound A reacts with sodium metal and forms B. On heating with conc. H_2SO_4, A gives diethyl ether. A and B are respectively
(a) C_2H_5OH and C_2H_5ONa
(b) C_3H_7OH and C_3H_7ONa
(c) CH_3OH and CH_3ONa
(d) C_4H_9OH and C_4H_9ONa

54. Ethanol when reacted with PCl_5 gives **A**, $POCl_3$ and HCl. **A** reacts with silver nitrite to form **B** (major product) and AgCl. A and B respectively are
(a) C_2H_5Cl and $C_2H_5OC_2H_5$ (b) C_2H_6 and $C_2H_5OC_2H_5$
(c) C_2H_5Cl and $C_2H_5NO_2$ (d) C_2H_6 and $C_2H_5NO_2$

55. Ethylene reacts with 1% cold alkaline $KMnO_4$ to form
(a) oxalic acid (b) ethylene glycol
(c) ethyl alcohol (d) HCHO

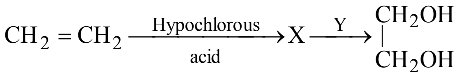
56. $CH_2=CH_2 \xrightarrow[Ag]{O_2} X \xrightarrow[473\text{ K}]{\text{Steam}} Y$

The compound Y is
(a) ethanol (b) ethanal
(c) epoxyethane (d) ethylene glycol

57. Osmium tetraoxide is a reagent used for
(a) hydroxylation of acetylenes
(b) hydroxylation of olefins to give *cis*-diols
(c) hydroxylation of olefins to form trans- diols
(d) hydroxylation of carbonyl compounds

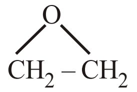
58. *trans*-Cyclohexane-1, 2-diol can be obtained by the reaction of cyclohexene with
(a) $KMnO_4$ (b) OsO_4
(c) peroxyformic acid (d) SeO_2

59. In the reaction sequence



$$CH_2=CH_2 \xrightarrow[\text{acid}]{\text{Hypochlorous}} X \xrightarrow{Y} \begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}$$

X and Y respectively are:

(a)  and heat
(b) CH_3CH_2Cl and NaOH
(c) CH_3CH_2OH and H_2SO_4
(d) CH_2ClCH_2OH and $NaHCO_3$

60. When ethylene glycol is heated with acidified potassium permanganate, the main organic compound obtained is
(a) oxalic acid (b) glyoxal
(c) formic acid (d) acetaldehyde

61. In the synthesis of glycerol from propene, compounds formed are
(a) Glycerol β-chlorohydrin and allyl chloride
(b) Glyceryl trichloride and glycerol α-chlorohydrin
(c) Allyl alcohol and α-chlorohydrin
(d) Allyl alcohol and monosodium glycerolate

62. Which of the following is not formed when glycerol reacts with HI?
(a) $CH_2=CH-CH_2I$ (b) $CH_2OH-CHI-CH_2OH$
(c) $CH_3-CH=CH_2$ (d) $CH_3-CHI-CH_3$

63. Acrolein is prepared from
(a) glycerol (b) 1, 2-ethanediol
(c) ethyl alcohol (d) acetone

64. Glycerol on heating with oxalic acid at 110°C gives
(a) ethanol (b) ethanal
(c) ether (d) formic acid

65. With oxalic acid, glycerol at 503 K gives
(a) allyl alcohol (b) formic acid
(c) glyceraldehyde (d) None of these

66. When benzenediazonium chloride is treated with water, the compound formed is
(a) C_6H_5COOH (b) C_6H_5OH
(c) C_6H_6 (d) $C_6H_5NH_2$

67. Phenol is
(a) a base stronger than ammonia
(b) an acid stronger than carbonic acid
(c) an acid weaker than carbonic acid
(d) a neutral compound

68. Which of the following is most acidic?
(a) Phenol (b) Benzyl alcohol
(c) *m*-Chlorophenol (d) Cyclohexanol

69. Which of the following fact(s) explain(s) as to why p-nitrophenol is more acidic than phenol?
I. –I Effect of nitro group.
II. Greater resonance effect of p-nitrophenoxy group
III. Steric effect of bulky nitro group
(a) I and II (b) I and III
(c) II and III (d) II alone

70. Which of the following is most acidic?
(a) Phenol (b) CH_3CH_2OH
(c) Picric acid (d) p-Nitrophenol

71. Which of the following will not be soluble in sodium bicarbonate?
(a) 2, 4, 6-Trinitrophenol
(b) Benzoic acid
(c) o-Nitrophenol
(d) Benzenesulphonic acid

72. The distillation of phenol with zinc dust gives
(a) C_6H_6 (b) $C_6H_5-C_6H_5$
(c) C_6H_{12} (d) $C_6H_5OC_6H_5$

73. Phenol on reduction with H_2 in presence of nickel catalyst gives
(a) benzene (b) toluene
(c) cyclohexane (d) cyclohexanol

74. In the Liebermann's nitroso reaction, sequential changes in the colour of phenol occurs as
(a) Brown or red $\longrightarrow$ green $\longrightarrow$ deep blue
(b) Red $\longrightarrow$ deep blue $\longrightarrow$ green
(c) Red $\longrightarrow$ green $\longrightarrow$ white
(d) White $\longrightarrow$ red $\longrightarrow$ green

75. The reaction of CO_2 with sodium phenoxide at 400 K results in
(a) benzoic acid (b) sodium benzoate
(c) sodium salicylate (d) salicylaldehyde

76. Phenol can be distinguished from ethyl alcohol by all reagents except
(a) NaOH (b) $FeCl_3$
(b) Br_2/H_2O (d) Na

77. Which one of the following compounds will be most readily attacked by an electrophile?
(a) Chlorobenzene (b) Benzene
(c) Phenol (d) Toluene

78. Phenol when heated with concentrated nitric acid gives
(a) anthranilic acid (b) p-nitrobenzoic acid
(c) picric acid (d) salicyclic acid

79. When phenol is treated with excess bromine water, it gives
(a) m-Bromophenol (b) o-and p-Bromophenols
(c) 2, 4-Dibromophenol (d) 2, 4, 6-Tribromophenol

80. What amount of bromine will be required to convert 2g of phenol into 2, 4, 6-tribromophenol?
(a) 4.0 (b) 6.0
(c) 10.22 (d) 20.44

81. Phenol on reaction with Br_2 in non-polar aprotic solvent furnishes
(a) 2, 4, 6-Tribromophenol (b) *p*-Bromophenol
(c) *o- and p*-Bromophenol (d) *m*-Bromophenol

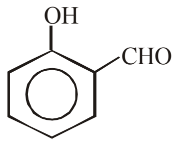
82. Which of the following is a Riemer-Tiemann reaction?
(a) $C_6H_5OH + CCl_4 \xrightarrow{NaOH} \text{Salicylic acid}$
(b) $C_6H_5OH + Zn \longrightarrow C_6H_6$
(c) $C_6H_5OH + NaOH \longrightarrow C_6H_5ONa$
(d) None of these

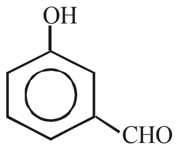
83. The following reaction is known as

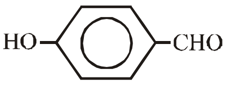
$$\text{Phenol} \xrightarrow[H^+]{CHCl_3/NaOH} \text{Salicylaldehyde}$$

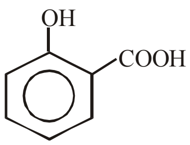
(a) Gattermann's aldehyde synthesis
(b) Duff's reaction
(c) Perkin's reaction
(d) Reimer-Tiemann's reaction

84. What is the major product obtained when phenol is treated with chloroform and aqueous alkali?

(a) 

(b) 

(c) 

(d) 

85. In the reaction of phenol with $CHCl_3$ and aqueous NaOH at 70ºC (343 K), the electrophile attacking the ring is
(a) $CHCl_3$ (b) $\cdot CHCl_2$
(c) $:CCl_2$ (d) $COCl_2$

86. Chemical name of salol is
(a) acetylsalicyclic acid (b) sodium salicylate
(c) phenyl salicylate (d) methyl salicylate

87. Which compound is known as oil of winter green?
(a) Phenyl benzoate (b) Phenyl salicylate
(c) Phenyl acetate (d) Methyl salicylate

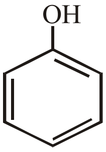
88. Reimer-Tiemann reaction involves
(a) carbonium ion intermediate
(b) carbene intermediate
(c) carbanion intermediate
(d) free radical intermediate

89. Aspirin is an acetylation product of
(a) p-Dihydroxybenzene (b) o-Hydroxybenzoic acid
(c) o-Dihydroxybenzene (d) m-Hydroxybenzoic acid

90. Dow's reaction involves
(a) electrophilic addition
(b) nucleophilic addition
(c) electrophilic substitution
(d) nucleophilic substitution

91. Phenol is heated with phthalic anhydride in presence of conc. H_2SO_4. The product gives pink colour with alkali. The product is
(a) phenolphthalein (b) bakelite
(c) salicylic acid (d) fluorescein

92. $o-\text{Xylene} \xrightarrow{HNO_3} X \xrightarrow[H_2SO_4]{\text{Phenol}} Y$. The product Y is
(a) Phthalic acid
(b) Isophthalic acid
(c) Phenolphthalein
(d) o-Hydroxysulphonic acid

93. 

$+C_2H_5I \xrightarrow[^-OC_2H_5]{\text{Anhydrous }(C_2H_5OH)}$

(a) $C_6H_5OC_2H_5$ (b) $C_2H_5OC_2H_5$
(c) $C_6H_5OC_6H_5$ (d) C_6H_5I

94. Ether is obtained from ethyl alcohol
(a) in presence of H_2SO_4 at 413 K
(b) in presence of H_2SO_4 at 474 K
(c) in presence of H_2SO_4 at 383 K
(d) in presence of H_2SO_4 at 273 K

95. Diethyl ether is prepared by passing vapours of ethyl alcohol over a heated catalyst under high temperature and pressure. The catalyst is
(a) SiO_2 (b) CuO
(c) Al_2O_3 (d) Ag_2O

96. In Williamson's synthesis, ethoxyethane is prepared by
(a) passing ethanol over heated alumina
(b) heating sodium ethoxide with ethyl bromide
(c) treating ethyl alcohol with excess of H_2SO_4 at 430-440 K
(d) heating ethanol with dry Ag_2O

97. Which of the following cannot be made by using Williamson's synthesis?
(a) Methoxybenzene
(b) Benzyl p-nitrophenyl ether
(c) Methyl tertiary butyl ether
(d) Di-tert-butyl ether

98. The reagent used for the preparation of higher ethers from halogenated ethers is
(a) Conc. H_2SO_4 (b) Sodium alkoxide
(c) Dry silver oxide (d) Grignard reagent

99. Which of the following reactions will not result in the formation of anisole?
(a) Phenol + dimethyl sulphate in presence of a base
(b) Sodium phenoxide is treated with methyl iodide
(c) Reaction of diazomethane with phenol
(d) Reaction of methylmagnesium iodide with phenol

100. Which of the following has strongest hydrogen bonding?
(a) Ethyl amine (b) Ethanal
(c) Ethyl alcohol (d) Diethyl ether

101. Ether which is liquid at room temperature is
(a) $C_2H_5OCH_3$ (b) CH_3OCH_3
(c) $C_2H_5OC_2H_5$ (d) None of these

102. When ether is exposed in air for sometimes, an explosive substance produced is
(a) Peroxide (b) TNT
(c) Oxide (d) Superoxide

103. Heating methyl phenyl ether with HI gives
(a) methanol + iodobenzene
(b) methyl iodide + iodobenzene
(c) methyl alcohol + benzyl alcohol
(d) methyl iodide + phenol

104. An aromatic ether is not cleaved by HI even at 525 K. The compound is
(a) $C_6H_5OCH_3$ (b) $C_6H_5OC_6H_5$
(c) $C_6H_5OC_3H_7$ (d) Tetrahydrofuran

105. Which of the following compounds is resistant to nucleophilic attack by hydroxyl ions?
(a) Methyl acetate (b) Acetonitrile
(c) Acetamide (d) Diethyl ether

106. Acetic anhydride reacts with diethyl ether in the presence of anhydrous $AlCl_3$ to give
(a) CH_3COOCH_3 (b) $CH_3CH_2COOCH_3$
(c) $CH_3COOCH_2CH_3$ (d) CH_3CH_2OH

107. When diethyl ether is treated with excess of Cl_2 in the presence of sunlight, then the product formed is
(a) $CH_3CHCl-O-CH_2CH_3$
(b) $CH_3CHCl-O-CHClCH_3$
(c) $CCl_3CCl_2OCCl_2CCl_3$
(d) $CH_3CCl_2-O-CHClCH_3$

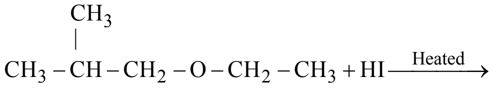
108. In the following reaction.

$C_2H_5OC_2H_5+4H\xrightarrow{\text{Red P + HI}}2X+H_2O$; X is
(a) ethane (b) ethylene
(c) butane (d) propane

109. The ether that undergoes electrophilic substitution reactions is
(a) $CH_3OC_2H_5$ (b) $C_6H_5OCH_3$
(c) CH_3OCH_3 (d) $C_2H_5OC_2H_5$

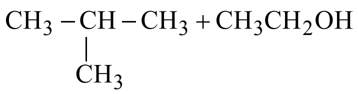
Exercise-3 | PAST COMPETITION MCQs

1. In the reaction: **[CBSE-PMT 2007]**

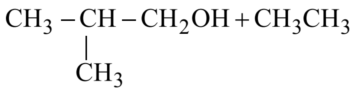


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-O-CH_2-CH_3+HI\xrightarrow{\text{Heated}}$$

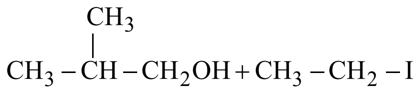
Which of the following compounds will be formed?

(a)


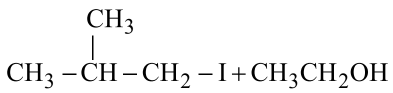
$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3+CH_3CH_2OH$$

(b)


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH+CH_3CH_3$$

(c)


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2OH+CH_3-CH_2-I$$

(d)


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-I+CH_3CH_2OH$$

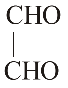
2. Consider the following reaction, **[CBSE-PMT 2009]**

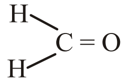
$$\text{ethanol}\xrightarrow{PBr_3}X\xrightarrow{\text{alc.KOH}}Y\xrightarrow[\text{(ii) } H_2O\text{, heat}]{\text{(i) } H_2SO_4 \text{ room temperature}}Z;$$

the product Z is:
(a) $CH_3CH_2-O-CH_2-CH_3$
(b) $CH_3-CH_2-O-SO_3H$
(c) CH_3CH_2OH
(d) $CH_2=CH_2$

3. $H_2COH \cdot CH_2OH$ on heating with periodic acid gives: **[CBSE-PMT 2009]**

(a) 2 HCOOH

(b)

$\overset{CHO}{\underset{CHO}{|}}$

(c) 2


(d) $2\,CO_2$

4. Consider the following reaction: **[CBSE-PMT 2009]**

$$\text{Phenol} \xrightarrow{\text{Zn dust}} X \xrightarrow[\text{Anhydrous } AlCl_3]{CH_3Cl} Y \xrightarrow{\text{Alkaline } KMnO_4} Z$$

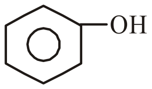
The product Z is:

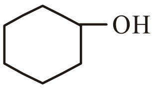
(a) benzaldehyde (b) benzoic acid

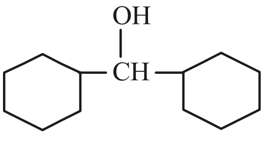
(c) benzene (d) toluene

5. Which one of the following compounds has the most acidic nature? **[CBSE-PMT 2010]**

(a)


(b)


(c)


(d)


6. Among the following four compounds **[CBSE-PMT 2010]**

(i) phenol (ii) methylphenol

(iii) meta-nitrophenol (iv) para-nitrophenol

the acidity order is :

(a) ii > i > iii > iv (b) iv > iii > i > ii

(c) iii > iv > i > ii (d) i > iv > iii > ii

7. When glycerol is treated with excess of HI, it produces: **[CBSE-PMT 2010]**

(a) glycerol triiodide (b) 2–iodopropane

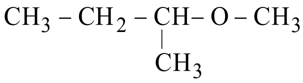
(c) allyl iodide (d) propene

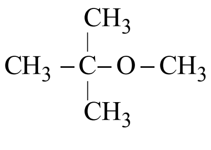
8. Which of the following compounds can be used as antifreeze in automobile radiators ? **[CBSE-PMT 2012]**

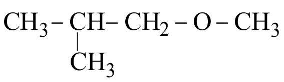
(a) Methyl alcohol (b) Glycol

(c) Nitrophenol (d) Ethyl alcohol

9. Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI? **[NEET 2013]**

(a)

$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-O-CH_3$

(b)

$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-O-CH_3$

(c)

$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-O-CH_3$

(d) $CH_3-CH_2-CH_2-CH_2-O-CH_3$

10. An ether is more volatile than an alcohol having the same molecular formula. This is due to **[AIEEE 2003]**

(a) alcohols having resonance structures

(b) inter-molecular hydrogen bonding in ethers

(c) inter-molecular hydrogen bonding in alcohols

(d) dipolar character of ethers

11. During dehydration of alcohols to alkenes by heating with conc. H_2SO_4 the initiation step is **[AIEEE 2003]**

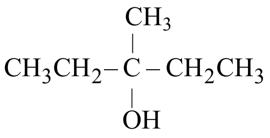
(a) formation of carbocation

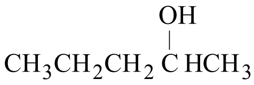
(b) elimination of water

(c) formation of an ester

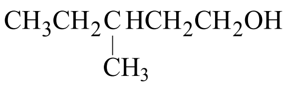
(d) protonation of alcohol molecule

12. Among the following compounds which can be dehydrated very easily is **[AIEEE 2004]**

(a)

$CH_3CH_2-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_2CH_3$

(b)

$CH_3CH_2CH_2\overset{OH}{\overset{|}{C}}HCH_3$

(c) $CH_3CH_2CH_2CH_2CH_2OH$

(d)

$CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCH_2CH_2OH$

13. The best reagent to convert pent-3-en-2-ol into pent-3-in-2-one is **[AIEEE 2005]**

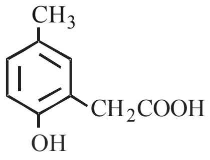
(a) pyridinium chloro-chromate

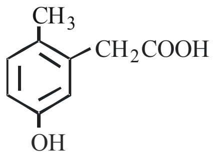
(b) chromic anhydride in glacial acetic acid

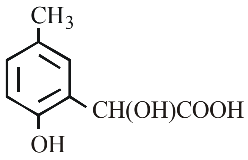
(c) acidic dichromate

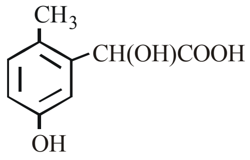
(d) acidic permanganate

14. p -cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form, the compound B. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is **[AIEEE 2005]**

(a)


(b)


(c)


(d)


15. Phenyl magnesium bromide reacts with methanol to give **[AIEEE 2006]**

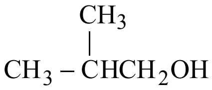
(a) a mixture of toluene and Mg(OH)Br

(b) a mixture of phenol and Mg(Me)Br

(c) a mixture of anisole and Mg(OH)Br

(d) a mixture of benzene and Mg(OMe)Br

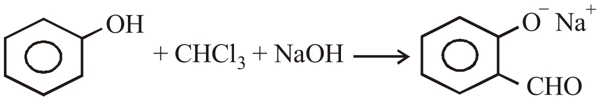
16. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is **[AIEEE 2006]**

(a) 
$CH_3-\overset{\overset{\large CH_3}{|}}{C}HCH_2OH$

(b) $PhCHOHCH_3$

(c) $CH_3CH_2CH(OH)CH_2CH_3$

(d) $C_6H_5CH_2CH_2OH$

17. 

The electrophile involved in the above reaction is **[AIEEE 2006]**

(a) trichloromethyl anion $(\overset{\ominus}{C}Cl_3)$

(b) formyl cation $(\overset{\oplus}{C}HO)$

(c) dichloromethyl cation $(\overset{\oplus}{C}HCl_2)$

(d) dichlorocarbene $(:CCl_2)$

18. In the following sequence of reactions,

$$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow[\text{ether}]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$$

the compound D is **[AIEEE 2007]**

(a) propanal (b) butanal

(c) *n*-butyl alcohol (d) *n*-propyl alcohol.

19. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives **[AIEEE 2008]**

(a) 2, 4, 6-trinitrobenzene (b) *o*-nitrophenol

(c) *p*-nitrophenol (d) nitrobenzene

20. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is **[AIEEE 2009]**

(a) salicylaldehyde (b) salicylic acid

(c) phthalic acid (d) benzoic acid

21. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$, is **[AIEEE 2010]**

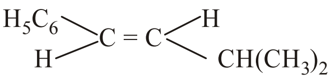
(a) 2-Butanol (b) 2- Methylpropan-2-ol

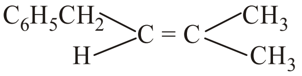
(c) 2-Methylpropanol (d) 1- Butanol

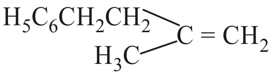
22. The main product of the following reaction is

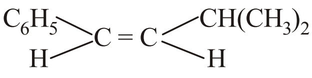
$$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{\text{conc.}H_2SO_4} ?$$

[AIEEE 2010]

(a) 

(b) 

(c) 

(d) 

23. The correct order of acid strength of the following compounds : **[AIEEE 2011 RS]**

(A) Phenol (B) *p*–Cresol

(C) *m*–Nitrophenol (D) *p*–Nitrophenol

(a) D > C > A > B (b) B > D > A > C

(c) A > B > D > C (d) C > B > A > D

24. Consider the following reaction :

$C_2H_5OH + H_2SO_4 \longrightarrow$ Product

Among the following, which one cannot be formed as a product under any conditions ? **[AIEEE 2011 RS]**

(a) Ethylene

(b) Acetylene

(c) Diethyl ether

(d) Ethyl-hydrogen sulphate

25. Phenol is heated with a solution of mixture of KBr and $KBrO_3$. The major product obtained in the above reaction is : **[AIEEE 2011]**

(a) 2-Bromophenol (b) 3-Bromophenol

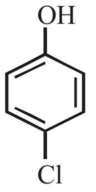
(c) 4-Bromophenol (d) 2, 4, 6-Tribromophenol

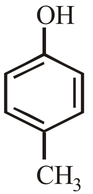
26. Which of the following reagents may be used to distinguish between phenol and benzoic acid? **[AIEEE 2011]**

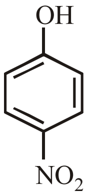
(a) Aqueous NaOH (b) Tollen's reagent

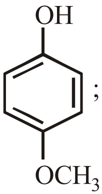
(c) Molisch reagent (d) Neutral $FeCl_3$

27. Arrange the following compounds in order of decreasing acidity : **[JEE M 2013]**


(I) ;

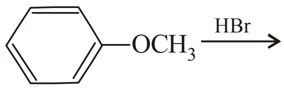

(II) ;

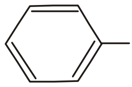

(III) ;

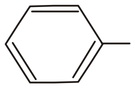

(IV) ;

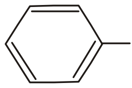
(a) II > IV > I > III (b) I > II > III > IV

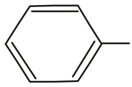
(c) III > I > II > IV (d) IV > III > I > II

28. In the reaction  the products are **[IIT-JEE 2010]**

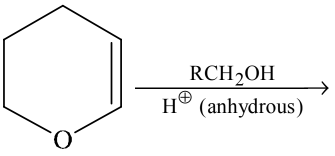
(a)  OCH$_3$and H_2

(b)  Br and CH_3Br

(c)  Br and CH_3OH

(d)  OH and CH_3Br

29. The major product of the following reaction is



[IIT-JEE 2011]

(a) a hemiacetal (b) an acetal

(c) an ether (d) an ester

Exercise-4 | Applied MCQs

1. Which one/ones of the following reactions will yield 2-propanol?

I. $CH_2=CH-CH_3+H_2O \xrightarrow{H^+}$

II. $CH_3-CHO \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgI}$

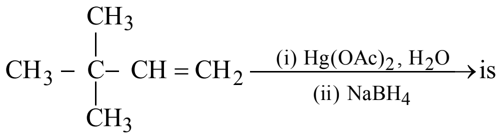
III. $CH_2O \xrightarrow[(ii)\ H_2O]{(i)\ C_2H_5MgI}$

IV. $CH_2=CH-CH_3 \xrightarrow{\text{Neutral } KMnO_4}$

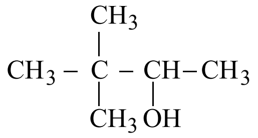
(a) I and II (b) II and III
(c) III and I (d) II and IV

2. The reagent required to convert propene to 1-propanol is
(a) B_2H_6 followed by H_2O_2/NaOH
(b) Conc. H_2SO_4 followed by hydrolysis with boiling water
(c) HBr followed by hydrolysis with aqueous KOH
(d) $Hg(OCOCH_3)_2$ followed by reduction with $NaBH_4$

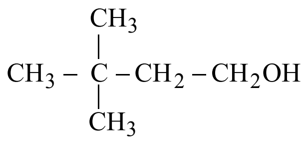
3. The product of the following reaction,



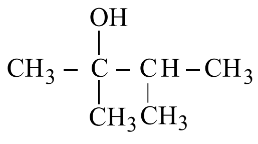
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2 \xrightarrow[(ii)\ NaBH_4]{(i)\ Hg(OAc)_2,\ H_2O} \text{is}$$

(a)


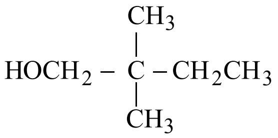
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{OH}{CH}-CH_3$$

(b)


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2OH$$

(c)


$$CH_3-\overset{OH}{\underset{CH_3}{C}}-\underset{CH_3}{CH}-CH_3$$

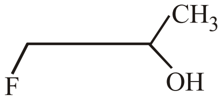
(d)


$$HOCH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2CH_3$$

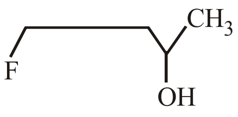
4. Oxymercuration-demercuration reaction of 1-methylcyclohexene gives
(a) *cis*-2-Methylcyclohexanol
(b) *trans*-2-Methylcyclohexanol
(c) 1-Methylcyclohexanol
(d) mixture of *cis*- and *trans*-2-Methylcyclohexanol

5. Correct increasing order of acidity is as follows
(a) H_2O, C_2H_2, H_2CO_3, phenol
(b) C_2H_2, H_2O, H_2CO_3, phenol
(c) phenol, C_2H_2, H_2CO_3, H_2O
(d) C_2H_2, H_2O, phenol, H_2CO_3

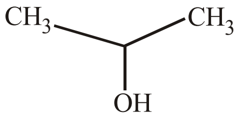
6. The order of reactivity of the following alcohols towards conc. HCl is



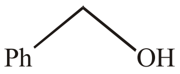
(I)



(II)



(III)



(IV)

(a) I > II > III > IV (b) I > III > II > IV
(c) IV > III > II > I (d) IV > III > I > II

7. 3 moles of ethanol react with one mole of phosphorus tribromide to form 3 moles of bromoethane and one mole of X. Which of the following is X?
(a) H_3PO_4 (b) H_3PO_2
(c) HPO_3 (d) H_3PO_3

8. Which one of the following pairs of compounds can be distinguished by means of iodoform test?
(a) CH_3OH and $CH_3CH_2CH_2OH$
(b) CH_3CH_2OH and $CH_3CHOHCH_3$
(c) $CH_3CH_2CH_2OH$ and $CH_3CHOHCH_3$
(d) $C_6H_5CH_2OH$ and CH_3OH

9. Identify X in the following sequence:

$$\underset{(X)}{C_3H_8O} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} C_3H_6O \xrightarrow[I_2+NaOH]{\text{warm}} CHI_3$$

(a) $CH_3CH_2CH_2OH$ (b) $CH_3CHOHCH_3$
(c) $CH_3OCH_2CH_3$ (d) CH_3CH_2CHO

10. What is Z in the following sequence of reactions?

$$Z \xrightarrow{PCl_5} X \xrightarrow{\text{Alc.KOH}} Y \xrightarrow[(ii)\ H_2O;\ \text{boil}]{(i)\ \text{Conc. } H_2SO_4} Z$$

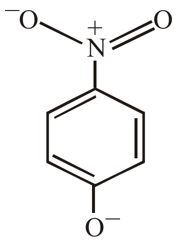
(a) $CH_3CH_2CH_2OH$ (b) $CH_3CHOHCH_3$
(c) $(CH_3CH_2)_2CHOH$ (d) $CH_3CH=CH_2$

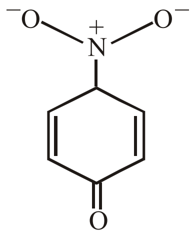
11. A compound is soluble in conc. H_2SO_4. It does not decolourise bromine in carbon tetrachloride but is oxidised by chromic anhydride in aqueous sulphuric acid within two seconds, turning orange solution to blue, green and then opaque. The original compound is
(a) a primary alcohol (b) a tertiary alcohol
(c) an alkane (d) an ether

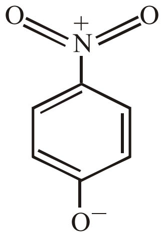
12. An organic compound **A** reacts with methyl magnesium iodide to form an addition product which on hydrolysis forms the compound **B**. Compound **B** gives blue colour salt in Victor Meyer's test. The compounds **A** and **B** are respectively
(a) acetaldehyde, tertiary butyl alcohol
(b) acetaldehyde, ethyl alcohol
(c) acetaldehyde, isopropyl alcohol
(d) acetone, isopropyl alcohol

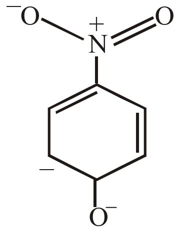
13. The ionisation constant of phenol is higher than that of ethanol because
(a) phenoxide ion is a stronger base than ethoxide ion
(b) phenoxide ion is stabilized through delocalization
(c) phenoxide ion is less stable than ethoxide ion
(d) phenoxide ion is bulkier than ethoxide ion

14. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is

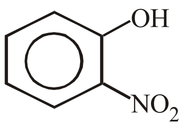
(a)


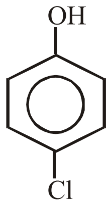
(b)


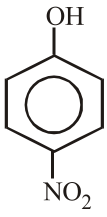
(c)


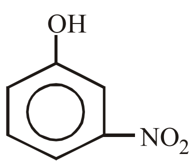
(d)


15. Which of the following is the strongest acid?

(a)


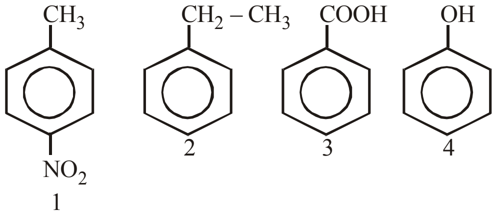
(b)


(c)


(d)


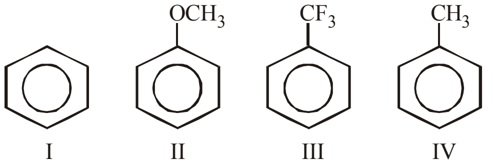
16. The reaction of an aromatic acyl chloride and phenol in the presence of a base such as NaOH or pyridine is called
(a) Kolbe's reaction
(b) Perkin's reaction
(c) Sandmeyer's reaction
(d) Schotten-Baumann's reaction

17. Which will undergo Friedel-Crafts alkylation reaction easily?



(a) 1, 2 and 4 (b) 1 and 3
(c) 2 and 4 (d) 1 and 2

18. The order or reactivity of the following towards electrophilic substitution reaction is



(a) I > II > III > IV (b) II > III > I > IV
(c) III > I > IV > II (d) II > IV > I > III

19. An organic compound of molecular formula $C_4H_{10}O$ does not react with sodium. With excess of HI, it gives only one type of alkyl halide. The compound is
(a) Ethoxyethane (b) 2-Methoxypropane
(c) 1-Methoxypropane (d) 1-Butanol

20. Product C in the reaction,

$$C_2H_5Br \xrightarrow[\text{(aqueous)}]{\text{NaOH}} A \xrightarrow{\text{Na}} B \xrightarrow{CH_3I} C \text{ will be}$$

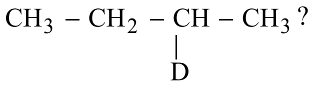
(a) propane (b) ethyl iodide
(c) ethane (d) ethyl methyl ether

21. Identify Z in the sequence:

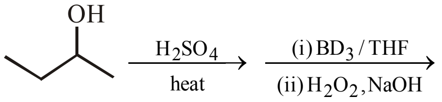
$$CH_3CH_2CH = CH_2 \xrightarrow{HBr/H_2O_2} Y \xrightarrow{C_2H_5ONa} Z$$

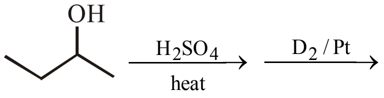
(a) $(CH_3)_2COHCH_2CH_3$
(b) $CH_3CH_2CH(CH_3)–O–CH_2CH_3$
(c) $CH_3(CH_2)_3–O–CH_2CH_3$
(d) $CH_3(CH_2)_4–O–CH_3$

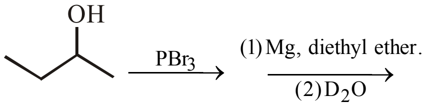
22. Which of the following reactions would convert 2-butanol into deuterated compound

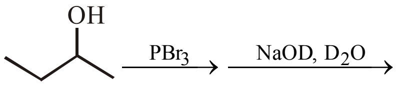


$$CH_3 - CH_2 - \underset{\displaystyle D}{\underset{|}{CH}} - CH_3\ ?$$

(a)


(b)


(c)


(d)


23. Which of the following pairs of reagents would give 4-methyl-2-pentanol ?

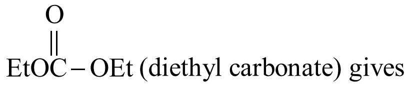
(a) $(CH_3)_2CHLi, CH_3COCH_3$

(b) $(CH_3)_2CHCH_2Li, CH_3CHO$

(c) $(CH_3)_2CHLi, CH_3CH_2CHO$

(d) $CH_3CH_2Li, (CH_3)_2CH.CHO$

24. Reaction of excess of Grignard reagent with

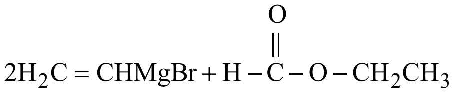


$EtO\overset{\overset{O}{\|}}{C}-OEt$ (diethyl carbonate) gives

(a) ketone (b) tert. alcohol

(c) ester (d) secondary alcohol

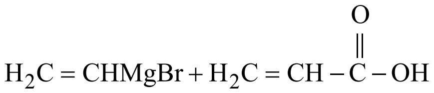
25. Which of the following would give, 1, 4 - pentadien-3-ol with minimum by product ?

(a) 

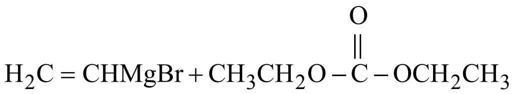
$2H_2C=CHMgBr+H-\overset{\overset{O}{\|}}{C}-O-CH_2CH_3$ followed by neutralisation

(b) 

$H_2C=CH-\underset{\underset{Br}{|}}{CH}-CH=CH_2+H_2O$

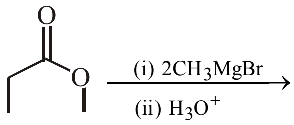
(c) 

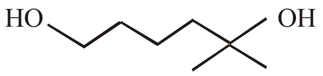
$H_2C=CHMgBr+H_2C=CH-\overset{\overset{O}{\|}}{C}-OH$

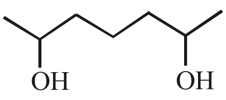
(d) 

$H_2C=CHMgBr+CH_3CH_2O-\overset{\overset{O}{\|}}{C}-OCH_2CH_3$

26. What is the product of the following reaction



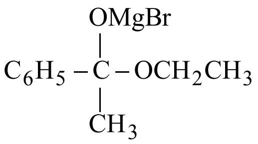
(a) 

(b) 

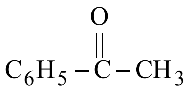
(c) Both (a) and (b)

(d) None of these

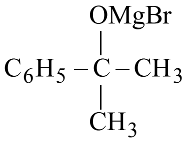
27. Which of the following are intermediates in the reaction of excess of CH_3MgBr with $C_6H_5COOC_2H_5$ to make 2-phenyl - 2-propanol ?

A. 

$C_6H_5-\overset{\overset{OMgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-OCH_2CH_3$

B. 

$C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$

C. 

$C_6H_5-\overset{\overset{OMgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

(a) A and B (b) A, B and C

(c) A and C (d) B and C

28. Which of the following cannot be made by reduction of ketone or aldehyde with $NaBH_4$ in methanol ?

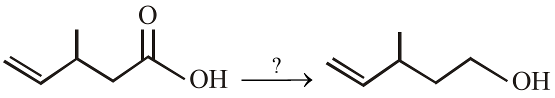
(a) 1 - butanol

(b) 2 - butanol

(c) 2 - methyl - 1- propanol

(d) 2 - methyl - 2- propanol

29. The following change can be carried out with



(a) $NaBH_4$ (b) $LiAlH_4$

(c) H_2/Pt (d) PCC/CH_2Cl_2

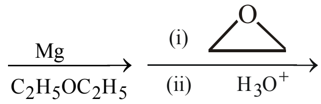
30. Formation of which compound given below from 1 - butanol needs an oxidising agent?

(a) $CH_3CH_2CH_2CH_2Br$ (b) $CH_3CH_2CH_2CH=O$

(c) $(CH_3CH_2CH_2CH_2)_2O$ (d) $CH_3-CH_2CH=CH_2$

31. Which of the following synthesis gives 3-methyl-1- hexanol?

(a) 2 - bromohexane $\xrightarrow[C_2H_5OC_2H_5]{Mg}$ $\xrightarrow[(ii)\ H_3O^+]{(i)\ H_2C=O}$

(b) 2 - bromopentane 

(c) 3 - bromopentane $\xrightarrow[C_2H_5OC_2H_5]{Mg}$ $\xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3CH=O}$

(d) 1 - bromobutane $\xrightarrow[C_2H_5OC_2H_5]{Mg}$ $\xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3COCH_3}$

32. Which of the following diols would cleave into two fragments with HIO_4

(a) 1, 3-hexanediol (b) 2, 4-hexanediol

(c) 1, 6-hexanediol (d) 3, 4-hexanediol

33. What is the product of the following sequence of reactions?

$$(CH_3)_2C=CH.CH_2CH_3 \xrightarrow[(ii)\ H_2O_2,OH^-]{(i)\ BH_3/THF} \xrightarrow[CH_2Cl_2]{PCC} \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr}$$

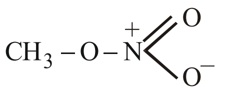
(a) 2, 4 - dimethyl - 3 - pentanol

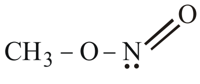
(b) 2, 3 - dimethyl - 3 - pentanol

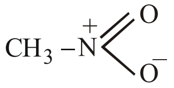
(c) 2, 3 - dimethyl - 2 - pentanol

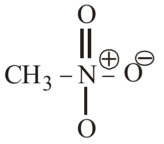
(d) 2, 2 - dimethyl - 3 - pentanol

34. The product formed with CH_3OH and HNO_3

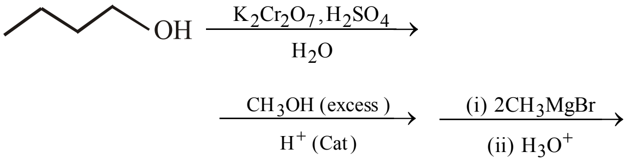
(a) 

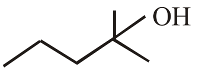
(b) 

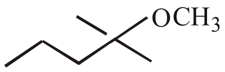
(c) 

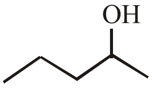
(d) 

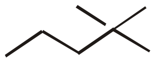
35. The end product of the following sequence of reactions



(a) 

(b) 

(c) 

(d) 

36. Which yields isopropyl methyl ether with little or no by products ?

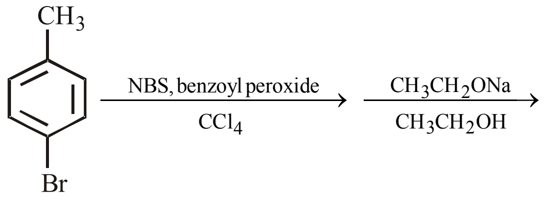
(a) $(CH_3)_2CHO^-Na^+ + CH_3I \longrightarrow$

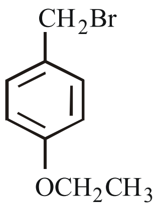
(b) $CH_3O^-Na^+ + (CH_3)_2CHI \longrightarrow$

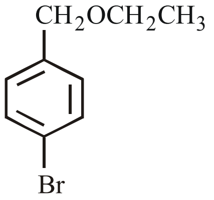
(c) $(CH_3)_2CHOH + CH_3OH \xrightarrow{H_2SO_4}$

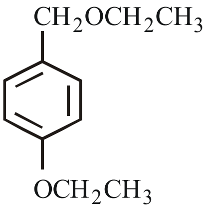
(d) All of these

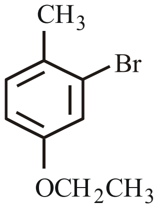
37. What is the major product of the following reaction ?



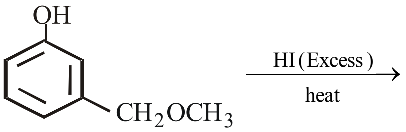
(a) 

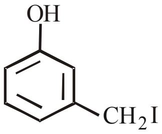
(b) 

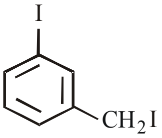
(c) 

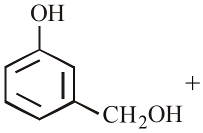
(d) 

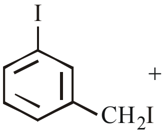
38. The correct products of the following reaction

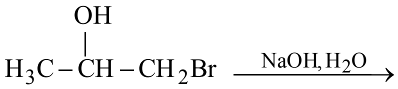


(a) 

(b) 

(c)  + CH_3I

(d)  $+CH_3I$

39. The reaction  $H_3C-\underset{}{\overset{OH}{\overset{|}{C}H}}-CH_2Br \xrightarrow{NaOH, H_2O}$

 can be described as

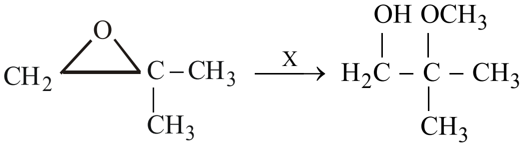
(a) Acid-base reaction followed by an intramolecular S_N1 reacton

(b) Acid- base reaction followed by an intermolecular Williamson ether synthesis

(c) E_2 reaction followed by an addition reaction to a double bond

(d) S_N2 reaction following an intramolecular Williamson ether synthesis

40. What is X in the following reaction ?



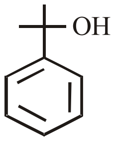
(a) CH_3OH, H_2SO_4

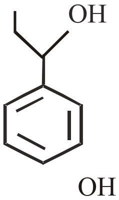
(b) $CH_3OH, CH_3O^-\overset{+}{Na}$

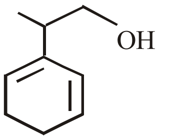
(c) H_2O / H_2SO_4 followed by CH_3OH

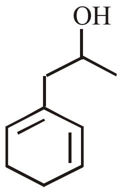
(d) CH_3MgBr / ether followed by H_3O^+

41. Benzene reacts with 2 - methyl oxirane in the presence of Anhy. $AlCl_3$ it give a product of $C_9H_{12}O$. Identify the product

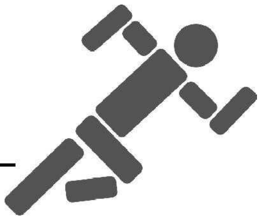
(a) 

(b) 

(c) 

(d) 

Hints & Solutions



EXERCISE 1

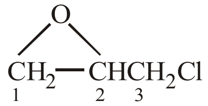
4. NaOH. It will dissolve phenol only.
5. Methanol or pyridine.
6. R = alkyl, R′ = aryl
11. (*a*) Diethyl ether is formed
    (*b*) ethylmethyl ether is formed

19. (c) **20. (c)** **21. (c)** **22. (c)** **23. (a)**
24. (b) **25. (d)** **26. (b)**

EXERCISE 2

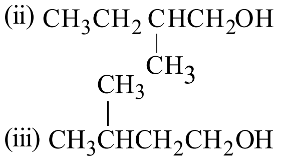
1. (a) Methyl alcohol (CH_3OH) is also known as carbinol. Hence vinyl carbinol is $CH_2 = CH - CH_2OH$

2. (c)



3. (b) $C_4H_{10}O$: (*i*) $C_2H_5OC_2H_5$ (*ii*) $CH_3OC_3H_7$
(iii) $CH_3OCH(CH_3)_2$

4. (b) (i) $CH_3CH_2CH_2CH_2CH_2OH$



(ii) $CH_3CH_2\underset{CH_3}{\underset{|}{C}}HCH_2OH$

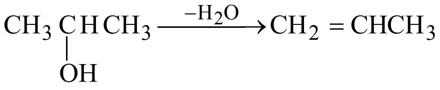
(iii) $CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2OH$

(iv) $(CH_3)_3CCH_2OH$

5. (b) Only 2-butanol ($CH_3\overset{*}{C}HOHCH_2CH_3$) has a chiral carbon.

6. (b) Butane-2, 3-diol–$CH_3CHOHCHOHCH_3$, is identical to tartaric acid since it too has two similar chiral carbon atoms. Hence it has three stereoisomeric forms: (+)–, (–)– and *meso* –; out of which only two are optically active, *meso* – form is optically inactive.

7. (b) Since the compound is formed by hydration of an alkene, to get the structure of alkene remove a molecule of water from the alcohol.



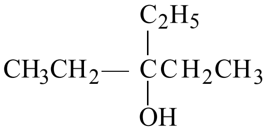
$$CH_3\underset{OH}{\underset{|}{C}}HCH_3 \xrightarrow{-H_2O} CH_2 = CHCH_3$$

Isopropyl alcohol Propylene

8. (c)
9. (b)
10. (d)

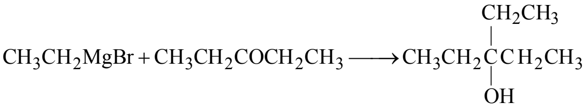
11. (d) Grignard reagents (CH_3MgBr) react with ketones (CH_3COCH_3) to form *tert*-alcohols (Me_3COH).

12. (c) First write down the structure of the required compound, observe the nature of functional group, and review the



$$CH_3CH_2\text{—}\overset{C_2H_5}{\overset{|}{\underset{OH}{\underset{|}{C}}}}CH_2CH_3$$

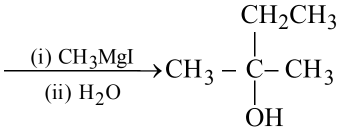
memory for preparing the required functional group. Here the required compound is a 3° alcohol having three ethyl groups, so only combination given in option *c* will introduce three ethyl groups.



$$CH_3CH_2MgBr + CH_3CH_2COCH_2CH_3 \longrightarrow CH_3CH_2\overset{CH_2CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}CH_2CH_3$$

13. (b) Esters react with Grignard reagent to form *tert*-alcohols having at least two alkyl groups, introduced through Grignard reagent, identical, the third introduced through ester may be similar or different.

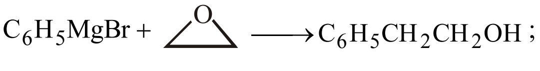
$$CH_3COOC_2H_5 + CH_3MgI \xrightarrow{H_2O} CH_3COCH_3$$



$$\xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgI} CH_3 - \overset{CH_2CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}} - CH_3$$

14. (c) 1-Phenylethanol ($C_6H_5\overset{1}{C}HOH\overset{2}{C}H_3$) is a secondary alcohol which can be prepared from C_6H_5CHO by the reaction of a Grignard reagent (CH_3MgX), with combination of CH_3I + Mg.

15. (d) 2-Phenylethanol, $\overset{1}{C}H_2OH\overset{2}{C}H_2C_6H_5$, is a 1° alcohol which can be prepared from C_6H_5MgBr by treating with ethylene oxide (note that HCHO will introduce only one carbon atom, i.e. it will give $C_6H_5CH_2OH$ and not $C_6H_5CH_2CH_2OH$).

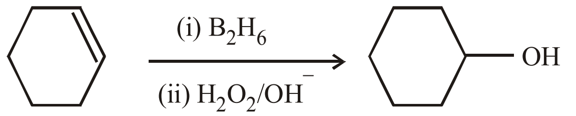


$$C_6H_5MgBr + HCHO \longrightarrow C_6H_5CH_2OH$$

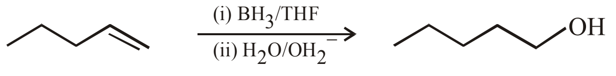
16. (a) $$3CH_2 = CH_2 \xrightarrow{B_2H_6} (CH_3CH_2)_3B \xrightarrow{H_2O_2/OH^-} 3CH_3CH_2OH$$

Hydroboration-oxidation of alkenes leads to hydration (in *anti*-Markownikoff's way).

17. (c)



18. (a) Hydroboration-oxidation leads to *anti*-Markownikoff's hydration, thus



1-Pentanol

19. (a)

20. (c) $\underbrace{CO + H_2}_{\text{Water gas}} \xrightarrow[573\,K,\,200\,atm]{CuO/ZnO/Cr_2O_3} CH_3OH$

21. (d)

22. (d) Magnesium reacts with ethanol to form magnesium ethoxide which then reacts with water to regenerate ethanol along with $Mg(OH)_2$.

$$Mg + 2C_2H_5OH \longrightarrow \underset{\text{Mag. ethoxide}}{(C_2H_5O)_2Mg} \xrightarrow{2H_2O}$$

$$2C_2H_5OH + \underset{\text{weak base}}{Mg(OH)_2}$$

Other reagents react with ethanol and do not regenerate ethanol.

$$C_2H_5OH \xrightarrow{Na} C_2H_5ONa$$

$$\xrightarrow{H_2O} C_2H_5OH + \underset{\text{Strong base}}{NaOH} \quad \text{(Reaction not possible)}$$

$$C_2H_5OH \xrightarrow{HCl} C_2H_5Cl \xrightarrow{H_2O} \text{No reaction}$$

Distillation of aqueous ethanol leads to azeotropic mixture.

23. (d)

$$(C_2H_5O)_2Mg + H_2O \xrightarrow{\text{distill}} \underset{\text{(distillate)}}{2C_2H_5OH} + \underset{\text{(residue)}}{Mg(OH)_2}$$

24. (d)

25. (a) Among isomeric alcohols surface area decreases from 1° to 2° to 3° alcohols and hence the boiling point.

26. (b) Number of active hydrogen in a compound corresponds to the number of moles of CH_4 evolved per mole of the compound.

$$\mathbf{-NH_2, -SH, -OH \text{ or } -C \equiv CH \xrightarrow{CH_3MgI} CI}$$

$$\mathbf{CH_4 \uparrow (2CH_4 \text{ from } -NH_2)}$$

27. (d) Since 1 mole of compound X reacts with Na to evolve 1 mole of H_2 gas, therefore the compound should have 2 active hydrogen atoms per mole which is possible only in option *d*.

$$CH_2O\mathbf{H}CH_2CH_2CH_2O\mathbf{H} + 2Na$$

$$\longrightarrow NaOCH_2CH_2CH_2CH_2ONa + 2H$$

28. (b) Other options are acids, only Na metal is a base.

29. (d) In ethane (C_2H_6) and benzene (C_6H_6) hydrogen atoms are present on sp^3 and sp^2 hybridised carbon atom, so these are very weak acids as compared to CH ≡ CH (having *sp* carbon) and CH_3OH (having electronegative oxygen) To decide whether CH≡CH or CH_3OH is a stronger acid, consider the following reaction

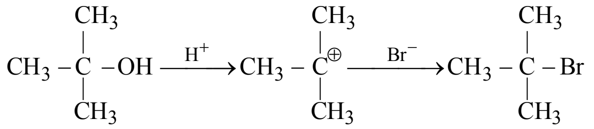
$$HC \equiv C^-Na^+ + \underset{\text{(Stronger acid)}}{CH_3OH} \longrightarrow \underset{\text{(Weaker acid)}}{HC \equiv CH} + CH_3O^-Na^+$$

Since a stronger acid displaces a weaker acid from its salts, therefore, CH_3OH is a stronger acid than HC≡CH.

Alternatively, CH_3O^- is a weaker base than $HC \equiv C^-$ because oxygen can accommodate negative charge easily.

30. (c) Reactivity increases as the nucleophilicity of the halide ion increases, i.e. $I^- > Br^- > Cl^-$.

31. (d) Since carbocations are formed as intermediate, more stable the carbocation, higher will be the reactivity of the parent compound (alcohol). 2-Methylpropan-2-ol generates a 3° carbocation, so it will react fastest; other three generates either 1° or 2° carbocations.

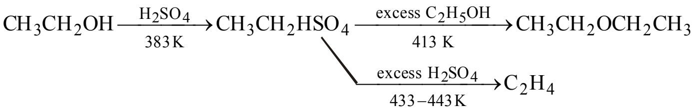


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow{H^+} CH_3-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}} \xrightarrow{Br^-} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br$$

2-Methyl-2-propanol

32. (a) In presence of acid, alcohols always form carbocations as intermediates.

33. (b) Other three compounds, viz $CH_3CH_2HSO_4$, C_2H_4 and $CH_3CH_2OC_2H_5$ are formed



$$CH_3CH_2OH \xrightarrow[383K]{H_2SO_4} CH_3CH_2HSO_4 \xrightarrow[413\ K]{\text{excess } C_2H_5OH} CH_3CH_2OCH_2CH_3$$

$$CH_3CH_2HSO_4 \xrightarrow[433-443K]{\text{excess } H_2SO_4} C_2H_4$$

34. (c) **35. (d)** **36 (b)** **37. (b)**

38. (b)

39. (c) $CH_2 = CH_2 \xleftarrow[650K]{Al_2O_3} CH_3CH_2OH \xrightarrow[525K]{Al_2O_3}$

$$CH_3CH_2OCH_2CH_3$$

40. (b) Dehydration of CH_3OH gives carbene (methylene), an unstable intermediate.

$$CH_3OH \xrightarrow{H_2SO_4} \underset{\text{Carbene}}{[:CH_2]} + H_2O$$

41. (a) Phenol does not react with heated Cu at 300°C.

42. (c) **43. (b)** **44. (d)** **45. (d)**

46. (a)

47. (c) (a) $CH_3CH_2CH_2OH \xrightarrow[\text{or } K_2Cr_2O_7/H+]{\text{alk. KMnO}_4} CH_3CH_2CHO$

$\longrightarrow CH_3CH_2COOH \xrightarrow{\text{Fehling sol.}} \text{No reaction}$

(b) $CH_3CHOHCH_3 \xrightarrow[\text{or } K_2Cr_2O_7/H+]{\text{alk. KMnO}_4} CH_3COCH_3$

$\longrightarrow CH_3COOH \xrightarrow{\text{Fehling sol.}} \text{No reaction}$

(c) $CH_3CH_2CH_2OH \xrightarrow{Cu} CH_3CH_2\,CHO \xrightarrow[\text{solution}]{\text{Fehling}} \underset{\text{(red)}}{Cu_2O\downarrow}$

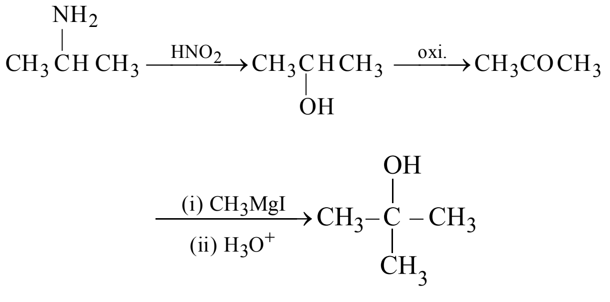
$CH_3CHOHCH_3 \xrightarrow{Cu} CH_3COCH_3 \xrightarrow[\text{solution}]{\text{Fehling}} \text{No reaction}$

(d) $CH_3CH_2CH_2OH$ or $CH_3CHOHCH_3 \xrightarrow{\text{Conc. }H_2SO_4}$

$CH_3CH = CH_2$

48. (c)

49. (d)



$$CH_3\overset{NH_2}{\overset{|}{C}H}CH_3 \xrightarrow{HNO_2} CH_3\underset{OH}{\underset{|}{C}H}CH_3 \xrightarrow{\text{oxi.}} CH_3COCH_3$$

$$\xrightarrow[\text{(ii) }H_3O^+]{\text{(i) }CH_3MgI} CH_3-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$$

2-methyl –2 propanol

50. (a)

51. (d) Since the compound ($C_4H_{10}O$) react with sodium, it must be alcohol (option *b, c, or d*). As it is oxidised to carbonyl compound which does not reduce Tollen's reagent, the carbonyl compound should be a ketone and thus $C_4H_{10}O$ should be a secondary alcohol, i.e. *sec*-butyl alcohol; other two given alcohols are 1°.

52. (c) Alcoholic iodine with NaOH ($C_2H_5OH + I_2 + NaOH$) gives iodoform due to haloform reaction.

53. (a) $C_2H_5OC_2H_5 \xleftarrow{\text{Conc. }H_2SO_4} A \xrightarrow{Na} B$

Given reactions indicate that A and B should be C_2H_5OH and C_2H_5ONa respectively.

54. (c) $\underset{B}{C_2H_5NO_2} \xleftarrow{AgNO_2} C_2H_5OH \xrightarrow{PCl_5}$

$\underset{[A]}{C_2H_5Cl} + POCl_3 + HCl$

55. (b) **56. (d)** **57. (b)** **58. (c)**

59. (d)

60. (a) Acidic $KMnO_4$ is a strong oxidising agent, so it oxidises both the CH_2OH groups completely to COOH

$HOH_2CCH_2OH \xrightarrow{KMnO_4,\ H^+} \underset{\text{Oxalic acid}}{HOOC\,COOH}$

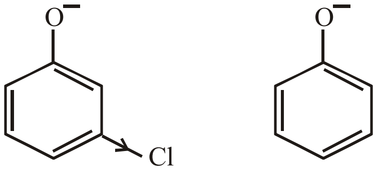
61. (a) Consult text.

62. (b) Since 1° is more reactive than 2° toward HI, latter can react only when both 1° alcoholic groups have reacted.

63. (a) **64. (d)** **65. (a)** **66. (b)**

67. (c) Conjugate base of phenol, i.e. phenoxide ion is a weaker base than the HCO_3^-, conjugate base of H_2CO_3. This is due to resonance, in HCO_3^- in which all resonating structures are equivalent.

68. (c) Phenols are more acidic than alcohols, hence phenol and *m*-chlorophenol are more acidic than benzyl alcohol and cyclohexanol. Further due to –I effect of Cl, negative charge is more dispersed than that in phenoxide, hence *m*-chlorophenoxide is more stable causing deprotonation of *m*-chlorophenol easier than that of phenol.



(negative charge dispersed due to –I effect of Cl)

69. (a)

70. (c) Picric acid has three electron-withdrawing $-NO_2$ groups, so its phenolic group exhibits strong acidic character like that of –COOH.

71. (c) 2, 4, 6-Trinitrophenol, benzoic acid and benzenesulphonic acid are more acidic than carbonic acid and hence dissolve in $NaHCO_3$ solution. In contrast, *o*-nitrophenol is less acidic than carbonic acid and hence does not dissolve in $NaHCO_3$ solution.

72. (a) **73. (d)** **74. (b)** **75. (c)**

76. (d) Sodium reacts with both phenol and ethyl alcohol to evolve H_2, hence it can't be used to distinguish phenol from ethyl alcohol

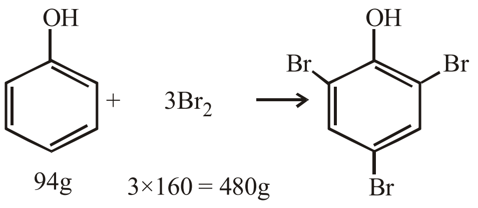
77. (c) Recall that more is the electron-releasing character of a group present in benzene nucleus, more readily the compound will be attacked by an electrophile. Thus the increasing order of attack by an electrophile among the given compound is

Chlorobenzene < Benzene < Toluene < phenol

78. (c) Picric acid is 2,4,6-trinitrophenol, hence obtained by nitration of phenol

79. (d) Phenol has activating (electron-releasing) –OH group and bromine water supplies Br^+ ion easily, hence under such conditions reaction does not stop at monobromo- or dibromo- stage; but a fully brominated (2,4, 6-tribromophenol) compound is the final product

80. (c)



Thus 94g of phenol require $Br_2 = 480$ g

2g of phenol require $Br_2 = \dfrac{480}{94} \times 2 = 10.22$g

81. (c) In presence of non-protic solvent such as $CHCl_3$ or CCl_4, concentration of electrophile (Br^+) is less, hence reaction stops at the monobromo stage

82. (a) **83. (d)** **84. (a)**

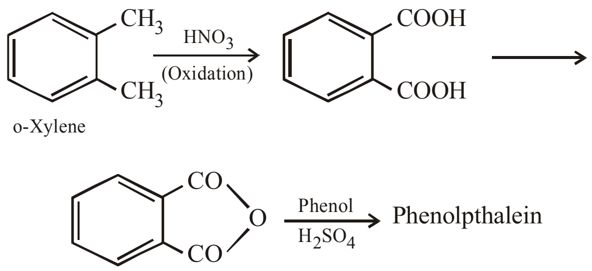
85. (c) $CHCl_3 \xrightarrow{OH^-} \underset{\substack{\text{Dichlorocarbene} \\ \text{(electron-deficient species)}}}{:CCl_2} + Cl^-$

86. (c) **87. (d)** **88. (b)**

89. (b) **90. (d)**

91. (a) Phenolphthalein gives pink colour with alkali

92. (c)



o-Xylene

Phthalic anhydride, X (Y)

93. (a) **94. (a)** **95. (c)** **96. (b)**

97. (d) The two components should be $(CH_3)_3CONa + (CH_3)_3CBr$. However, tert-alkyl halides tend to undergo elimination reaction rather than substitution leading to the formation of an alkene, $Me_2C=CH_2$

98. (d) $CH_3OCH_3 \xrightarrow{Cl_2,\, hv} \underset{\text{Halogenated ether}}{CH_3OCH_2Cl}$

$$\xrightarrow[\text{(ii) dry ether}]{\text{(i) RMgX}} \underset{\text{Higher ether}}{CH_3OCH_2R}$$

99. (d) Phenol has active (acidic) hydrogen so it reacts with CH_3MgI to give CH_4, and not anisole

$$C_6H_5OH + CH_3MgI \longrightarrow CH_4 + C_6H_5OMgI$$

100. (c)

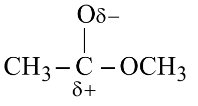
101. (c) CH_3OCH_3 and $C_2H_5OCH_3$ are gaseous in nature.

102. (a)

103. (d) Iodide ion attacks the smaller alkyl group forming alkyl iodide, while the larger alkyl group appears in the form of alcohol or phenol.

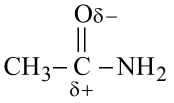
104. (b) Due to greater electronegativity of sp^2-hybridized carbon atoms of the benzene ring, diaryl ethers are not attacked by nucleophiles like I^-.

105. (d) Diethyl ether, being a Lewis base, is not attacked by nucleophiles, while all others contain electrophilic carbon, hence attacked by nucleophiles like OH^- ions.



$$CH_3-\underset{\delta+}{\overset{O\delta-}{\overset{|}{C}}}-OCH_3$$

$$CH_3-\overset{\delta+}{C}\equiv\overset{\delta-}{N}$$



$$CH_3-\underset{\delta+}{\overset{O\delta-}{\overset{||}{C}}}-NH_2$$

$$C_2H_5-\ddot{\underset{..}{O}}-C_2H_5$$

106. (c) $\underset{\text{Ether}}{(CH_3CH_2)_2O} + \underset{\text{Acid anhydride}}{(CH_3CO)_2O}$

$$\xrightarrow{\text{anhy. } AlCl_3} \underset{\text{Ester}}{CH_3COOCH_2CH_3}$$

107. (c) Ethers react with Cl_2 in presence of light to form fully chlorinated product (all hydrogen atoms of the alkyl groups are replaced by chlorine).

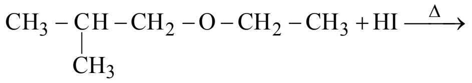
108. (a) Ethers are reduced by red P and HI to alkanes through alkyl iodides

$$C_2H_5OC_2H_5 \xrightarrow{\text{red P+HI}} 2C_2H_5I \xrightarrow{\text{red P+HI}} 2C_2H_6$$

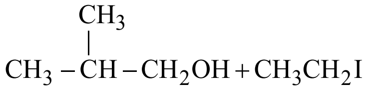
109. (b)

EXERCISE 3

1. (c) In the cleavage of mixed ethers having two different alkyl groups, the alcohol and alkyl iodide that form depend on the nature of alkyl group. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide therefore

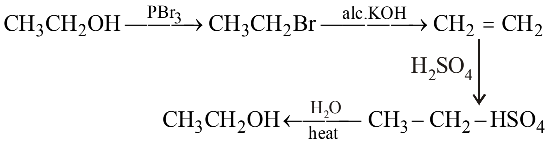


$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-O-CH_2-CH_3+HI \xrightarrow{\Delta}$$



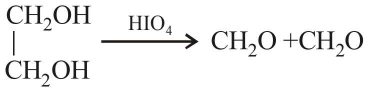
$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2OH+CH_3CH_2I$$

2. (c)



$$\begin{tikzcd} CH_3CH_2OH \arrow[r, "PBr_3"] & CH_3CH_2Br \arrow[r, "alc.KOH"] & CH_2=CH_2 \arrow[d, "H_2SO_4"'] \\ & CH_3CH_2OH & CH_3-CH_2-HSO_4 \arrow[l, "H_2O"', "heat"] \end{tikzcd}$$

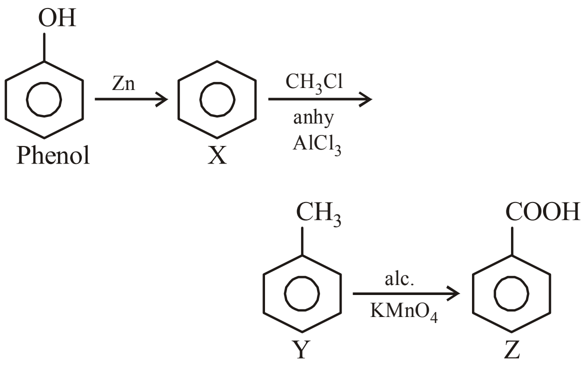
3. (c) 1, 2 – Diols, when treated with an aqueous solution of periodic acid give aldehyde



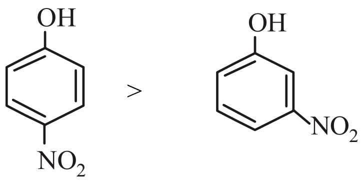
$$\underset{CH_2OH}{\overset{CH_2OH}{|}} \xrightarrow{HIO_4} CH_2O + CH_2O$$

Note that a 1° alcohol gives CH_2O. Since in glycol both the OH groups, are primary hence give 2 molecules of CH_2O as by product.

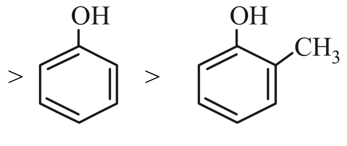
4. (b)



5. (b) Phenol is most acidic because its conjugate base is stabilised due to resonance, while the rest three compounds are alcohols, hence, their corrosponding conjugate bases do not exhibit resonance

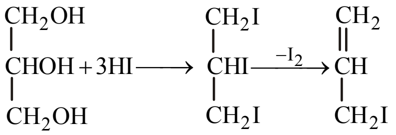
6. **(b)** 

(iv) (iii)
(– I and – M effects, both increase acidity) (only – I effect)

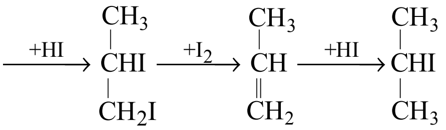


(i) (ii)
(+ I effect of CH_3 group decreases acidity)

7. **(b)** Glycerol when treated with excess HI produces 2–iodopropane



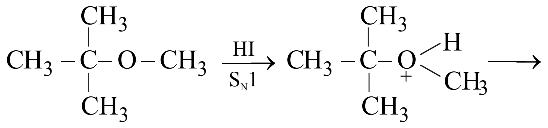
$$\begin{matrix}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix} + 3HI \longrightarrow \begin{matrix}CH_2I\\ |\\ CHI\\ |\\ CH_2I\end{matrix} \xrightarrow{-I_2} \begin{matrix}CH_2\\ ||\\ CH\\ |\\ CH_2I\end{matrix}$$



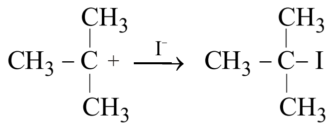
$$\xrightarrow{+HI} \begin{matrix}CH_3\\ |\\ CHI\\ |\\ CH_2I\end{matrix} \xrightarrow{+I_2} \begin{matrix}CH_3\\ |\\ CH\\ ||\\ CH_2\end{matrix} \xrightarrow{+HI} \begin{matrix}CH_3\\ |\\ CHI\\ |\\ CH_3\end{matrix}$$

8. **(b)** Glycol is used as an antifreeze in automobiles.

9. **(b)** The reaction will proceed via S_N1 or S_N2 based on nature of alkyl group. If alkyl group attached is 3°. The reaction will proceed through the S_N1 mechanism and if alkyl group is primary reaction will proceed through S_N2 mechanism.



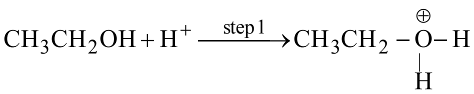
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-CH_3 \xrightarrow[S_N1]{HI} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{+}{O}\begin{matrix}H\\ CH_3\end{matrix} \longrightarrow$$



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{}^{+} \xrightarrow{I^-} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-I$$

(Highly stable)

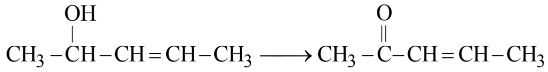
10. **(c)** In ether, there is no H-bonding while alcohols have intermolecular H-bonding

11. **(d)** 

$$CH_3CH_2OH + H^+ \xrightarrow{\text{step 1}} CH_3CH_2-\underset{\underset{H}{|}}{\overset{\oplus}{O}}-H$$

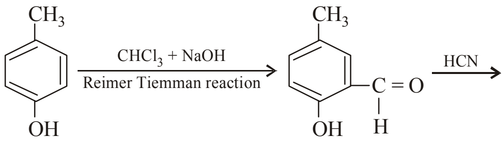
Protonated alcohol

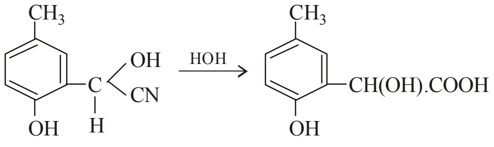
12. **(a)** 3-methyl pentanol-3 will be dehydrated most readily since it produces tertiary carbonium ion as intermediate.

13. **(a)** 

$$CH_3-\overset{\overset{OH}{|}}{C}H-CH=CH-CH_3 \longrightarrow CH_3-\overset{\overset{O}{||}}{C}-CH=CH-CH_3$$

Pyridiminum chloro-chromate (PCC) is specific for the conversion.

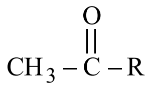
14. **(c)** 



Cyanohydrin

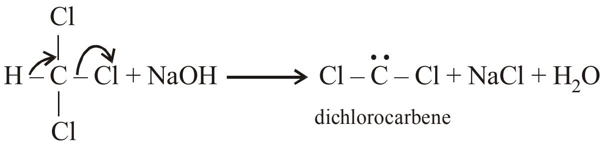
15. **(d)** $CH_3OH + C_6H_5MgBr \longrightarrow CH_3O.MgBr + C_6H_6$

16. **(b)** The compounds containing CH_3CHOH – R or



$CH_3-\overset{\overset{O}{||}}{C}-R$ (R = H, alkyl or aryl) give CHI_3 with I_2 and NaOH.

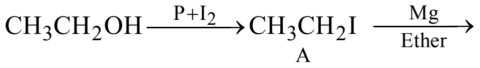
17. **(d)** This is Riemer-Tiemann reaction and the electrophile is dichlorocarbene.



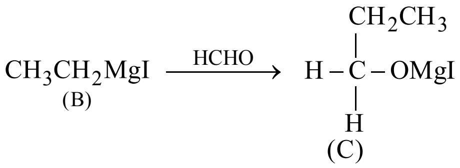
$$H-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-Cl + NaOH \longrightarrow Cl-\ddot{C}-Cl + NaCl + H_2O$$

dichlorocarbene

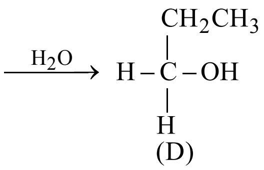
α-elimination

18. **(d)** 

$$CH_3CH_2OH \xrightarrow{P+I_2} \underset{A}{CH_3CH_2I} \xrightarrow[\text{Ether}]{Mg}$$



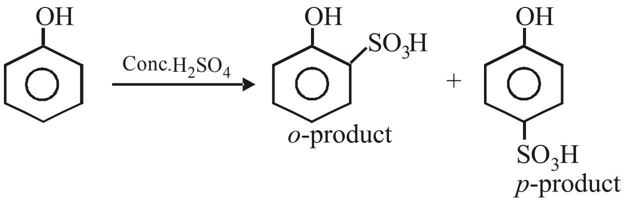
$$\underset{(B)}{CH_3CH_2MgI} \xrightarrow{HCHO} H-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{H}{|}}{C}}-OMgI \quad (C)$$



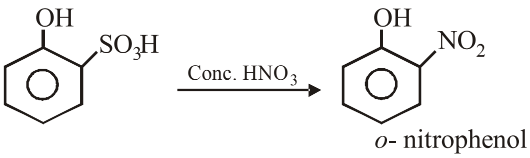
$$\xrightarrow{H_2O} H-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{H}{|}}{C}}-OH \quad (D)$$

n–propyl alcohol

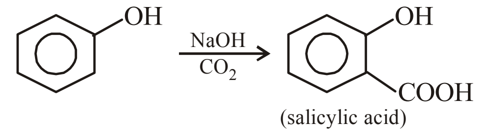
19. **(b)** Phenol on reaction with conc. H_2SO_4 gives a mixture of *o*- and *p*- products (i.e., $–SO_3H$ group, occupies *o*-, *p*- position). At room temperature *o*-product is more stable, which on treatment with conc. HNO_3 will yield *o*-nitrophenol.



At room temperature o- product is more stable

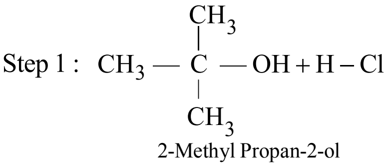


20. (b)



21. (b) Tertiary alcohols react fastest with conc. HCl and anhydrous $ZnCl_2$ (lucas reagent) as its mechanism proceeds through the formation of stable tertiary carbocation.

Mechanism



Step 1 : $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH+H-Cl$

2-Methyl Propan-2-ol

$$\rightleftharpoons (CH_3)_3C-\overset{+}{O}H_2+Cl^-$$

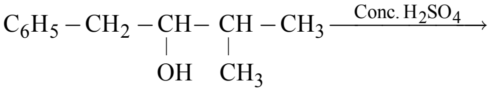
Step 2 : $(CH_3)_3C-\overset{+}{O}H_2 \rightleftharpoons \underset{3^\circ \text{ Carbocation}}{(CH_3)_3C^+} + H_2O$

Step 3 : $(CH_3)_3C^+ + Cl^- \rightleftharpoons \underset{\text{t-Butyl chloride}}{(CH_3)_3C-Cl}$

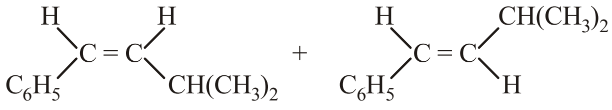
22. (a) Whenever dehydration can produce two different alkenes, major product is formed according to **Saytzeff rule** *i.e.* more substituted alkene (alkene having lesser number of hydrogen atoms on the two doubly bonded carbon atoms) is the major product.

Such reactions which can produce two or more structural isomers but one of them in greater amount than the other are called **regioselective** *; in case a reaction is 100% regioselective, it is termed as* **regiospecific.**

In addition to being regioselective, alcohol dehydrations are **stereoselective** (*a reaction in which a single starting material can yield two or more stereoisomeric products, but gives one of them in greater amount than any other).*



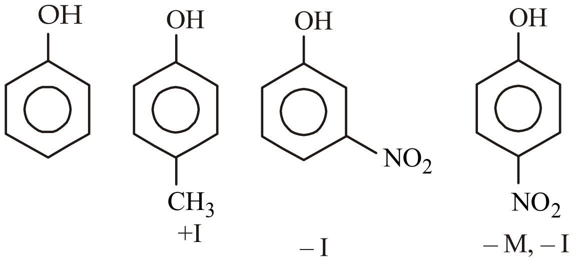
$$C_6H_5-CH_2-\underset{OH}{CH}-\underset{CH_3}{CH}-CH_3 \xrightarrow{\text{Conc. } H_2SO_4}$$



cis
(minor)
(less stable due to bulky groups lying on same side)

trans
(major)
(more stable)

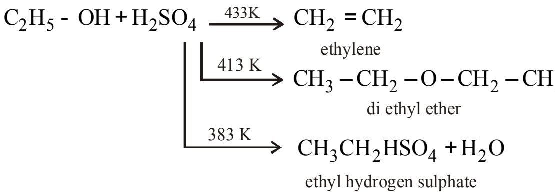
23. (a)



(A) (B) (C) (D)

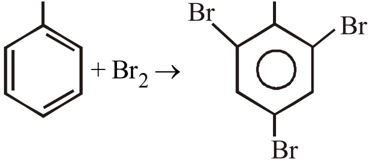
Electron withdrawing substituents increases the acidity of phenols; while electron releasing substituents decreases acidity. Further the particular effect (acidity increasing or decreasing) is more when a substituent is present in o-orp position to phenolic group. Thus the correct order will be D > C > A > B

24. (b)



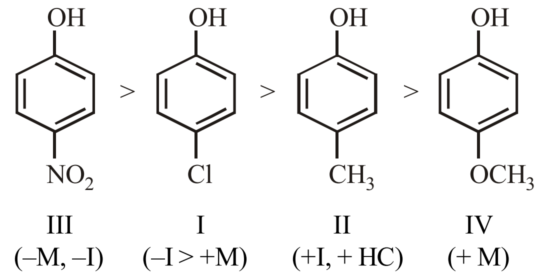
Acetylene is not formed under any conditions.

25. (d) $5KBr+KBrO_3+3H_2O \rightarrow 3Br_2+6KOH$

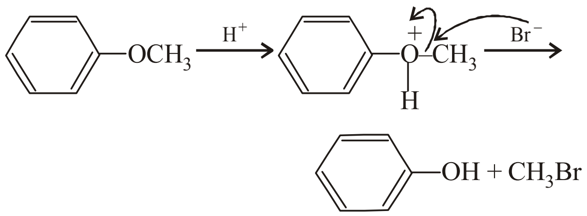


26. (d) Phenol gives a violet colour with neutral ferric chloride solution whereas benzoic acid does not give this test.

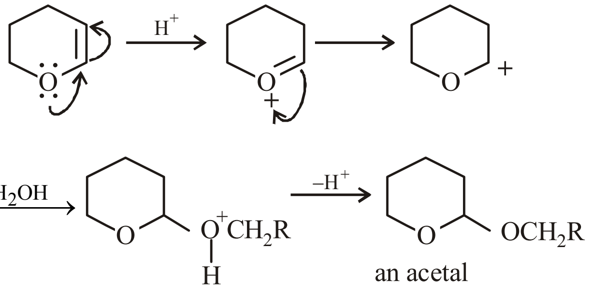
27. (c) Electron withdrawing substituents like $-NO_2$, Cl increase the acidity of phenol while electron releasing substituents like $-CH_3$, $-OCH_3$ decreases acidity. hence the correct order of acidity will be



28. (d)

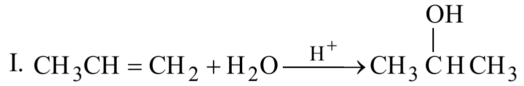


29. (b)



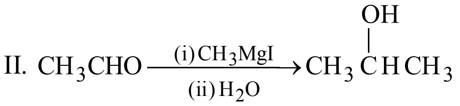
EXERCISE 4

1. (a) I.



$$CH_3CH=CH_2+H_2O\xrightarrow{H^+}CH_3\overset{\overset{OH}{|}}{C}HCH_3$$

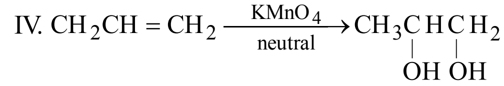
II.



$$CH_3CHO\xrightarrow[(ii)\,H_2O]{(i)\,CH_3MgI}CH_3\overset{\overset{OH}{|}}{C}HCH_3$$

III. $CH_2O\xrightarrow[(ii)\,H_2O]{(i)\,C_2H_5MgI}C_2H_5CH_2OH$

IV.



$$CH_2CH=CH_2\xrightarrow[\text{neutral}]{KMnO_4}CH_3\underset{OH}{\underset{|}{C}}H\underset{OH}{\underset{|}{C}}H_2$$

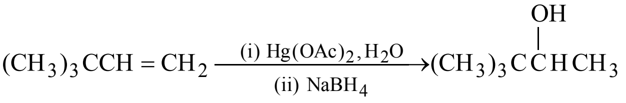
2. (a) *Anti*-Markovnikov's hydration by hydroboration-oxidation of alkenes.

$$CH_3CH=CH_2\xrightarrow[(ii)\ H_2O_2\,/\,OH^-]{(i)\ B_2H_6}CH_3CH_2CH_2OH$$

Anti – Markovnikov's product

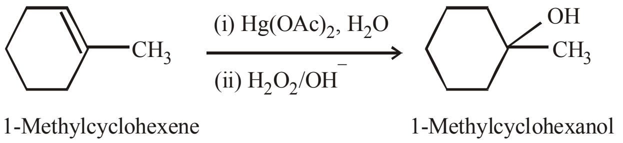
Other three options will lead Markovnikov's hydration, i.e. $CH_3CH=CH_2\longrightarrow CH_3CHOHCH_3$

3. (a) Recall that oxymercuration-reduction of alkenes lead to hydration in Markovnikov's way. Thus



$$(CH_3)_3CCH=CH_2\xrightarrow[(ii)\ NaBH_4]{(i)\ Hg(OAc)_2,H_2O}(CH_3)_3C\overset{\overset{OH}{|}}{C}HCH_3$$

4. (c) Similar as above question (Markovnikov's hydration)



5. (d) Such questions can be solved by considering the relative basic character of their conjugated bases which for H_2O, C_2H_2, H_2CO_3 and C_6H_5OH are

$${}^-OH,\ HC\equiv C\bar{:},\ HCO_3^-,\ C_6H_5O^-$$

More the possibility for the dispersal of the negative charge, weaker will be the base. Thus the relative basic character of the four bases is

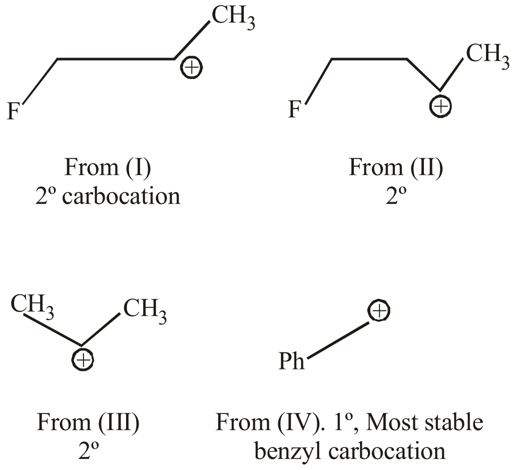
$$HCO_3^- < C_6H_5O^- < {}^-OH < HC\equiv C^-$$

HCO_3^-	$C_6H_5O^-$	${}^-OH$
Eqivalent resonating	Non-equivalent structures	Oxygen can accommodate negative charge easily

Due to resonance

Thus the acidic character of the four corresponding acids will be $H_2CO_3 > C_6H_5OH > H_2O > HC\equiv CH$

6. (c) The order of reactivity depends upon the stability of the carbocations formed.



Remember that presence of electron-withdrawing group intensifies i.e., destabilises the carbocation thus (i) and (ii) are less stable than (iii). Further (i) is less stable than (ii) because –I effect is more pronounced in (i) due to less distance between F and positive charge. Thus the stability order of the four carbocations and reactivity of their parent alcohols will be

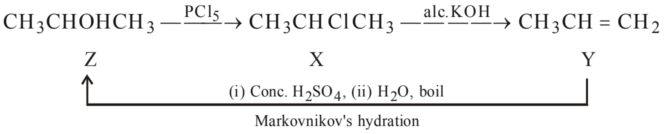
IV > III > II > I

7. (d) $3C_2H_5OH+PBr_3\longrightarrow 3C_2H_5Br+\underset{[X]}{H_3PO_3}$

8. (c)

9. (b) Since the compound X (C_3H_6O) gives iodoform test, it must have $-COCH_3$ groups hence it should be CH_3COCH_3. Therefore X should be $CH_3CHOHCH_3$.

10. (b) Reagents used in the various steps indicate that the compound Z has an alcoholic group. This set of reactions is possible only when Z is $CH_3CHOHCH_3$.



$$\underset{Z}{CH_3CHOHCH_3} \xrightarrow{PCl_5} \underset{X}{CH_3CHClCH_3} \xrightarrow{alc.KOH} \underset{Y}{CH_3CH=CH_2}$$

$$Y \xrightarrow[\text{Markovnikov's hydration}]{\text{(i) Conc. } H_2SO_4\text{, (ii) } H_2O\text{, boil}} Z$$

In options *a* and *c*, Y cannot be converted back into d by the given series of reactions.

11. (a) Solubility of the compound in conc. H_2SO_4 indicates that it can be an alkene, alcohol or an ether. The inability to discharge bromine colour indicates absence of an alkene. Hence the compound is an alcohol which should be primary because it is readily (within 2 seconds) oxidised by CrO_3 in sulphuric acid.

12. (c) In such reactions, first write down the sequence of reactions and then proceed backward/forward from a known compound, reagent, or known fact (test).

$$A \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgI} B \xrightarrow{\text{Victor Meyer test}} \text{Blue colour}$$

Appearance of blue colour in Victor Meyer test indicates that B is 2° alcohol and thus A must be an aldehyde other than HCHO. Thus among the given options, only option (*c*) is correct.

13. (b)

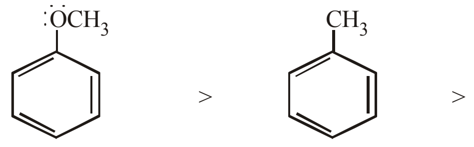
14. (c) Since N is an element of second period, it cannot contain more than 10 electrons in its valence shell; hence resonance structure (*c*) is most unlikely.

15. (c) Due to greater electron-withdrawing effect of NO_2, and also due to additional resonance due to $–NO_2$ group in the phenoxide ion, nitrophenols are stronger acids than chlorophenol. Further since resonance in *p*-nitrophenoxide ion is more important than that in *m*-nitrophenoxide ion, former is more stable, hence *p*-nitrophenol is more acidic than *m*-nitrophenol. *o*-Nitrophenol is least acidic among the three isomers due to *ortho*-effect.

16. (d)

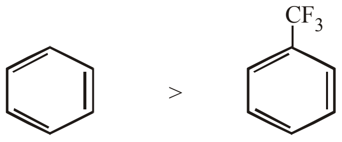
17. (c) Friedel-Crafts alkylation is an electrophilic substitution reaction, hence it occurs readily with compounds having electron-releasing groups

18. (d)



II IV

($–OCH_3$ is more electron-releasing than $–CH_3$)



I

(No group is present) ($–CF_3$ is electron- withdrawing)

19. (a) $C_4H_{10}O \xrightarrow{\text{excess of HI}} \text{only RI}$

Since the compound ($C_4H_{10}O$) does not react with sodium, oxygen must be in the form of ether (R–OR). Further since a single alkyl halide is formed, the two alkyl groups must be same, hence ether is $C_2H_5OC_2H_5$.

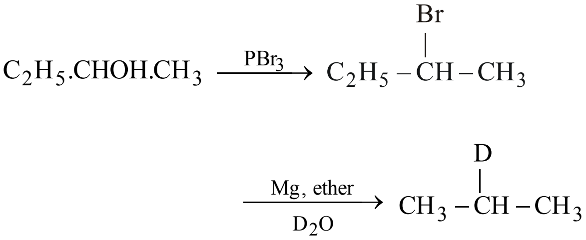
20. (d)

21. (c) $CH_3CH_2CH=CH_2 \xrightarrow{HBr/H_2O_2} CH_3CH_2CH_2CH_2Br$

$\xrightarrow{C_2H_5ONa} CH_3(CH_2)_3OC_2H_5$

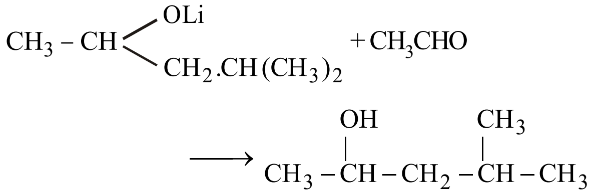
In presence of H_2O_2, HBr adds in *anti*-Markovnikov's way (peroxide effect).

22. (c)



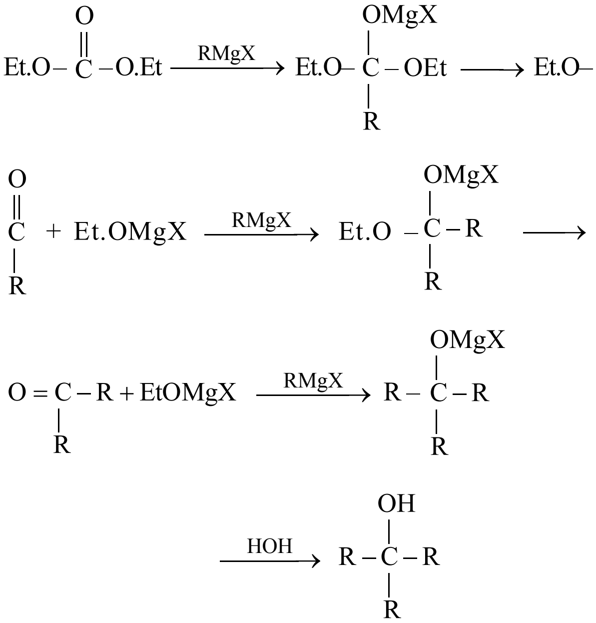
$$C_2H_5.CHOH.CH_3 \xrightarrow{PBr_3} C_2H_5-\overset{Br}{\overset{|}{C}H}-CH_3 \xrightarrow[D_2O]{\text{Mg, ether}} CH_3-\overset{D}{\overset{|}{C}H}-CH_3$$

23. (b)



$$CH_3-CH\begin{cases}OLi\\CH_2.CH(CH_3)_2\end{cases} + CH_3CHO \longrightarrow CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_3$$

24. (b)

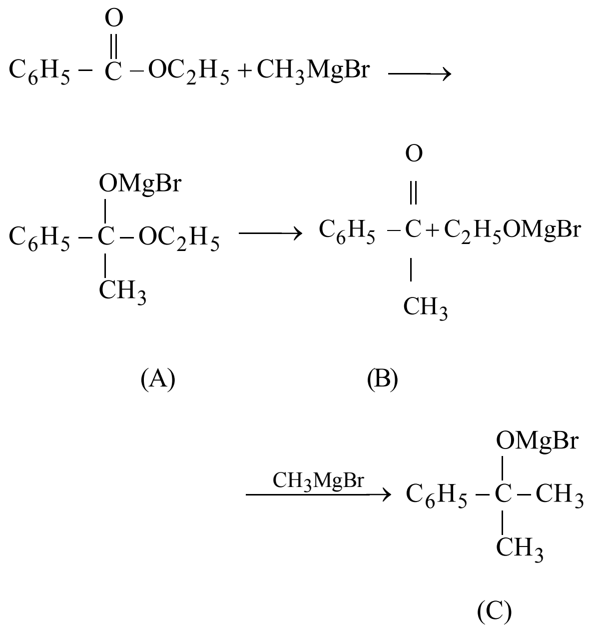


$$Et.O-\overset{O}{\overset{\|}{C}}-O.Et \xrightarrow{RMgX} Et.O-\underset{R}{\underset{|}{\overset{OMgX}{\overset{|}{C}}}}-OEt \longrightarrow Et.O-\underset{R}{\underset{|}{\overset{O}{\overset{\|}{C}}}} + Et.OMgX \xrightarrow{RMgX} Et.O-\underset{R}{\underset{|}{\overset{OMgX}{\overset{|}{C}}}}-R \longrightarrow$$

$$O=\underset{R}{\underset{|}{C}}-R + EtOMgX \xrightarrow{RMgX} R-\underset{R}{\underset{|}{\overset{OMgX}{\overset{|}{C}}}}-R \xrightarrow{HOH} R-\underset{R}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-R$$

25. (a) **26. (a)**

27. (b)



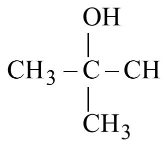
$C_6H_5-\overset{\overset{O}{\|}}{C}-OC_2H_5+CH_3MgBr \longrightarrow$

$C_6H_5-\underset{\underset{CH_3}{|}}{\overset{\overset{OMgBr}{|}}{C}}-OC_2H_5 \longrightarrow C_6H_5-\underset{\underset{CH_3}{|}}{\overset{\overset{O}{\|}}{C}}+C_2H_5OMgBr$

(A) (B)

$\xrightarrow{CH_3MgBr} C_6H_5-\underset{\underset{CH_3}{|}}{\overset{\overset{OMgBr}{|}}{C}}-CH_3$

(C)

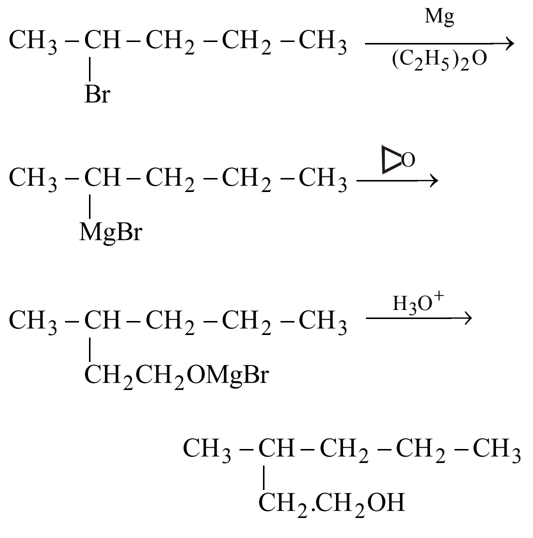


28. (d) 2-methyl-2-propanol is $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$. It cannot be obtained by reduction of an aldehyde or ketone with $NaBH_4$.

29. (b) $LiAlH_4$ will give the desired compound.

30. (b) $CH_3CH_2CH_2CH_2OH \xrightarrow{\text{Oxidation}} CH_3CH_2.CH_2CHO$

31. (b)



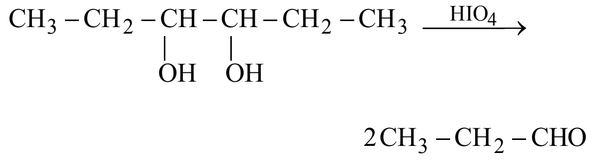
$CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_2-CH_3 \xrightarrow[(C_2H_5)_2O]{Mg}$

$CH_3-\underset{\underset{MgBr}{|}}{CH}-CH_2-CH_2-CH_3 \xrightarrow{\triangleright O}$

$CH_3-\underset{\underset{CH_2CH_2OMgBr}{|}}{CH}-CH_2-CH_2-CH_3 \xrightarrow{H_3O^+}$

$CH_3-\underset{\underset{CH_2.CH_2OH}{|}}{CH}-CH_2-CH_2-CH_3$

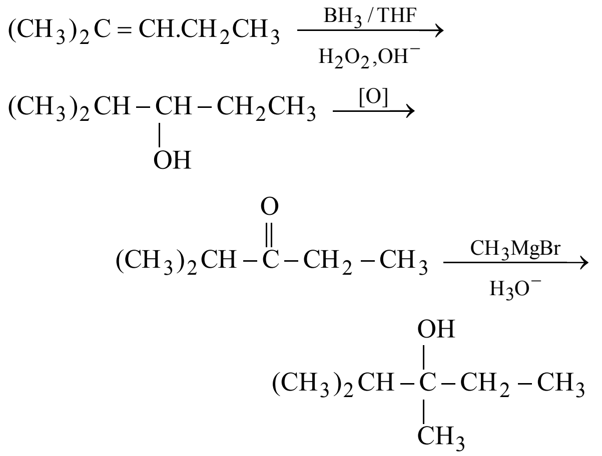
32. (d)



$CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 \xrightarrow{HIO_4}$

$2CH_3-CH_2-CHO$

33. (b)



$(CH_3)_2C=CH.CH_2CH_3 \xrightarrow[H_2O_2,OH^-]{BH_3/THF}$

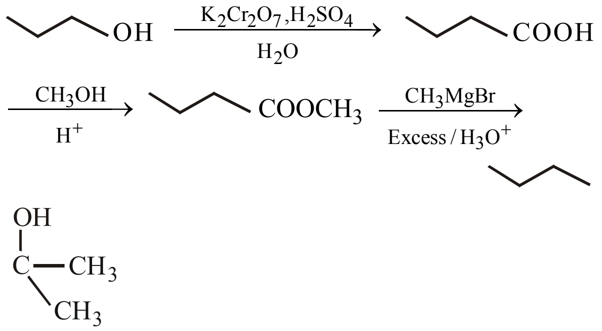
$(CH_3)_2CH-\underset{\underset{OH}{|}}{CH}-CH_2CH_3 \xrightarrow{[O]}$

$(CH_3)_2CH-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 \xrightarrow[H_3O^-]{CH_3MgBr}$

$(CH_3)_2CH-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CH_3$

34. (a)

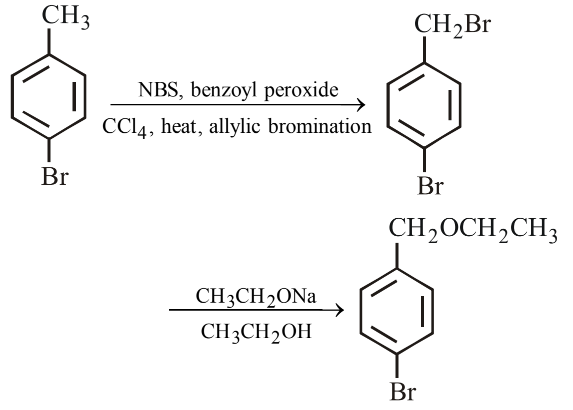
35. (a)



36. (a) $(CH_3)_2CHO^-\overset{+}{Na}+CH_3I \longrightarrow$

$(CH_3)_2CH-O-CH_3+NaI$

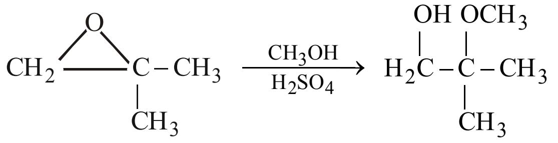
37. (b)



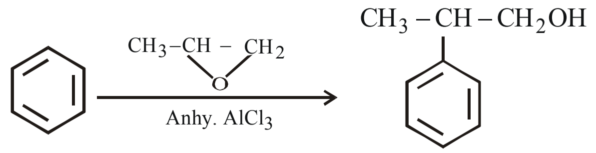
38. (a) With excess of conc. HI iodises are formed from ether or alcohol but nuclear OH is not replaced by I.

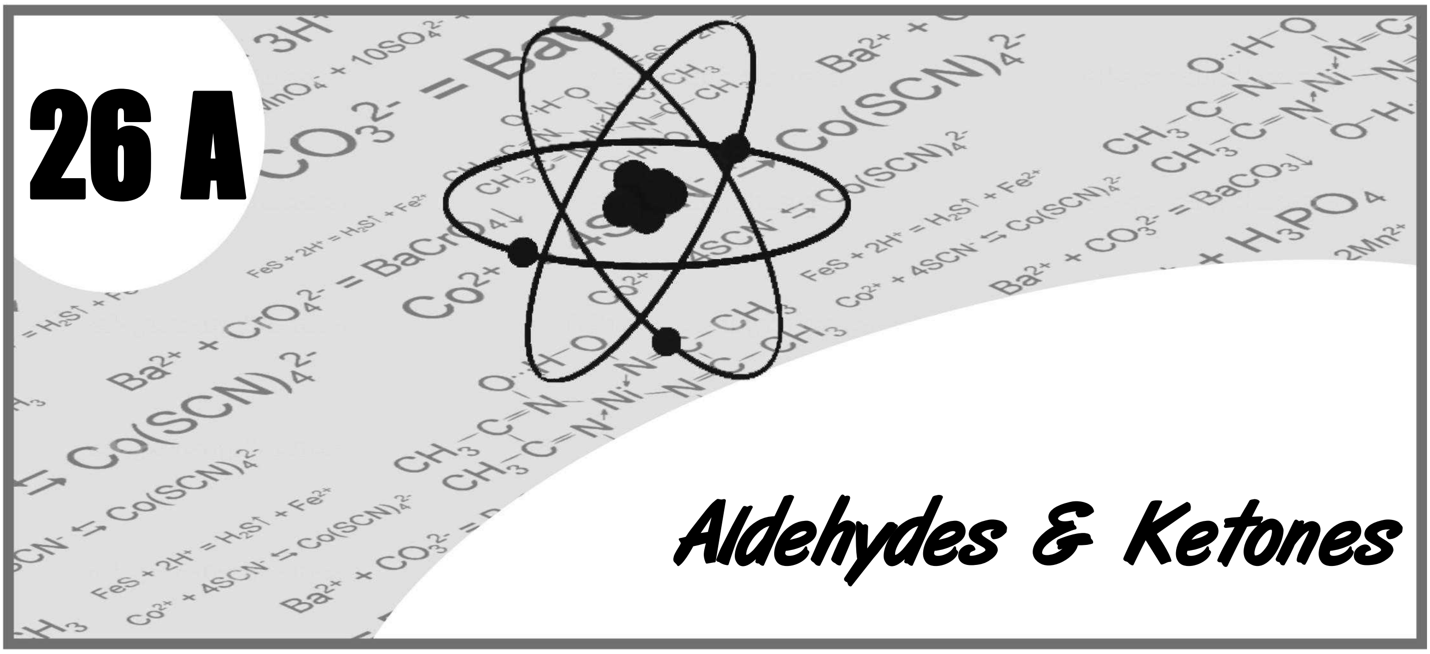
39. (b)

40. (a)



41. (c)





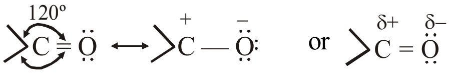
26 A

Aldehydes & Ketones

Aldehydes and Ketones are characterised by the presence of Carbonyl group $>C = O$ in their molecules. Aldehydes contain group $\begin{matrix} H \\ R \end{matrix}\!\!>C = O$ and ketones the $\begin{matrix} R \\ R \end{matrix}\!\!>C = O$. If the groups attached to carbonyl carbon are the same, the ketone is symmetrical and if they are different the ketone is unsymmetrical.

NATURE OF CARBONYL GROUP :

The carbon and oxygen of the carbonyl group are sp^2 hybridised and the carbonyl double bond is made of one σ bond and one π bond.



The electronegativity of oxygen is much higher than that of carbon, the π electron cloud is displaced towards the oxygen. Therefore the C–O bond is polar in nature and carbonyl compounds possess dipole moment (2.3 to 2.8 D)

NOMENCLATURE OF ALDEHYDES :

There are two systems

(i) ***Common system :*** The suffix **"-ic acid"** is replaced by the suffix **"-aldehyde"**

(ii) ***IUPAC system :*** The suffix "**-e**" of alkane is replaced by the suffix "**-al**".

Compound	Common name	IUPAC name
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal

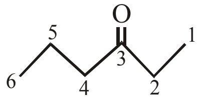
NOMENCLATURE OF KETONES :

(i) ***Common system :*** Symmetrical ketones are named as dialkyl ketone and name of unsymmetrical ketone is obtained by naming the alkyl groups alphabetically and adding the thrid word ketone.

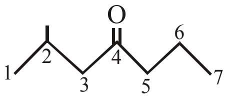
(ii) ***IUPAC system :*** The suffix "**-e**" of corresponding alkane is replaced by "**-one**"

Compound	Common name	IUPAC name
$H_3C.COCH_3$	dimethyl ketone (acetone)	Propanone
$H_3C.COC_2H_5$	ethyl methyl ketone	butanone

In higher ketones the numbering of C-atoms is must to show the position of carbonyl group. eg. :



3-hexanone

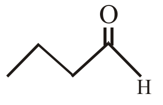


2-methyl-4-heptanone

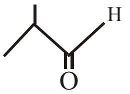
ISOMERISM IN ALDEHYDES :

Aldehydes exhibit two types of isomerism

(i) ***Chain isomerism :*** Example

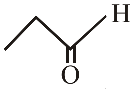


n-butyraldehyde

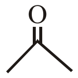


Iso-butyraldehyde

(ii) ***Functional isomerism :***

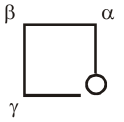


Propanal

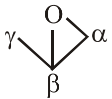


Acetone

Allylalcohol



α, γ propylene oxide

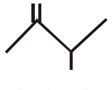


α, β - propylene oxide

(iii) Isomersim in ketones : They exhibit three types of isomersim

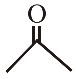
(a) Chain isomerism :

2-pentanone

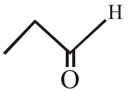


3-methyl-2-butanone

(b) ***Functional isomersim :***



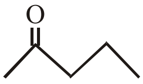
Acetone



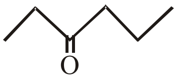
Propanal

Allylalcohol

(c) ***Position isomerism :***



2-pentanone



3-pentanone

GENERAL METHODS OF PREPARATION OF ALDEHYDES :

(i) ***Controlled oxidation of primary alcohols :*** Oxidising agents $K_2Cr_2O_7/H_2SO_4$ or $KMnO_4/H_2SO_4$

$$R-CH_2OH \xrightarrow{[O]} RCHO + H_2O$$

$$R\ CH_2OH \xrightarrow{PCC} RCHO$$

PCC is pyridinium chloro chromate known as **Collin's reagent** and is specific for oxidation of 1° alcohol to aldehyde.

(ii) ***Dehydrogenation of primary alcohol :***

$$RCH_2OH \xrightarrow{Cu\ 575K} RCHO + H_2$$

(iii) ***By Rosenmund's reduction from acid chloride :***

$$RCOCl + H_2 \xrightarrow[S\text{ or quinoline}]{Pd/BaSO_4} RCHO + HCl$$

(iv) ***Hydration of Alkynes (Kucherov's reaction) :***

$$HC\equiv CH \xrightarrow[40\%\ H_2SO_4]{1\%\ HgSO_4} [\ CH_2 = CH-OH\ ] \rightarrow CH_3CHO$$

(v) ***Reductive ozonolysis of alkenes :***

$$R-CH\equiv CH-R \xrightarrow[ii)\ Zn/H_2O]{i)\ O_3} 2RCHO + H_2O_2$$

(vi) ***Distillation of Calcium salt of fatty acid with calcium formate :***

$$(RCOO)_2Ca + (HCOO)_2Ca \xrightarrow{\text{distillation}} 2RCHO + 2CaCO_3$$

(vii) ***From acid :***

$$RCOOH + HCOOH \xrightarrow[575\ K]{MnO} RCHO + H_2O + CO_2$$

$$2HCOOH \xrightarrow[575\ K]{MnO} HCHO + H_2O + CO_2$$

(viii) ***Waker's process :***

$$CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow[H_2O]{PdCl_2.CuCl_2} CH_3.CHO$$

(ix) ***Oxo process :***

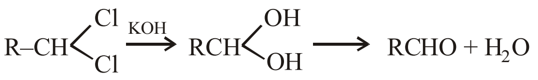
$$R-CH = CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} R.CH_2.CH_2CHO$$

(x) ***Stephen's reduction of nitriles :***

$$R-C\equiv N + 2H \xrightarrow{SnCl_2/HCl} \underset{\text{Aledimine}}{R-CH = NH}$$

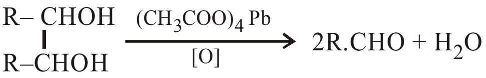
$$R.CHO + NH_3 \xleftarrow{H_2O}$$

(xi) ***Hydrolysis of Geminal halides :***



$$R\text{–}CH\begin{matrix}Cl\\Cl\end{matrix} \xrightarrow{KOH} RCH\begin{matrix}OH\\OH\end{matrix} \longrightarrow RCHO + H_2O$$

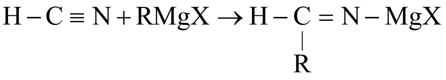
(xii) ***From Glycols :***



$$\begin{matrix}R-CHOH\\ |\\ R\text{–}CHOH\end{matrix} \xrightarrow[{[O]}]{(CH_3COO)_4Pb} 2R.CHO + H_2O$$

(xiii) ***From Grignard's reagent :***

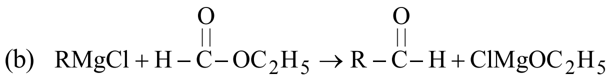
(a)



$$H-C\equiv N + RMgX \rightarrow H-\underset{\underset{R}{|}}{C} = N-MgX$$

$$\xrightarrow{H_2O} RCHO + NH_3 + HOMgX$$

(b)



$$RMgCl + H-\overset{\overset{O}{||}}{C}-OC_2H_5 \rightarrow R-\overset{\overset{O}{||}}{C}-H + ClMgOC_2H_5$$

(xiv) From acid chloride by the use of lithium t-butoxy aluminium hydride

$$RCOCl + LiAl(O-t-Bu)_3H \xrightarrow{-78°C}$$

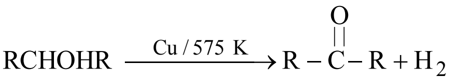
$$RCHO + LiCl + Al(O-t-Bu)_3$$

GENERAL METHODS OF PREPARATION OF KETONES ONLY :

(i) Oxidation of 2° alcohol. Oxidising agent $K_2Cr_2O_7/H_2SO_4$ or $KMnO_4/H_2SO_4$

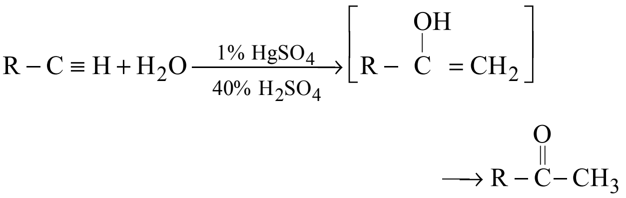
$$R.CHOHR \xrightarrow{[O]} R-CO-R + H_2O$$

(ii) ***Dehydrogenation of 2° alcohols :***



$$RCHOHR \xrightarrow{Cu/575\ K} R-\overset{\overset{O}{||}}{C}-R + H_2$$

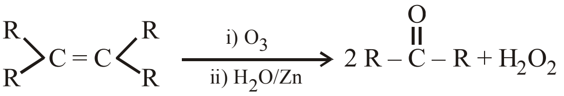
(iii) ***Hydration of alkynes :***



$$R-C\equiv H + H_2O \xrightarrow[40\%\ H_2SO_4]{1\%\ HgSO_4} \left[R-\overset{\overset{OH}{|}}{C} = CH_2\right]$$

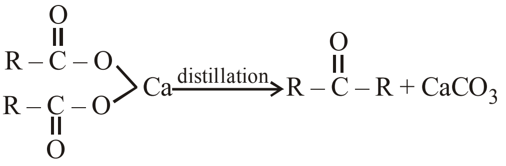
$$\longrightarrow R-\overset{\overset{O}{||}}{C}-CH_3$$

(iv) ***Reductive ozonolysis of alkenes :***



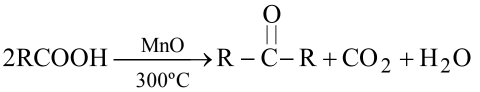
$$\begin{matrix}R\\R\end{matrix}\!\!>C=C<\!\!\begin{matrix}R\\R\end{matrix} \xrightarrow[ii)\ H_2O/Zn]{i)\ O_3} 2\ R-\overset{\overset{O}{||}}{C}-R + H_2O_2$$

(v) ***From Calcium salt of an acid :***



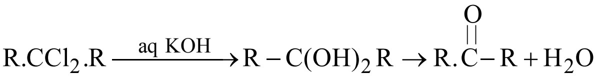
$$\begin{matrix}\overset{\overset{O}{||}}{R-C-O}\\ \underset{\underset{O}{||}}{R-C-O}\end{matrix}\!\!>Ca \xrightarrow{\text{distillation}} R-\overset{\overset{O}{||}}{C}-R + CaCO_3$$

(vi) ***From acid :***



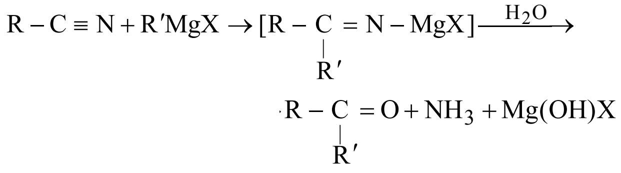
$$2RCOOH \xrightarrow[300°C]{MnO} R-\overset{\overset{O}{||}}{C}-R + CO_2 + H_2O$$

(vii) ***Hydrolysis of non-terminal gem.halide :***



$$R.CCl_2.R \xrightarrow{aq\ KOH} R-C(OH)_2R \rightarrow R.\overset{\overset{O}{||}}{C}-R + H_2O$$

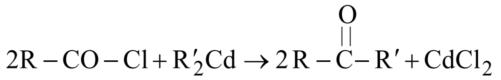
(viii) ***From Grignard's reagents :***



$$R-C\equiv N + R'MgX \rightarrow [R-\underset{\underset{R'}{|}}{C} = N-MgX] \xrightarrow{H_2O}$$

$$R-\underset{\underset{R'}{|}}{C} = O + NH_3 + Mg(OH)X$$

(ix) ***From acid chlorides :***

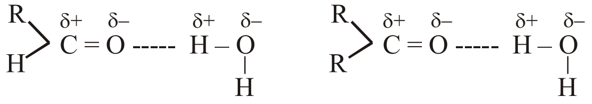


$$2R-CO-Cl+R'_2Cd \rightarrow 2R-\overset{O}{\overset{||}{C}}-R'+CdCl_2$$

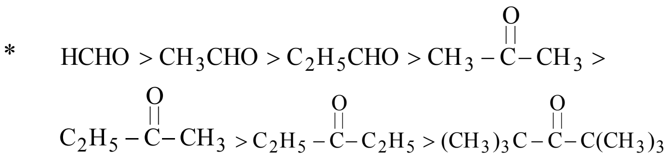
PHYSICAL PROPERTIES :

Formaldehyde is a gas and its 40% aqueous solution was known as formalin but now it is 40% HCHO, 8% CH_3OH, 52% H_2O. They are polar in nature and have higher values of b.p. Lower members are soluble in water.

Lower aldehydes and ketones (C_1-C_4) are soluble in water due to presence of H–bonding.



REACTIVITY :

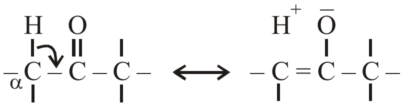


$$* \quad HCHO > CH_3CHO > C_2H_5CHO > CH_3-\overset{O}{\overset{||}{C}}-CH_3 > C_2H_5-\overset{O}{\overset{||}{C}}-CH_3 > C_2H_5-\overset{O}{\overset{||}{C}}-C_2H_5 > (CH_3)_3C-\overset{O}{\overset{||}{C}}-C(CH_3)_3$$

* It is due to + I effect of alkyl groups which decreases the +ve charge on carbonyl carbon.

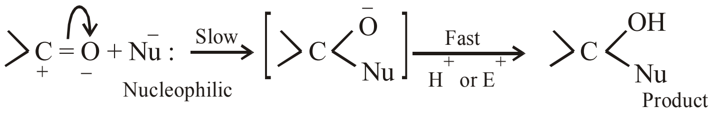
* Steric hinderance : The bulky alkyl group hinder the approach of nucleophile.

* α-hydrogen atom is acidic in nature due to Resonance



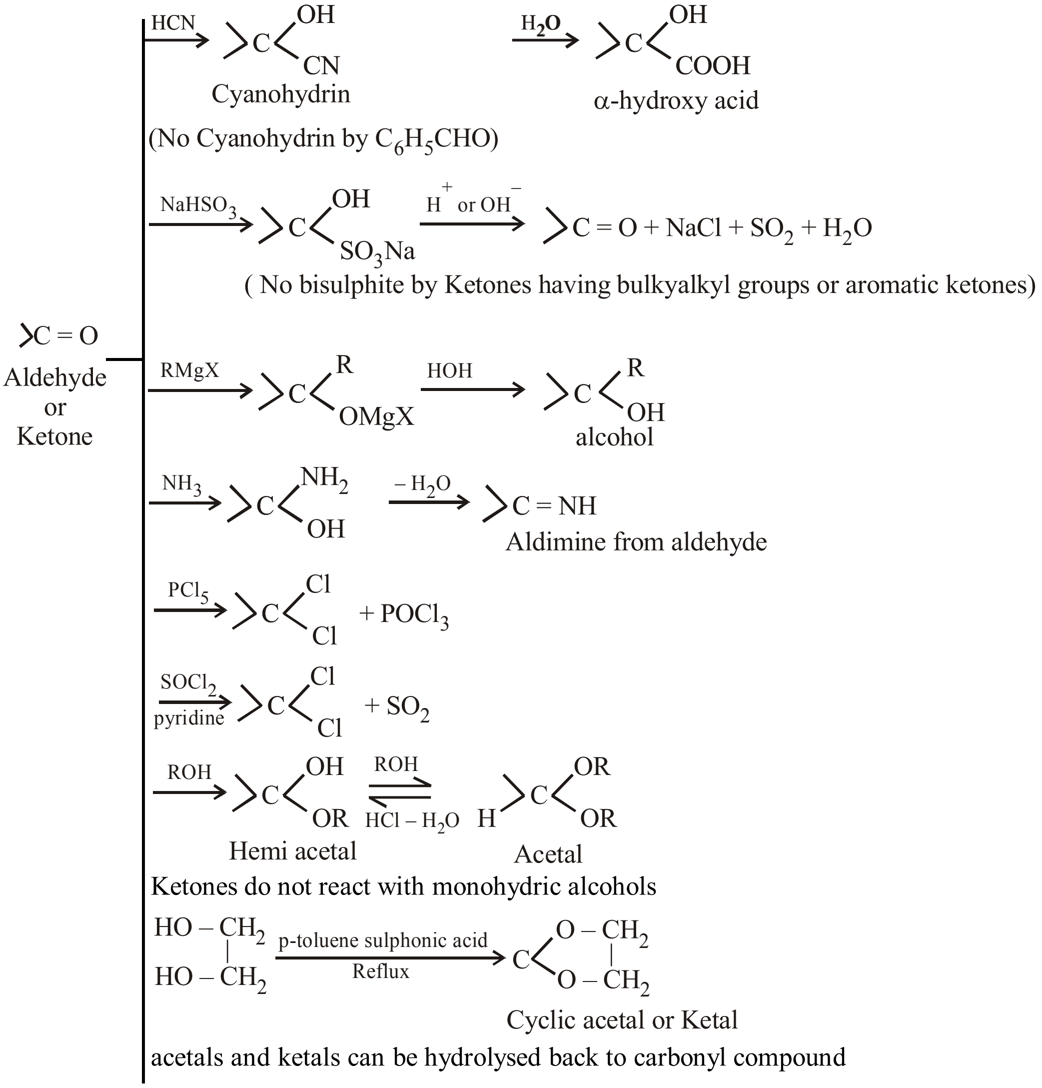
CHEMICAL PROPERTIES :

(i) ***Addition reactions :*** Their addition reactions are known as nucleophilic addition reactions



$$>\underset{+}{C}=\underset{-}{O}+\overset{-}{Nu}: \xrightarrow{\text{Slow}} \left[>C<^{\bar{O}}_{Nu}\right] \xrightarrow[\overset{+}{H}\text{ or }\overset{+}{E}]{\text{Fast}} >C<^{OH}_{Nu}$$

Nucleophilic Product



$$>C=O \xrightarrow{HCN} >C<^{OH}_{CN} \xrightarrow{H_2O} >C<^{OH}_{COOH}$$

Cyanohydrin α-hydroxy acid

(No Cyanohydrin by C_6H_5CHO)

$$>C=O \xrightarrow{NaHSO_3} >C<^{OH}_{SO_3Na} \xrightarrow{\overset{+}{H}\text{ or }\overset{-}{OH}} >C=O+NaCl+SO_2+H_2O$$

(No bisulphite by Ketones having bulkyalkyl groups or aromatic ketones)

$>C=O$ Aldehyde or Ketone

$$>C=O \xrightarrow{RMgX} >C<^{R}_{OMgX} \xrightarrow{HOH} >C<^{R}_{OH}$$

alcohol

$$>C=O \xrightarrow{NH_3} >C<^{NH_2}_{OH} \xrightarrow{-H_2O} >C=NH$$

Aldimine from aldehyde

$$>C=O \xrightarrow{PCl_5} >C<^{Cl}_{Cl} + POCl_3$$

$$>C=O \xrightarrow[\text{pyridine}]{SOCl_2} >C<^{Cl}_{Cl} + SO_2$$

$$>C=O \xrightarrow{ROH} >C<^{OH}_{OR} \underset{HCl-H_2O}{\overset{ROH}{\rightleftharpoons}} H>C<^{OR}_{OR}$$

Hemi acetal Acetal

Ketones do not react with monohydric alcohols

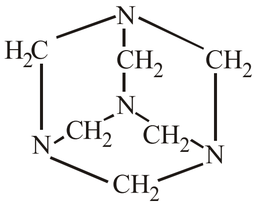
$$\begin{matrix}HO-CH_2\\ |\\ HO-CH_2\end{matrix} \xrightarrow[\text{Reflux}]{\text{p-toluene sulphonic acid}} C<\begin{matrix}O-CH_2\\ |\\ O-CH_2\end{matrix}$$

Cyclic acetal or Ketal

acetals and ketals can be hydrolysed back to carbonyl compound

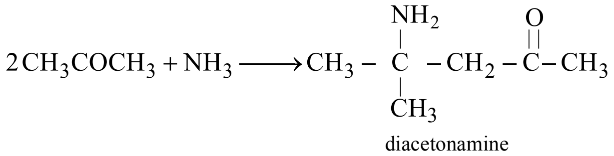
The followings reaction in different ways with NH_3

(a) $$6HCHO + 4NH_3 \longrightarrow \underset{\text{Hexamethylene tetramine or Urotropine}}{(CH_2)_6N_4} + 6H_2O$$

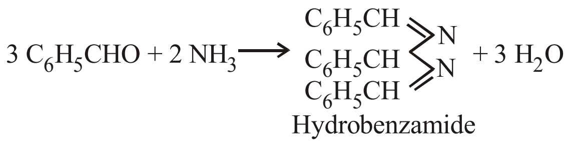


(Urotropine),
Heterocyclic compound

It is used as urinary antiseptic.

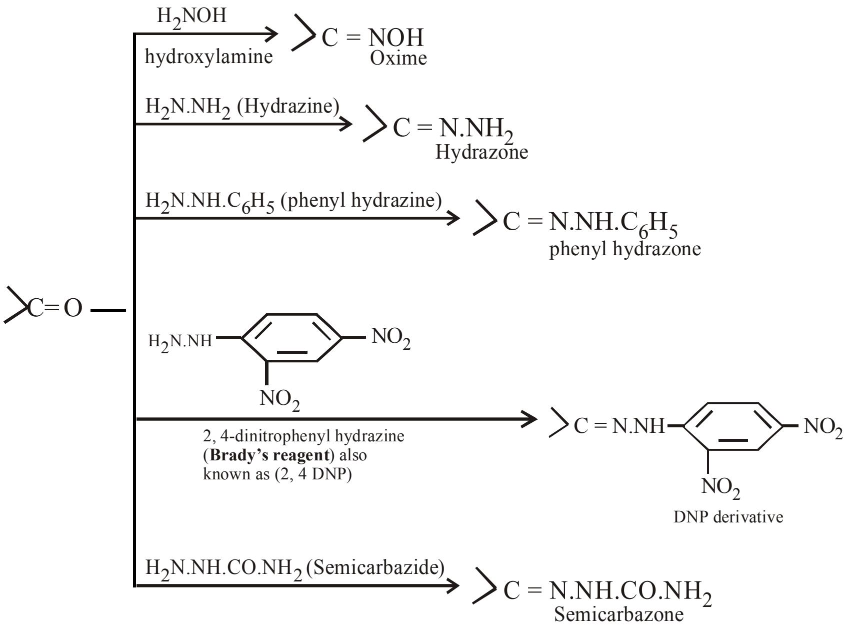
(b)


$$2CH_3COCH_3 + NH_3 \longrightarrow \underset{\text{diacetonamine}}{CH_3-\overset{\overset{NH_2}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{O}{||}}{C}-CH_3}$$

(c)


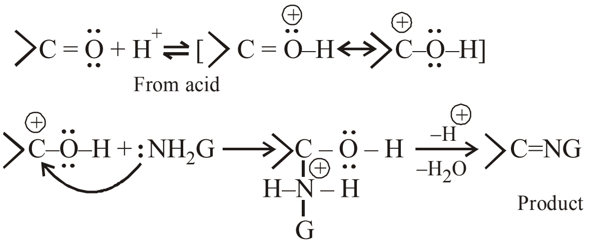
Hydrobenzamide

(ii) ***Nucleophilic addition reactions with elimination of water molecule :***



The control of pH is must for these reactions. The optimum value is around 3.5.

Control of pH during formation of ammonia derivatives :

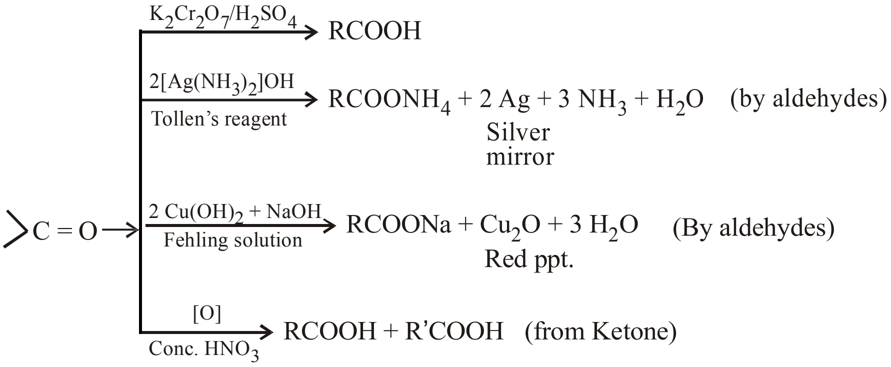


At low pH : H^+ concentration is very high. The carbonyl compound and ammonia derivative, both protonated and latter cannot act as nucleophile $(\overset{+}{N}H_3G)$.

At high pH : H^+ concentration is too small. The protonation of carbonyl group will not occur and reaction will not occur smoothly.

Hence optimum pH of the medium is around **3.5**.

(iii) ***Oxidation:***



$$>C=O \xrightarrow{K_2Cr_2O_7/H_2SO_4} RCOOH$$

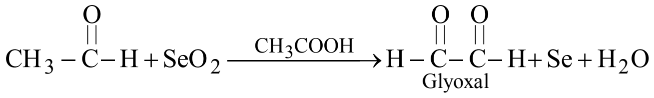
$$>C=O \xrightarrow[\text{Tollen's reagent}]{2[Ag(NH_3)_2]OH} RCOONH_4 + \underset{\text{Silver mirror}}{2\,Ag} + 3\,NH_3 + H_2O \quad \text{(by aldehydes)}$$

$$>C=O \xrightarrow[\text{Fehling solution}]{2\,Cu(OH)_2 + NaOH} RCOONa + \underset{\text{Red ppt.}}{Cu_2O} + 3\,H_2O \quad \text{(By aldehydes)}$$

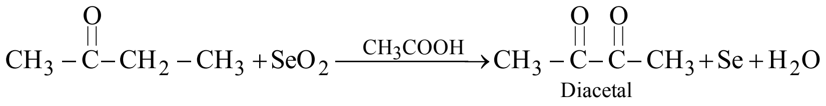
$$>C=O \xrightarrow[\text{Conc. } HNO_3]{[O]} RCOOH + R'COOH \quad \text{(from Ketone)}$$

*Ketones are oxidised by strong oxidising agents such as Conc. HNO_3, $K_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$

******Oxidation with*** SeO_2 : The CH_3 group adjacent to $-\overset{O}{\overset{||}{C}}-$ is oxidised to – CHO and $>CH_2$ group is oxidised to $>C=O$ group.

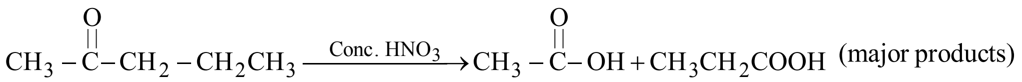


$$CH_3-\overset{O}{\overset{||}{C}}-H+SeO_2 \xrightarrow{CH_3COOH} \underset{\text{Glyoxal}}{H-\overset{O}{\overset{||}{C}}-\overset{O}{\overset{||}{C}}-H}+Se+H_2O$$



$$CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3+SeO_2 \xrightarrow{CH_3COOH} \underset{\text{Diacetal}}{CH_3-\overset{O}{\overset{||}{C}}-\overset{O}{\overset{||}{C}}-CH_3}+Se+H_2O$$

* ***Popoff's rule*** : During oxidation of unsymmertrical ketone the carbonyl group is retained by smaller alkyl group.

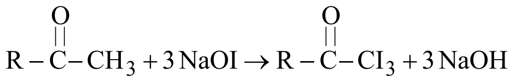


$$CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_2CH_3 \xrightarrow{\text{Conc. } HNO_3} CH_3-\overset{O}{\overset{||}{C}}-OH+CH_3CH_2COOH \text{ (major products)}$$

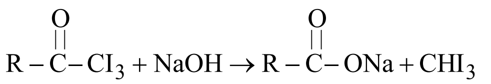
* ***Jone's reagent*** : Acidfied $K_2Cr_2O_7$ i.e. chromic acid and sulphuric acid mixture

* ***Haloform reaction*** : Oxidation of acetaldehyde or methyl ketones with Sodium Hypohalite (NaOX) or (X_2 + NaOH) gives haloform CHX_3. The reaction is of practical value to identify these compounds by forming CHI_3.

$$2\,NaOH+I_2 \rightarrow NaI+NaOI+H_2O$$



$$R-\overset{O}{\overset{||}{C}}-CH_3+3\,NaOI \rightarrow R-\overset{O}{\overset{||}{C}}-CI_3+3\,NaOH$$

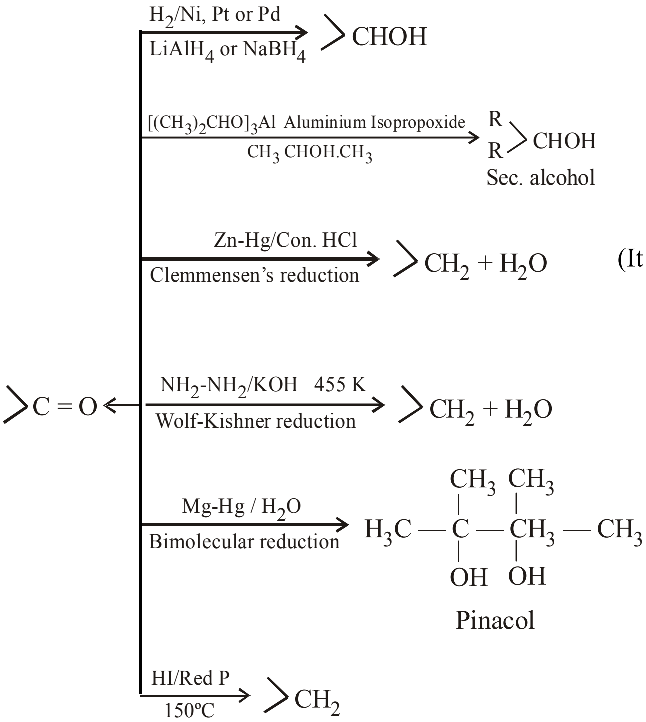


$$R-\overset{O}{\overset{||}{C}}-CI_3+NaOH \rightarrow R-\overset{O}{\overset{||}{C}}-ONa+CHI_3$$

Bayer-Villiger oxidation : Oxidation of aliphatic Ketones by organic per acids, e.g. perbenzoic acid, peracetic acid or monoperthalic acid to form esters or their hydrolysed products :

$$RCOR \xrightarrow{\text{peracid}} RCOOR \xrightarrow{H^+} RCOOH+ROH$$

(iv) ***Reduction :***

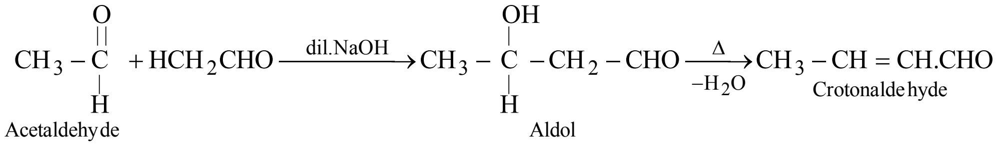


The reaction is called **Meerwein Ponndorf reduction,** $-NO_2, -CH_2=CH_2-C\equiv C-$ groups are not reduced

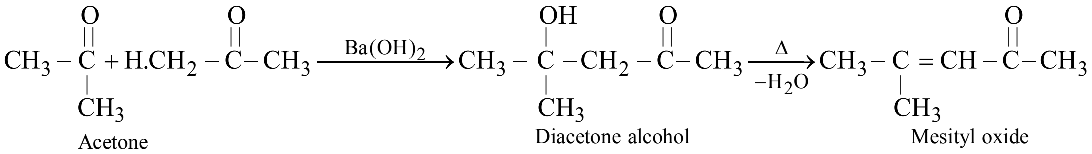
(It is easier to perform but fails for acid sensitive and high molecular weight substrates)

(v) ***Condensation reactions :***

1. ***Aldol Condensation :*** Aldehydes and Ketones having at least one α-hydrogen atom in presence of dil. alkali give β- hydroxy aldehyde or β-hydroxy ketone, which on heating gives α,β–unsaturated carbonyl compound.

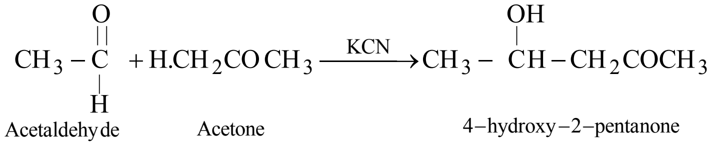


$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{||}}{\underset{\underset{H}{|}}{C}}} + HCH_2CHO \xrightarrow{dil.NaOH} \underset{\text{Aldol}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-CHO} \xrightarrow[-H_2O]{\Delta} \underset{\text{Crotonaldehyde}}{CH_3-CH=CH.CHO}$$

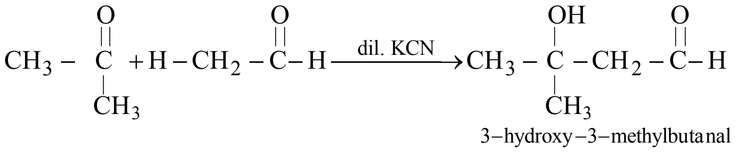


$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{||}}{\underset{\underset{CH_3}{|}}{C}}} + H.CH_2-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow{Ba(OH)_2} \underset{\text{Diacetone alcohol}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{O}{||}}{C}-CH_3} \xrightarrow[-H_2O]{\Delta} \underset{\text{Mesityl oxide}}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH-\overset{\overset{O}{||}}{C}-CH_3}$$

2. ***Crossed Aldol Condensation :***

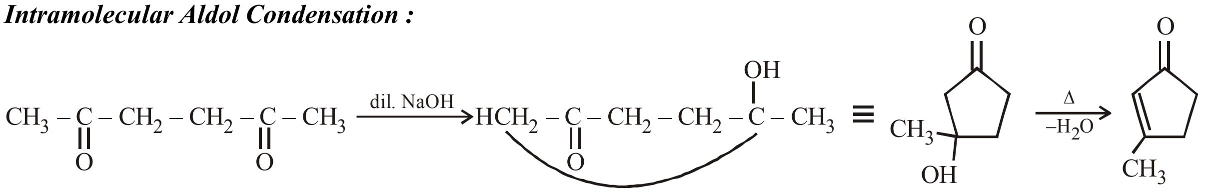


$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{||}}{\underset{\underset{H}{|}}{C}}} + \underset{\text{Acetone}}{H.CH_2COCH_3} \xrightarrow{KCN} \underset{\text{4-hydroxy-2-pentanone}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_2COCH_3}$$



$$CH_3-\overset{\overset{O}{||}}{\underset{\underset{CH_3}{|}}{C}} + H-CH_2-\overset{\overset{O}{||}}{C}-H \xrightarrow{dil.\ KCN} \underset{\text{3-hydroxy-3-methylbutanal}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{O}{||}}{C}-H}$$

3. ***Intramolecular Aldol Condensation :***



Hexa-2,5-dione

3-methyl-3-hydroxy cyclopentanone

3-methyl cyclo pent-2-ene-1-one

(4) Cannizzaro's reaction : Aldehydes containing no α-hydrogen atom on warming with 50% NaOH or KOH undergo disproportionation i.e. self oxidation - reduction known as cannizzaro's reaction.

$$2\,HCHO + NaOH \xrightarrow{50\%\,NaOH} HCOONa + CH_3OH$$

$$2\,C_6H_5CHO + NaOH \xrightarrow{50\%\ NaOH} C_6H_5COONa + C_6H_5CH_2OH$$

$$2\,Cl_3C.CHO + NaOH \rightarrow \underset{\text{Oxidation products}}{Cl_3C.COONa} + \underset{\text{Reduction products}}{Cl_3C.CH_2OH}$$

* 2-methyl propanal $(CH_3)_2CH.CHO$ has α-hydrogen atom but gives Cannizzaro's reaction.

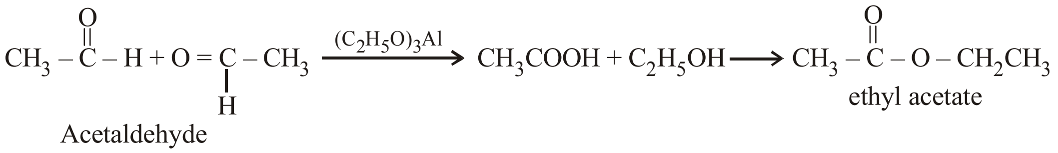
$$2(CH_3)_2CH.CHO \xrightarrow[NaOH]{200°C} (CH_3)_2CH.COONa + (CH_3)_2CH.CH_2OH$$

Aldehydes containing α-H atoms on heating with conc. alkali give brown resinous mass by undergoing repeated aldol condensation.

(5) Crossed Cannizzaro's reaction :

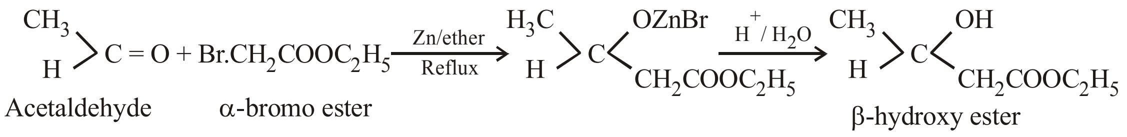
$$C_6H_5CHO + HCHO \xrightarrow{50\%\,NaOH} C_6H_5CH_2OH + HCOONa$$

(6) Tischenko reaction : Aldehydes containing α-hydrogen atom with aluminium ethoxide give esters.

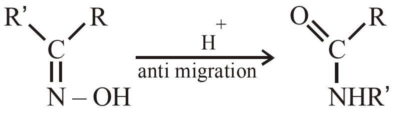


$$\underset{\text{Acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + O=\underset{H}{\underset{|}{C}}-CH_3 \xrightarrow{(C_2H_5O)_3Al} CH_3COOH + C_2H_5OH \longrightarrow \underset{\text{ethyl acetate}}{CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3}$$

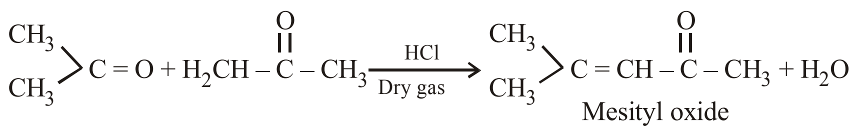
(7) Reformatsky reaction : It is the reaction between an α-bromoacid ester and a carbonyl compound (aldehyde or ketone) in the presence of zinc to form a β-hydroxy ester.

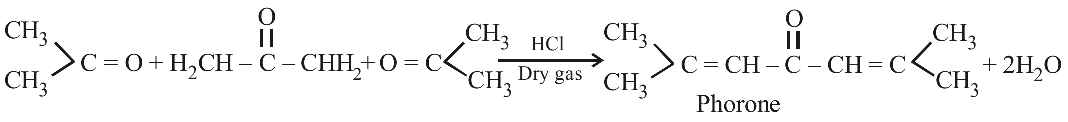


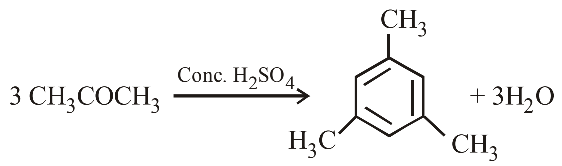
(8) Beckmann's rearrangement : It is rearrangement of keto oxime to N-substituted acid amide in presence of Conc. H_2SO_4, PPA, $SOCl_2$, PCl_5 etc.



(9) Condensation products of acetone :



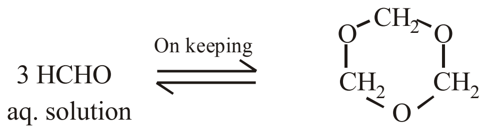




Mesitylene

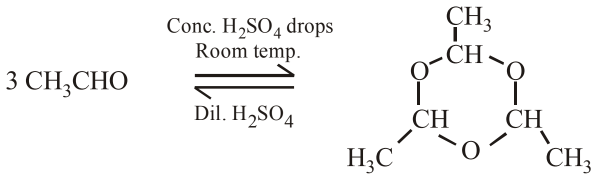
Above reactions are not aldol condensations.

(10) Polymers of formaldehydes : $$\underset{\text{aq. solution}}{n\ HCHO} \xrightleftharpoons{\text{Evaporation}} \underset{\text{Solid paraformaldehyde}}{(CH_2O)_n}$$

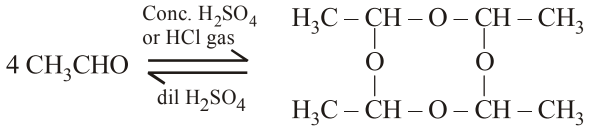


Trioxane
(meta formaldehyde)

(11) Polymers of acetaldehyde :



Para aldehyde
(pleasant smelling liquid,
used as hypnotic and soporofic)
(sleep producing)



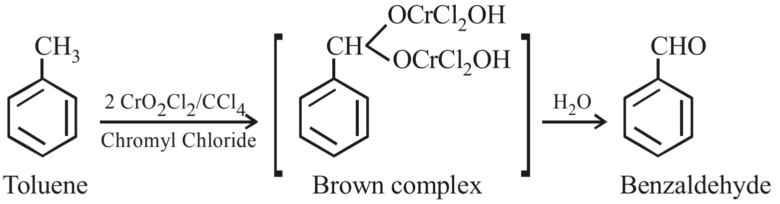
Metaldehyde
(used as solid fuel in spirit lamps)

Aromatic aldehydes and Ketones

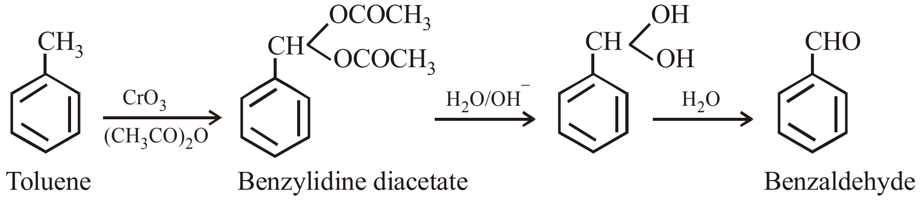
BENZALDEHYDE:

Preparation :

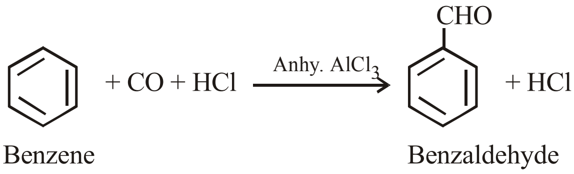
(i) ***Etard's oxidation :***



(ii) ***Oxidation of toluene :***



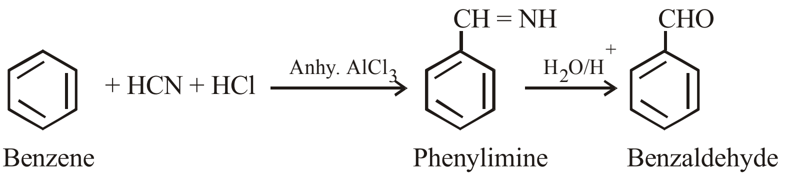
(iii) ***Gattermann Koch Synthesis :***

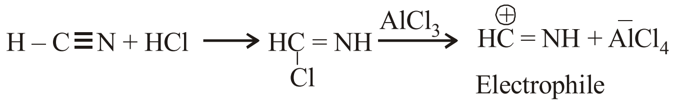


(Combination of CO + HCl act as formyl chloride HCOCl)

It is an electrophilic substitution reaction, **the electrophile is** $H\overset{+}{C}=O$ **formylium ion.**

(iv) ***Gattermann aldehyde synthesis :***

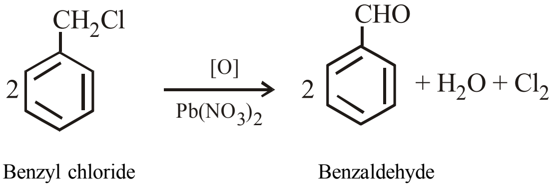




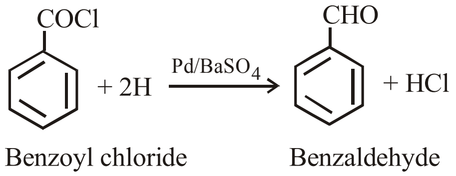
$$H-C\equiv N + HCl \longrightarrow \underset{\substack{| \\ Cl}}{HC}=NH \xrightarrow{AlCl_3} \overset{\oplus}{HC}=NH + \overset{-}{Al}Cl_4$$

Electrophile

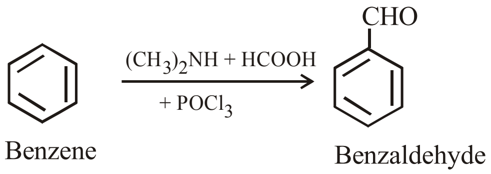
(v) ***From benzyl chloride :*** (Lab method)



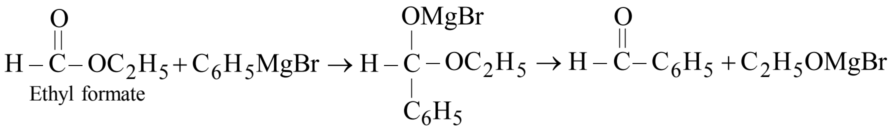
(vi) ***Rosenmund's reaction :***



(vii) ***Vilsmeyer reaction :***



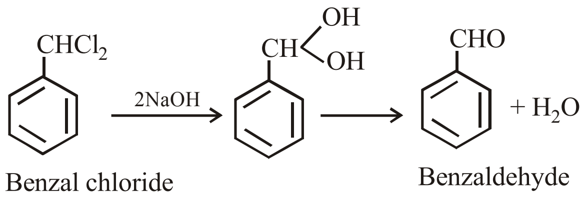
(viii) ***From Grignard's reaction :***



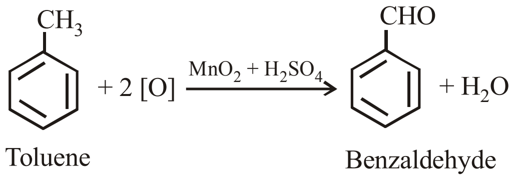
$$H-\overset{\overset{O}{\|}}{C}-OC_2H_5 + C_6H_5MgBr \rightarrow H-\underset{\underset{C_6H_5}{|}}{\overset{\overset{OMgBr}{|}}{C}}-OC_2H_5 \rightarrow H-\overset{\overset{O}{\|}}{C}-C_6H_5 + C_2H_5OMgBr$$

Ethyl formate

(ix) ***From Benzal chloride (manufacture) :***



(x) ***Manufacture :*** partial oxidation of toluene

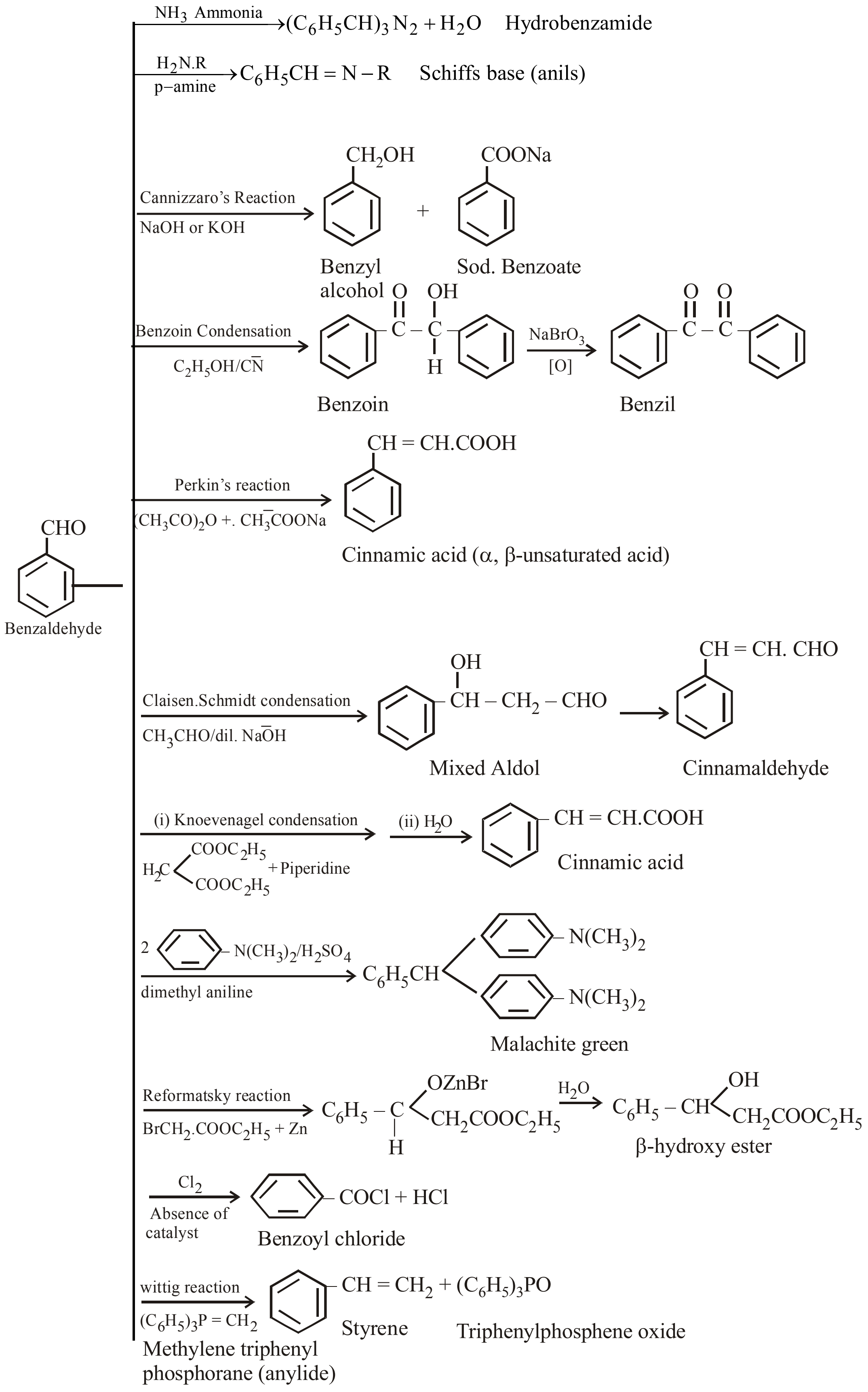


Properties :

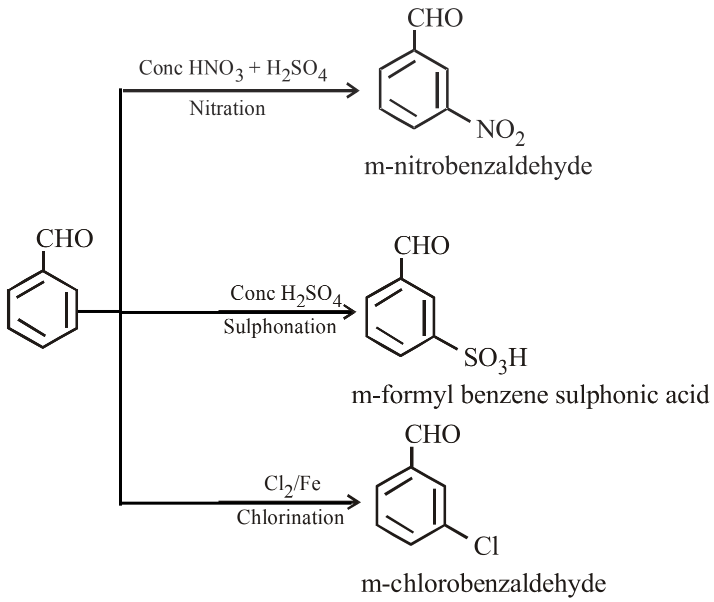
Colourless, highly refractive liquid b.p. 443K. It has smell of bitter almonds, slightly soluble in water. Steam volatile and poisonous.

Chemical properties : →

(i) Reaction of CHO group given by aromatic aldehydes



(ii) Reactions due to benzene nucleus : CHO group is meta directing with deactivation of benzene nucleus



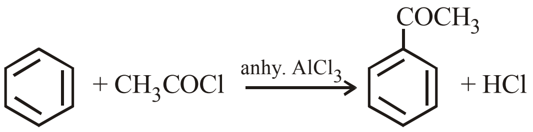
Benzaldehyde reduces Tollen's reagent but not Fehling solution.

Uses : (i) As flavouring agent (ii) In perfumes (iii) Manufacture of triphenyl methane dyes

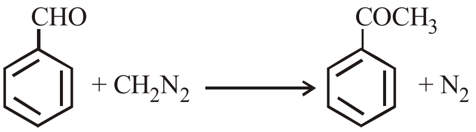
ACETOPHENONE:

Preparation

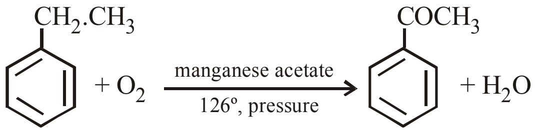
(i) ***By Friedel Craft's acylation :***



(ii) ***From benzaldehyde :***



(iii) ***Manufacture :***



Ethyl benzene

Properties : It is colourless crystalline compound m.p. 20°C, b.p. 202°C. At room temperature it is coloured liquid.

Chemical properties :

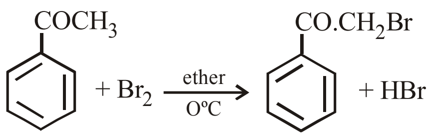
(i) Reactions due to $-\overset{\overset{O}{||}}{C}-CH_3$. It gives almost all reactions due >C = O group.

(ii) Reactions due to benzene nucleus : $-COCH_3$ is meta directing in nature. Hence electrophilic substitution reactions give meta derivative.

(iii) It give iodoform test.

(iv) ***Some important reactions are :***

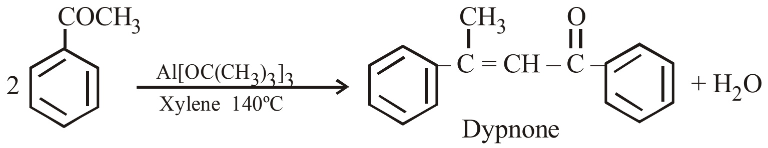
(a)



ω-bromoacetophenone
(phenacyl bromide)

Its vapour attack nose, throat and lungs. It is used as **tear gas**.

(b)



Uses: It is used as **hypnotic** in medicine.

TEST FOR ALDEHYDE :

1. **Tollen's reagent** (ammonical silver nitrate). All aldehydes give silver mirror.

   $\mathrm{RCHO + Ag_2O \rightarrow RCOOH + 2Ag}$

2. **Fehling Solution** (alkaline solution of Cu^{2+} complexed with Sodium potassium tartrate blue colour). All aldehydes give red colour except benzaldehyde.

   $\mathrm{RCHO + 2CuO \rightarrow RCOOH + \underset{Red}{Cu_2O}}$

3. **Benedict's solution** (Copper sulphate, sodium citrate and sodium carbonate solution). Aldehydes give reddish brown ppt.

4. **Schiff's reagent** (dilute solution of p-rosaniline hydrochloride decolourised with SO_2 or H_2SO_4). Aldehydes give pink colour. Acetone respond to this test slowly and o-hydroxy benzaldehyde does not give pink colour with schiff's reagent

   Note : Formic acid, tartaric acid, α-hydroxy ketones, glucose, fructose reduce Tollen reagent and Fehling solution.

Exercise-1 | NCERT BASED QUESTIONS

Very Short/ Short Answer Questions

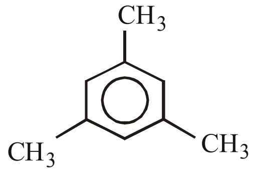
1. Give a chemical reaction when ethanal is heated with hydrogen iodide and red phosphorous under high pressure.
2. Which of the following does not give Cannizaro's reaction and why:
HCHO ; CH_3CHO ?
3. How is benzophenone reduced to diphenylmethane?
4. C_6H_5CHO gives a positive test with Tollen's reagent but not with Fehling's and Benedict's solution. Why?
5. A compound (A), $C_5H_{10}O$ forms phenyl hydrazone with phenyl hydrazine and gives negative Tollen's test and iodoform test. On reduction of compound (A), n-pentane is obtained. Identify the compound (A).
6. Explain why aldehydes get oxidised more readily than ketones.
7. What will be formed when formaldehyde is kept with a trace of sulphuric acid ?
8. To what oxidation state does ethanal reduce Cu (II)?
9. Out of acetophenone and benzophenone, which gives iodoform test? Write reaction involved.
10. What type of reactions are given by the carbonyl group in aldehyde and ketones?
11. An organic compound (A), which has a characteristic odour, on treatment with NaOH gives two compound (B) and (C). Compound (A) has molecular formula C_7H_8O which on oxidation gives back compound (C). Compound (C) is the sodium salt of an acid. Compound (C) when heated with soda lime yields an aromatic hydrocarbon (D). Deduce the structures of (A), (B), (C) and (D).
12. During the preparation of ammonia derivatives from aldehydes or ketones, pH of the reaction is carefully controlled. Why?
13. Why formaldehyde gives Cannizzaro's reaction whereas acetaldehyde does not?
14. Name two methods which are commonly used to convert a $>C=O$ group into a $>CH_2$ group.

Long Answer Questions

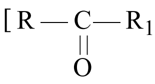
15. Give the reagents to bring about the following transformations:
    (*a*) Butan-1-ol to Butanal
    (*b*) Cyclohexanol to Cyclohexanone
    (*c*) Pent-3-en-2-ol to Pent-3-en-2-one
    (*d*) But-2-ene to Ethanal
    (*e*) But-1-yne to butan-2-one
    (*f*) p-Nitrotoluene to p-nitrobenzaldehyde.
16. How will you convert acetaldehyde into following compounds:
    (*a*) Butan-2-one
    (*b*) Butan-1,3-diol
    (*c*) But-2-enal
    (*d*) But-2-enoic acid
    (*e*) Butan-1-ol
    (*f*) But-2-enoic acid
17. The substance which add to alkenes are electrophilic reagents. In contrast, those which combine with aldehydes are mostly nucleophilic reagents. Explain.

Multiple Choice Questions

18. The reagent(s) which can be used to distinguish acetophenone from benzophenone is (are)
    (a) 2,4- Dinitrophenylhydrazine
    (b) Aqueous solution of $NaHSO_3$
    (c) Benedict reagent
    (d) $I_2$and Na_2CO_3.
19. Which of the following compound will undergo self aldol condensation in the presence of cold dilute alkali ?
    (a) $CH_2=CH-CHO$
    (b) $CH=C-CHO$
    (c) C_6H_5CHO
    (d) CH_3CH_2CHO.
20. $(CH_3)_3C–CHO$ does not undergo aldol condensation due to
    (a) three electron donating methyl groups
    (b) cleavage taking place between —C— CHO bond
    (c) absence of alpha hydrogen atom in the molecule
    (d) bulky $(CH_3)_3$ C—group
21.



The above compound describes a condensation polymer which can be obtained in two ways : either treating 3 molecules of acetone (CH_3COCH_3) with conc.H_2SO_4 or passing propyne ($CH_3C\equiv CH$) through a red hot tube. The polymer is
    (a) Phorone
    (b) Mesityl oxide
    (c) Deacetonyl alcohol
    (d) Mesitylene.
22. The cyanohydrin of a compound on hydrolysis gives an optically active α-hydroxy acid. The compound is
    (a) Diethyl ketone
    (b) Formaldehyde
    (c) Acetaldehyde
    (d) Acetone
23. Ketones



$[R - \underset{\underset{O}{\|}}{C} - R_1$, where $R = R_1$ = alkyl groups]

can be obtained in one step by
    (a) oxidation of primary alcohols
    (b) hydrolysis of esters
    (c) oxidation of tertiary alcohols
    (d) reaction of acid halides with alcohols

24. Which of the following is incorrect?

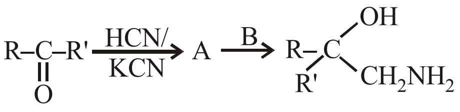
(a) $NaHSO_3$ is used in detection of carbonyl compound

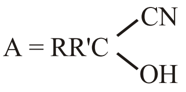
(b) $FeCl_3$ is used in detection of phenolic group

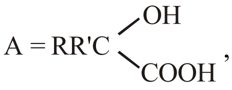
(c) Tollen is reagent is used in detection of unsaturation

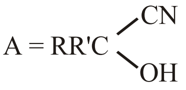
(d) Fehling solution is used in detection of glucose

25. A and B in the following reactions are



(a)  $, B = LiAlH_4$

(b)  $, B = NH_3$

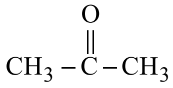
(c)  $, B = H_3O^{\oplus}$

(d) $A = RR'CH_2CN, B = NaOH$

26. Which one of the following on treatment with 50% aqueous sodium hydroxide yields the corresponding alcohol and acid?

(a) C_6H_5CHO

(b) $CH_3CH_2CH_2CHO$

(c)  $CH_3-\overset{\overset{O}{||}}{C}-CH_3$

(d) $C_6H_5CH_2CHO$

27. The product formed in aldol condensation is

(a) a beta-hydroxy aldehyde or a beta-hydroxy ketone

(b) an alpha-hydroxy aldehyde or ketone

(c) an alpha, beta unsaturated ester

(d) a beta-hydroxy acid

28. Which one of the following can be oxidised to the corresponding carbonyl compound?

(a) 2-hydroxy-propane

(b) Ortho-nitro-phenol

(c) Phenol

(d) 2-methyl-2 hydroxy-propane

Exercise-2 | CONCEPTUAL MCQs

1. In aldehydes and ketones, carbon of the carbonyl group is

(a) sp^3-hybridized (b) sp^2-hybridized

(c) sp-hybridized (d) unhybridized

2. Which of the following types of isomerism is exhibited by pentanone ?

(a) Chain isomerism (b) Position isomerism

(c) Functional isomerism (d) All of these

3. Which one of the statements about $HOH_2CCH(OH)CHO$ is not correct ? It

(a) is an isomer of 1, 3-dihydroxypropanone

(b) contains a tertiary alcoholic group

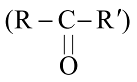
(c) has the same empirical formula as glucose

(d) can show optical isomerism

4. When acetylene is passed through dil. H_2SO_4 in the presence of $HgSO_4$, the compound formed is

(a) C_2H_5OH (b) acetone

(c) carbide of Hg (d) CH_3CHO

5. Ketones  $(R-\underset{\underset{O}{||}}{C}-R')$ where R and R' are alkyl group, can be obtained in one step by

(a) hydrolysis of esters

(b) oxidation of 1° alcohol

(c) oxidation of 2° alcohol

(d) reaction of alkyl halide with alcohols

6. Calcium formate on dry heating yields

(a) acetone (b) formaldehyde

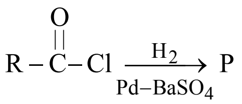
(c) acetic acid (d) acetaldehyde

7. Calcium acetate on heating results in

(a) acetone (b) acetaldehyde

(c) ethane (d) acetic anhydride

8. In the following reaction, product 'P' is


$$R-\overset{\overset{O}{||}}{C}-Cl \xrightarrow[Pd-BaSO_4]{H_2} P$$

(a) RCH_2OH (b) RCOOH

(c) RCHO (d) RCH_3

9. Hydrogenation of benzoyl chloride in the presence of Pd and $BaSO_4$ gives

(a) benzyl alcohol (b) benzaldehyde

(c) benzoic acid (d) phenol

10. In Rosenmund reaction,

(a) aldehydes are reduced to alcohols

(b) acids are converted to acid chlorides

(c) alcohols are reduced to hydrocarbons

(d) acid chlorides are reduced to aldehydes

11. Catalyst used in Rosenmund's reduction is

(a) $HgSO_4$ (b) anhydrous $AlCl_3$

(c) anhydrous $ZnCl_2$ (d) $Pd/BaSO_4$

12. The oxidation of toluene to benzaldehyde by chromyl chloride is called
(a) Rosenmund reaction
(b) Wurtz reaction
(c) Etard reaction
(d) Fittig reaction

13. Benzaldehyde can be prepared by the hydrolysis of
(a) benzal chloride
(b) benzotrichloride
(c) benzyl chloride
(d) benzonitrile

14. Which of the following reaction can produce $R-CO-Ar$?
(a) $ArCOCl + H-Ar \xrightarrow{AlCl_3}$
(b) $RCOCl + ArMgX \rightarrow$
(c) $ArCOCl + RMgX \rightarrow$
(d) $RCOCl + H-Ar \xrightarrow{AlCl_3}$

15. Which of the following compounds gives a ketone with Grignard's reagent?
(a) Formaldehyde
(b) Ethane nitrile
(c) Ethyl alcohol
(d) Methyl iodide

16. The conversion $PhCN \rightarrow PhCOCH_3$, can be achieved most conveniently by reaction with
(a) CH_3MgBr followed by hydrolysis
(b) $I_2 - NaOH, CH_3I$
(c) Dil. H_2SO_4 followed by reaction with CH_2N_2
(d) $LiAlH_4$ followed by reaction with CH_3I

17. The product (s) obtained via oxymercuration ($HgSO_4$ + H_2SO_4) of 1-butyne would be
(a) $CH_3CH_2COCH_3$
(b) $CH_3CH_2CH_2CHO$
(c) $CH_3CH_2CHO + HCHO$
(d) $CH_3CH_2COOH + HCOOH$

18. The addition of HCN to carbonyl compounds is an example of
(a) nucleophilic substitution
(b) electrophilic addition
(c) nucleophilic addition
(d) electrophilic substitution

19. Carbonyl compounds undergo nucleophilic addition because of
(a) electronegativity difference of carbon and oxygen atoms
(b) electromeric effect
(c) more stable anion with negative charge on oxygen atom and less stable carbonium ion
(d) None of these

20. Consider the following compounds :
I. HCHO II. CH_3CHO III. CH_3COCH_3
The reactivities of these compounds are such that
(a) III > II > I
(b) I > II > III
(c) III > I > II
(d) II > III > I

21. Which of the following compounds does not react with sodium bisulphite ?
(a) Benzaldehyde
(b) Acetophenone
(c) Acetone
(d) Acetaldehyde

22. Which of the following will react with water ?
(a) $CHCl_3$
(b) Cl_3CCHO
(c) CCl_4
(d) $ClCH_2CH_2Cl$

23. Acetal is produced by reacting an alcohol in the presence of dry HCl with
(a) acetaldehyde
(b) ketone
(c) ether
(d) carboxylic acid

24. $CH_3CHO + H_2NOH \rightarrow CH_3CH = NOH + H_2O$
The above reaction occurs at
(a) pH = 1
(b) pH = 4.5
(c) any value of pH
(d) pH = 12

25. Acetone oxime is obtained by reacting acetone with
(a) NH_3
(b) NH_2OH
(c) NH_2Na
(d) $NH_2.NH_2$

26. Formaldehyde reacts with ammonia to give
(a) hexamethylene tetramine
(b) formaldehyde-ammonia
(c) formalin
(d) hydrobenzamide

27. Which of the following reagents reacts differently with HCHO, CH_3CHO and CH_3COCH_3 ?
(a) HCN
(b) NH_2NH_2
(c) NH_2OH
(d) NH_3

28. Formaldehyde when reacted with methyl magnesium bromide gives
(a) C_2H_5OH
(b) CH_3COOH
(c) CH_3CHO
(d) HCHO

29. Which of the following products is formed when benzaldehyde is treated with CH_3MgBr and the addition product so obtained is subjected to acid hydrolysis ?
(a) A secondary alcohol
(b) A primary alcohol
(c) Phenol
(d) tert-Butyl alcohol

30. 1-Phenylethanol can be prepared by reaction of benzaldehyde with
(a) methyl bromide
(b) ethyl iodide and magnesium
(c) methyl bromide and aluminium bromide
(d) methyl iodide and magnesium

31. From which of the following tertiary butyl alcohol is obtained by the action of methyl magnesium iodide ?
(a) HCHO
(b) CH_3CHO
(c) CH_3COCH_3
(d) CO_2

32. When ethanal is heated with Fehling's solution it gives a precipitate of
(a) Cu
(b) CuO
(c) Cu_2O
(d) $Cu + Cu_2O + CuO$

33. Schiff's reagent gives pink colour with
(a) acetaldehyde
(b) acetone
(c) acetic acid
(d) methyl acetate

34. Schiff's reagent is
(a) resorcinol solution in dilute HCl
(b) rosaniline solution in water decolourised by SO_2
(c) alkaline $CuSO_4$ stabilized by Roschelle salt
(d) ammonical silver nitrate

35. Oxidation of acetaldehyde with selenium dioxide produces
(a) ethanoic acid (b) methanoic acid
(c) glyoxal (d) oxalic acid

36. Methyl ketones are usually characterized through
(a) the Tollen's reagent (b) the iodoform test
(c) the Schiff's test (d) the Benedict's reagent

37. $(CH_3)_2C=CHCOCH_3$ can be oxidised to $(CH_3)_2C=CHCOOH$ by
(a) Chromic acid (b) NaOI
(c) Cu at 300ºC (d) $KMnO_4$

38. Which of the following does not give iodoform test ?
(a) CH_3COCH_3 (b) CH_3OH
(c) CH_3CH_2OH (d) CH_3CHO

39. Which of the following will not give the iodoform test ?
(a) Acetophenone (b) Ethanal
(c) Benzophenone (d) Ethanol

40. Which of the following will not give iodoform test ?
(a) Ethanol (b) Ethanal
(c) Isopropyl alcohol (d) Benzyl alcohol

41. Acetone when reacted with conc. HCl and Zn-Hg gives
(a) CH_3CH_3 (b) $CH_3CH_2CH_3$
(c) CH_3COOH (d) $CH_3CHOHCH_3$

42. Reduction of a carbonyl group to a methylene group by alkaline decomposition of the hydrazone is known as
(a) Rosenmund's reduction
(b) Wolf-Kishner's reduction
(c) Clemmensen's reduction
(d) Sabatier and Senderen's reduction

43. Reduction of $>C=O$ to $>CH_2$ can be carried out with
(a) catalytic reduction
(b) Na/C_2H_5OH
(c) Wolf-Kishner reduction
(d) $LiAlH_4$

44. During reduction of carbonyl compounds by hydrazine and KOH, the first intermediate formed is
(a) $RC\equiv N$ (b) $RCONH_2$
(c) $RCH=NH$ (d) $RCH=NNH_2$

45. The reaction of $C_6H_5CH=CHCHO$ with $NaBH_4$ gives
(a) $C_6H_5CH_2CH_2CH_2OH$ (b) $C_6H_5CH=CHCH_2OH$
(c) $C_6H_5CH_2CH_2CHO$ (d) $C_6H_5CH_2CHOHCH_3$

46. If 3-hexanone is reacted with $NaBH_4$ followed by hydrolysis with D_2O, the product will be
(a) $CH_3CH_2CH(OH)CH_2CH_2CH_3$
(b) $CH_3CH_2CD(OH)CH_2CH_2CH_3$
(c) $CH_3CH_2CH(OD)CH_2CH_2CH_3$
(d) $CH_3CH_2CD(OD)CH_2CH_2CH_3$

47. Bimolecular reduction of acetone gives
(a) diacetoneamine (b) pinacol
(c) chloretone (d) propane

48. Pinacolone is
(a) 2, 3-Dimethyl-2, 3-butanediol
(b) 3,3-Dimethyl-2-butanone
(c) 1-Phenyl-2-propanone
(d) 1, 1-Diphenyl-1, 2-ethandiol

49. Formaldehyde when treated with KOH gives methanol and potassium formate. The reaction is known as
(a) Perkin reaction
(b) Claisen reaction
(c) Cannizaro reaction
(d) Knoevengel condensation

50. The reaction of benzaldehyde with alkali gives
(a) phenol + sodium benzoate
(b) benzene + Benzyl alcohol
(c) benzyl alcohol + sodium benzoate
(d) phenol + Benzene

51. Which of the following will give Cannizzaro reaction ?
(a) CH_3CHO (b) CH_3COCH_3
(c) $(CH_3)_3CCHO$ (d) CH_3CH_2CHO

52. Which of the following will respond to Cannizzaro's reaction ?
(a) 2,2-Dimethylpropanal (b) Acetaldehyde
(c) Propionaldehyde (d) Cinnamaldehyde

53. If formaldehyde and KOH are heated, then we get
(a) methane (b) methyl alcohol
(c) ethyl formate (d) acetylene

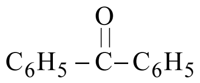
54. Cannizzaro's reaction is not given by
(a) Acetaldehyde (b) Formaldehyde
(c) Benzaldehyde (d) Trimethylacetaldehyde

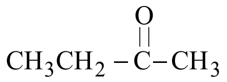
55. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives
(a) benzyl alcohol and sodium formate
(b) sodium benzoate and methyl alcohol
(c) sodium benzoate and sodium formate
(d) benzyl alcohol and methyl alcohol

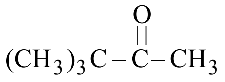
56. Conversion of acetaldehyde into ethyl acetate in presence of aluminium ethoxide is called
(a) Aldol condensation (b) Cope reaction
(c) Tischenko reaction (d) Benzoin condensation

57. Which of the following compounds will undergo self aldol condensation in the presence of cold dilute alkali?
(a) $CH_2=CH-CHO$ (b) $CH\equiv C-CHO$
(c) C_6H_5CHO (d) CH_3CH_2CHO

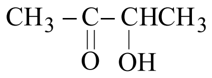
58. Which of the following gives aldol condensation?
(a) C_6H_5OH

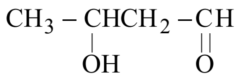
(b) 
$C_6H_5-\overset{\overset{\large O}{||}}{C}-C_6H_5$

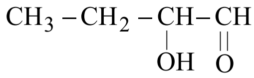
(c) 
$CH_3CH_2-\overset{\overset{\large O}{||}}{C}-CH_3$

(d) 
$(CH_3)_3C-\overset{\overset{\large O}{||}}{C}-CH_3$

59. The aldol condensation of acetaldehyde results in the formation of

(a) 
$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{C}HCH_3$

(b) 
$CH_3-\underset{\underset{OH}{|}}{C}HCH_2-\underset{\underset{O}{\|}}{C}H$

(c) 
$CH_3-CH_2-\underset{\underset{OH}{|}}{C}H-\underset{\underset{O}{\|}}{C}H$

(d) $CH_3CH_2OH+CH_3COOH$

60. Propanal on reaction with dilute NaOH forms
(a) $CH_3CH_2CH_2CH_2CH_2CHO$
(b) $CH_3CH_2CH(OH)CH_2CH_2CHO$
(c) $CH_3CH_2CH_2CH(OH)CH_2CHO$
(d) $CH_3CH_2CH(OH)CH(CH_3)CHO$

61. The base-catalysed aldol condensation will not occur with
(a) propionaldehyde
(b) benzaldehyde
(c) 2-methylpropionaldehyde
(d) acetone

62. Aldol condensation will not be observed in
(a) chloral (b) phenylacetaldehyde
(c) hexanal (d) nitromethane

63. Acetaldehyde reacts with phosphorus pentachloride to produce
(a) ethylene chloride (b) ethylidene chloride
(c) ethyl chloride (d) trichloroacetaldehyde

64. The product formed by the reaction of chlorine with benzaldehyde in the absence of catalyst is
(a) chlorobenzene (b) benzyl chloride
(c) benzoyl chloride (d) *o*-chlorobenzaldehyde

65. An example of Perkin's reaction is

(a) $C_6H_5CHO+CH_3NO_2 \xrightarrow{KOH} C_6H_5CH=CHNO_2$

(b) $C_6H_5CHO+(CH_3CO)_2O \xrightarrow{CH_3COONa} C_6H_5CH=CHCOOH$

(c) $C_6H_5CHO+CH_3CHO \xrightarrow{NaOH} C_6H_5CH=CHCHO$

(d) $C_6H_5CHO+CH_2(COOH)_2 \xrightarrow{Alc.NH_3} C_6H_5CH=CHCO_2H$

66. Aromatic aldehydes, in the presence of cyanide ion as catalyst, are converted to acyloins. This reaction is called
(a) Perkin reaction (b) Cannizzaro reaction
(c) Benzoin condensation (d) Claisen condensation

67. Benzaldehyde reacts with ethanolic KCN to give
(a) $C_6H_5CHOHCN$ (b) $C_6H_5CHOHCOC_6H_5$
(c) $C_6H_5CHOHCOOH$ (d) $C_6H_5CHOHCHOHC_6H_5$

68. Trioxane is a trimer of
(a) acetaldehyde (b) formaldehyde
(c) benzaldehyde (d) salicylaldehyde

69. Paraldehyde is formed by polymerisation of
(a) CH_3CHO (b) HCHO
(c) CH_3OH (d) CH_3CH_2OH

70. Which of the following does not give formaldehyde on heating or distillation ?
(a) Formalin (b) Trioxane
(c) Paraldehyde (d) Paraformaldehyde

71. Acetone on heating with conc. H_2SO_4 mainly gives
(a) mesitylene (b) mesityl oxide
(c) toluene (d) xylene

72. Which is not true about acetophenone ?
(a) It reacts with 2,4-dinitrophenylhydrazine to form 2, 4-dinitrophenylhydrazone
(b) It reacts with Tollen's reagent to form silver mirror
(c) It reacts with I_2/NaOH to form iodoform
(d) On oxidation with alkaline $KMnO_4$ followed by hydrolysis it gives benzoic acid

73. Benzophenone can be converted into benzene by using
(a) fused alkali
(b) anhydrous $AlCl_3$
(c) sodium amalgam in water
(d) acidified dichromate

74. Acetaldehyde cannot give
(a) Iodoform test (b) Lucas test
(c) Benedict's test (d) Tollen's test

75. Which of the following will give red precipitate when reacted with complexes formed by copper sulphate and sodium tartarate ?
(a) CH_3CHO (b) CH_3COCH_3
(c) CH_3COOH (d) C_2H_5COOH

76. Acetaldehyde and acetone can be distinguished by
(a) Molisch test (b) Bromoform test
(c) Solubility in water (d) Tollen's test

77. Which of the following is incorrect ?
(a) $FeCl_3$ is used in detection of phenols
(b) Fehling solution is used in detection of glucose
(c) Tollen's reagent is used in detection of unsaturation
(d) $NaHSO_3$ is used in detection of carbonyl compounds

78. Which of the following reagents is used to distinguish acetone and acetophenone ?
(a) $NaHSO_3$ (b) Grignard reagent
(c) Na_2SO_4 (d) NH_4Cl

79. Which of the following reagents cannot be used to distinguish between hexanal and 2-hexanone?
(a) Tollen's reagent (b) Br_2 in CCl_4
(c) I_2 in NaOH (d) Fehling solution

80. Aldehydes and ketones will not form crystalline derivatives with
(a) sodium bisulphite
(b) phenylhydrazine
(c) semicarbazide hydrochloride
(d) dihydrogen sodiumphosphate

81. The organic compound which will answer the Fehling solution test is
(a) ethanol (b) acetone
(c) maltose (d) benzaldehyde

82. An organic compound, C_3H_6O does not give a precipitate with 2, 4-dinitrophenylhydrazine reagent and does not react with metallic sodium. It could be
(a) $CH_3–CH_2–CHO$ (b) $CH_2=CH–CH_2OH$
(c) $CH_3–CO–CH_3$ (d) $CH_2=CH–O–CH_3$

83. An organic compound of molecular formula, C_3H_6O did not give a silver mirror with Tollen's reagent, but gave an oxime with hydroxylamine. It may be
(a) $CH_2 = CH - CH_2 - OH$ (b) $CH_3 - CH_2 - CHO$
(c) $CH_3 - CO - CH_3$ (d) $CH_2 = CH - OCH_3$

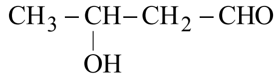
84. The end product (C) in the following sequence of reactions is

$$HC \equiv CH \xrightarrow[20\%\ H_2SO_4]{1\%\ HgSO_4} A \xrightarrow[H_2O]{CH_3MgX} B \xrightarrow{[O]} (C)$$

(a) acetic acid (b) isopropyl alcohol
(c) acetone (d) ethanol

85. Predict the product 'B' in the sequence of reactions

$$CH \equiv CH \xrightarrow[\%\ HgSO_4]{30\%\ H_2SO_4} A \xrightarrow{NaOH} B$$

(a) CH_3COONa (b) CH_3COOH
(c) CH_3CHO (d)

$\underset{\displaystyle OH}{CH_3 - \overset{}{CH} - CH_2 - CHO}$

86. The reaction of acetaldehyde with HCN followed by hydrolysis gives a product which exhibits
(a) metamerism (b) tautomerism
(c) enantiomerism (d) geometrical isomerism

87. $(CH_3)_2CO \xrightarrow[(HCl)]{NaCN} A \xrightarrow[\Delta]{H_3O^+}$

In the above sequence of reactions A and B are
(a) $(CH_3)_2C(OH)CN, (CH_3)_2C(OH)COOH$
(b) $(CH_3)_2C(OH)CN, (CH_3)_2C(OH)_2$
(c) $(CH_3)_2C(OH)CN, (CH_3)_2CHCOOH$
(d) $(CH_3)_2C(OH)CN, (CH_3)_2C=O$

88. In the reaction sequence

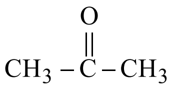
$$\text{Glycerol} \xrightarrow{KHSO_4/\Delta} X \xrightarrow{Zn-Hg/conc.HCl/\Delta}$$
$$Y \xrightarrow{NBS/CCl_4} Z$$; (Z) will be

(a) 1-Bromopropane (b) 2-Bromopropane
(c) 3-Bromopropene (d) 1, 2-Dibromopropane

89. A substance $C_4H_{10}O$ yields on oxidation a compound, C_4H_8O which gives an oxime and a positive iodoform test. The original substance on treatment with conc. H_2SO_4 gives C_4H_8. The structure of the compound is
(a) $CH_3CH_2CH_2CH_2OH$ (b) $CH_3CHOHCH_2CH_3$
(c) $(CH_3)_3COH$ (d) $CH_3CH_2–O–CH_2CH_3$

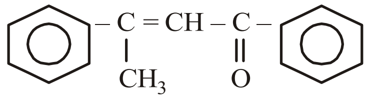
Exercise-3 | PAST COMPETITION MCQs

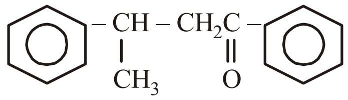
1. Reduction of aldehydes and ketones into hydrocarbons using zinc amalgam and conc. HCl is called
(a) Cope reduction **[CBSE-PMT 2007]**
(b) Dow reduction
(c) Wolf-Kishner reduction
(d) Clemmensen reduction.

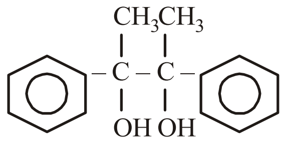
3. Which one of the following on treatment with 50% aqueous sodium hydroxide yields the corresponding alcohol and acid? **[CBSE-PMT 2007]**
(a) C_6H_5CHO (b) $CH_3CH_2CH_2CHO$
(c)

$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$
(d) $C_6H_5CH_2CHO$

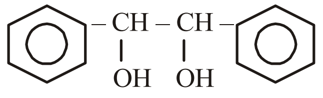
3. The product formed in Aldol condensation is
[CBSE-PMT 2007]
(a) a beta-hydroxy aldehyde or a beta-hydroxy ketone
(b) an alpha-hydroxy aldehyde or ketone
(c) an alpha, beta unsaturated ester
(d) a beta-hydroxy acid

4. Acetophenone when reacted with a base, C_2H_5ONa, yields a stable compound which has the structure.
[CBSE-PMT 2008]

(a)


(b)


(c)


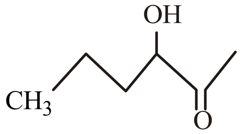
(d)


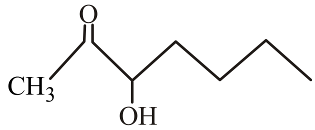
5. Which of the following reactions will not result in the formation of carbon-carbon bonds? **[CBSE-PMT 2010]**
(a) Reimer-Tieman reaction
(b) Cannizaro reaction
(c) Wurtz reaction
(d) Friedel-Crafts acylation

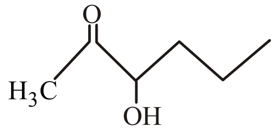
6. Following compounds are given: **[CBSE-PMT 2010]**
(i) CH_3CH_2OH
(ii) CH_3COCH_3
(iii) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}HOH$
(iv) CH_3OH

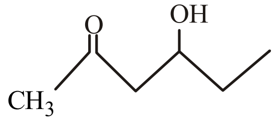
Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform?
(a) (i) and (ii)
(b) (i), (iii) and (iv)
(c) Only (ii)
(d) (i), (ii) and (iii)

7. Which one of the following compounds will be most readily dehydrated? **[CBSE-PMT 2010]**

(a) 

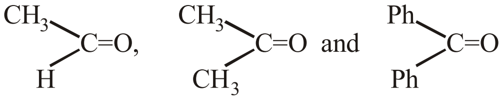
(b) 

(c) 

(d) 

8. Clemmensen reduction of a ketone is carried out in the presence of which of the following ? **[CBSE-PMT 2011]**
(a) Glycol with KOH
(b) Zn-Hg with HCl
(c) $LiAlH_4$
(d) H_2 and Pt as catalyst

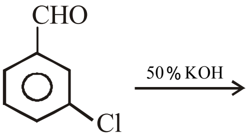
9. The order of reactivity of phenyl magnesium bromide (PhMgBr) with the following compounds **[CBSE-PMT 2011 M]**

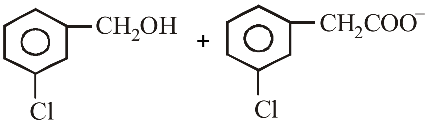


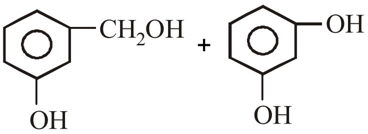
I II III

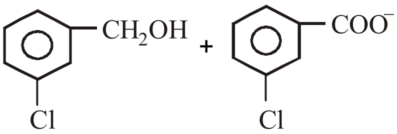
(a) III > II > I
(b) II > I > III
(c) I > III > II
(d) I > II > III

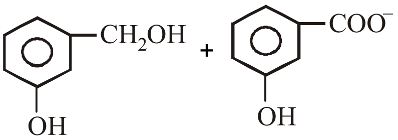
10. Predict the product in the given reaction. **[CBSE-PMT 2012]**



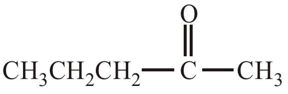
(a) 

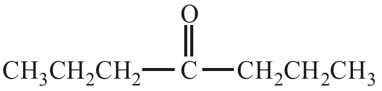
(b) 

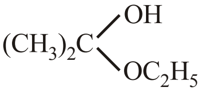
(c) 

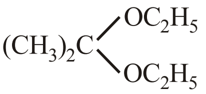
(d) 

11. Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is : **[CBSE-PMT 2012]**

(a) 
$CH_3CH_2CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

(b) 
$CH_3CH_2CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2CH_2CH_3$

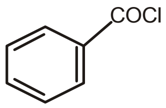
(c) 
$(CH_3)_2C\begin{matrix}\diagup OH\\ \diagdown OC_2H_5\end{matrix}$

(d) 
$(CH_3)_2C\begin{matrix}\diagup OC_2H_5\\ \diagdown OC_2H_5\end{matrix}$

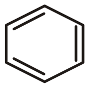
12. Consider the reaction : **[CBSE-PMT 2012 M]**
$$RCHO + NH_2NH_2 \rightarrow RCH = N - NH_2$$
What sort of reaction is it ?
(a) Electrophilic addition – elimination reaction
(b) Free radical addition – elimination reaction
(c) Electrophilic substitution – elimination reaction
(d) Nucleophilic addition – elimination reaction

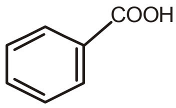
13. Which of the following compounds will give a yellow precipitate with iodine and alkali ? **[CBSE-PMT 2012 M]**
(i) Acetophenone
(ii) Acetamide
(iii) Methyl acetate
(iv) 2-Hydroxypropane
(a) (i), (ii) and (iii)
(b) (i) and (iv)
(c) (ii) and (iv)
(d) (i), (iii) and (iv)

14. Reaction by which Benzaldehyde cannot be prepared : **[NEET 2013]**

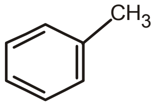
(a) 

+ H_2 in presence of Pd - $BaSO_4$

(b) 
+ CO + HCl in presence of anhydrous $AlCl_3$

(c) 

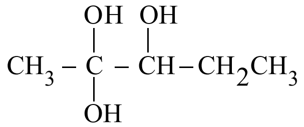
+ Zn/Hg and conc. HCl

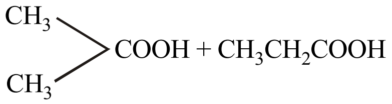
(d) 

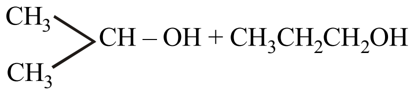
+ CrO_2Cl_2 in CS_2 followed by H_3O^+

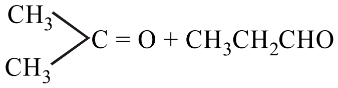
15. On vigorous oxidation by permanganate solution of (*AIEEE 2002*)

$(CH_3)_2C = CH - CH_2 - CHO$ gives

(a) 
$CH_3 - \underset{OH}{\overset{OH}{C}} - \overset{OH}{CH} - CH_2CH_3$

(b) 

(c) 

(d) 

16. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid? **[AIEEE 2004]**

(a) Butanal	(b) Benzaldehyde
(c) Phenol	(d) Benzoic acid

17. In Cannizzaro reaction given below **[AIEEE 2009]**

$$2PhCHO \xrightarrow{:\overset{\ominus}{O}H} PhCH_2OH + PhC\ddot{O}_2^{\ominus}$$

the slowest step is :

(a) the transfer of hydride to the carbonyl group

(b) the abstraction of proton from the carboxylic group

(c) the deprotonation of Ph CH_2OH

(d) the attack of : $\overset{\ominus}{O}H$ at the carboxyl group

18. Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds: **[AIEEE 2011 RS]**

(a) 1 – Pentene

(b) 2 – Pentene

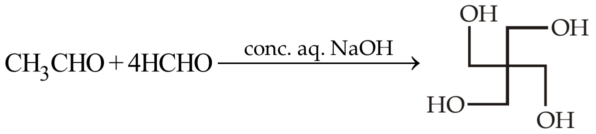
(c) 2 – Methyl – 2 – pentene

(d) 2 – Methyl – 1 – pentene

19. Iodoform can be prepared from all except : **[AIEEE 2012]**

(a) Ethyl methyl ketone	(b) Isopropyl alcohol
(c) 3-Methyl 2-butanone	(d) Isobutyl alcohol

20. The number of aldol reaction(s) that occurs in the given transformation is : **[IIT-JEE 2012]**



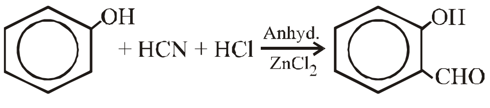
(a) 1	(b) 2
(c) 3	(d) 4

Exercise-4 | Applied MCQs

1. Oxidation of toluene with CrO_3 in the presence of $(CH_3CO)_2O$ gives a product (A) which on treatment with aqueous NaOH produces

(a) C_6H_5CHO	(b) $(C_6H_5CO)_2O$
(c) C_6H_5COONa	(d) 2, 4-Diacetyltoluene

2. The following reaction



is known as

(a) Perkin reaction

(b) Gattermann aldehyde synthesis

(c) Kolbe's reaction

(d) Gattermann-Koch reaction

3. The general order of reactivity of carbonyl compounds towards nucleophilic addition reactions is

(a) $H_2C = O > RCHO > ArCHO > R_2C = O > Ar_2C = O$

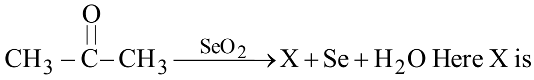
(b) $ArCHO > Ar_2C = O > RCHO > R_2C = O > H_2C = O$

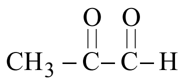
(c) $Ar_2C = O > R_2C = O > ArCHO > RCHO > H_2C = O$

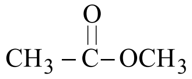
(d) $H_2C = O > R_2C = O > Ar_2C = O > RCHO > ArCHO$

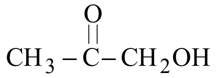
4. The most reactive compound towards formation of cyanohydrin on treatment with KCN followed by acidification is

(a) benzaldehyde	(b) *p*-nitrobenzaldehyde
(c) phenylacetaldehyde	(d) *p*-hydroxybenzaldehyde

5. 
$CH_3 - \overset{O}{\overset{||}{C}} - CH_3 \xrightarrow{SeO_2} X + Se + H_2O$ Here X is

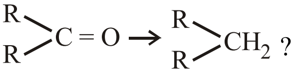
(a) 
$CH_3 - \overset{O}{\overset{||}{C}} - \overset{O}{\overset{||}{C}} - H$

(b) 
$CH_3 - \overset{O}{\overset{||}{C}} - OCH_3$

(c) 
$CH_3 - \overset{O}{\overset{||}{C}} - CH_2OH$

(d) None of these

6. Which one of the following reactions cannot be used for the reduction of



(a) Clemmensen reaction

(b) Wolf-Kishner reaction

(c) Wurtz reaction

(d) HI and red phosphorus at 200°C

7. Which one of the following pairs is not correctly matched ?

(a) $>C=O \rightarrow >CH_2$ (Clemmensen's reduction)

(b) $>C=O \rightarrow >CHOH$ (Wolf-Kishner's reduction)

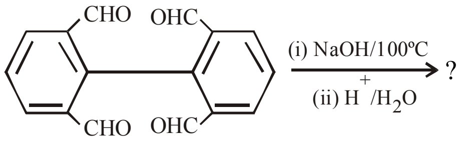
(c) $-COCl \rightarrow -CHO$ (Rosenmund's reduction)

(d) $-C \equiv N \rightarrow -HO$ (Stephen's reduction)

8. m-chlorobenzaldehyde on reaction with conc. KOH at room temperature gives

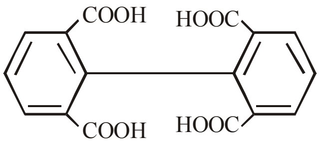
(a) Potassium m-chlorobenzoate and m-hydroxybenzaldehyde
(b) m-hydroxybenzaldeyde and m-chlorobenzyl alcohol
(c) m-chlorobenzyl alcohol and m-hydroxybenzyl alcohol
(d) Potassium m-chlorobenzoate and m-chlorobenzyl alcohol

9.

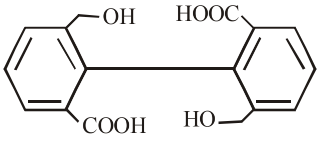


The major product in the above reaction is

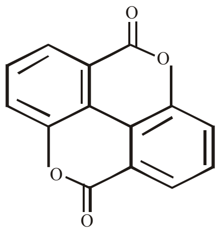
(a)



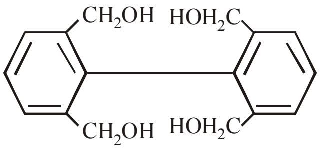
(b)



(c)



(d)



10. Consider the following statements :

I. Acetophenone can be prepared by oxidation of 1-phenylethanol
II. Acetophenone can be prepared by reaction of benzaldehyde with methyl magnesium bromide
III. Acetophenone can be prepared by Friedel-Craft's reaction of benzene with acetyl chloride
IV. Acetophenone can be prepared by distillation of calcium benzoate

Which of the above statements are correct ?

(a) II and III (b) I and IV
(c) I and III (d) III and IV

11. Which of the following statements regarding chemical properties of acetophenone are wrong?

I. It is reduced to methylphenylcarbinol by sodium and ethanol
II. It is oxidised to benzoic acid with acidified $KMnO_4$
III. It does not undergo electrophilic substitution like nitration at meta position
IV. It does not undergo iodoform reaction with iodine and alkali

(a) I and III (b) II and IV
(c) III and IV (d) I and II

12. The end product 'C' in the following sequence of chemical reactions is

$$CH_3COOH \xrightarrow{CaCO_3} A \xrightarrow{heat} B \xrightarrow{NH_2OH} C$$

(a) Acetaldehyde oxime (b) Formaldehyde oxime
(c) Methyl nitrate (d) Acetoxime

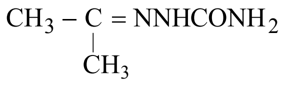
13. An organic compound 'A' has the molecular formula C_3H_6O. It undergoes iodoform test. When staturated with HCl it gives 'B' of molecular formula $C_9H_{14}O$. 'A' and 'B' respectively are

(a) Propanal and mesitylene
(b) Propanone and mesityl oxide
(c) Propanone and 2,6-dimethyl-2, 5-heptadien-4-one
(d) Propanone and mesitylene oxide

14. Compound 'A' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product 'B' (molecular formula C_3H_6O). 'B' forms a shining silver mirror on warming with ammonical silver nitrate. 'B' when treated with an aqueous solution of $H_2NCONHNH_2$.HCl and sodium acetate gives a product 'C'. Identify the structure of 'C'

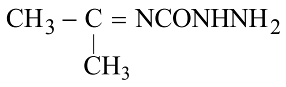
(a) $CH_3CH_2CH = NNHCONH_2$

(b)



$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{C}} = NNHCONH_2$

(c)



$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{C}} = NCONHNH_2$

(d) $CH_3CH_2CH = NCONHNH_2$

15. Match List I (Reaction) with List II (Reagent) and select the correct answer using the codes given below the lists:

List I	**List II**
I. Etard reaction	A. Alcoholic KOH
II. Hydroxylation	B. Anhydrous $AlCl_3$
III. Dehydro-halogenation	C. Chromyl chloride
IV. Friedel-Crafts reaction	D. Dilute alkaline $KMnO_4$

Codes

(a) I-A, II-B, III-C, IV-B (b) I-D, II-C, III-A, IV-B
(c) I-C, II-D, III-A, IV-B (d) I-B, II-A, III-D, IV-C

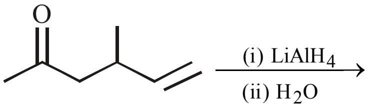
16. Match List I (Reaction) with List II (Name) and select the correct answer using the codes given below the lists:

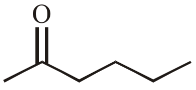
List I	**List II**
I. $R-CO-CH_3 \xrightarrow{Zn-Hg/HCl} R-CH_2-CH_3$	A. Friedel-Craft's reaction
II. $2C_6H_5CHO \xrightarrow{NaOH} C_6H_5COONa + C_6H_5CH_2OH$	B. Kolbe's reaction
III. $C_6H_6 + CH_3COCl \xrightarrow[AlCl_3]{Anhyd.} C_6H_5COCH_3$	C. Clemmensen's reaction
IV. $C_6H_5OH + CO_2 + NaOH \rightarrow HOC_6H_4COONa$	D. Cannizzaro's reaction

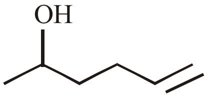
Codes :

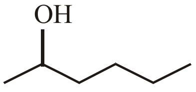
(a) I-A, II-B, III-C, IV-D
(b) I-B, II-A, III-C, IV-D
(c) I-C, II-D, III-A, IV-B
(d) I-D, II-C, III-A, IV-B

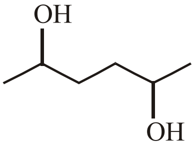
17. What is the product of the following reaction ?



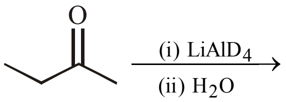
(a) 

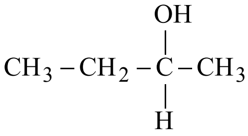
(b) 

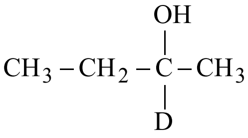
(c) 

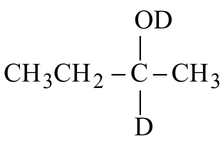
(d) 

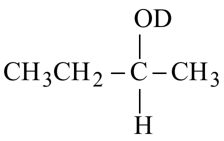
18. Give the product of the following reaction :



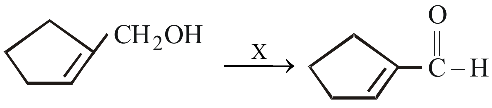
(a) 
$CH_3-CH_2-\overset{OH}{\underset{H}{C}}-CH_3$

(b) 
$CH_3-CH_2-\overset{OH}{\underset{D}{C}}-CH_3$

(c) 
$CH_3CH_2-\overset{OD}{\underset{D}{C}}-CH_3$

(d) 
$CH_3CH_2-\overset{OD}{\underset{H}{C}}-CH_3$

19. What is X in the following conversion ?



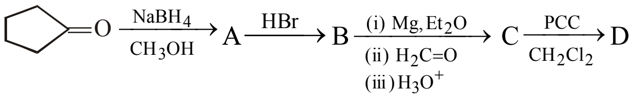
(a) $K_2Cr_2O_7, H_2SO_4 / H_2O$

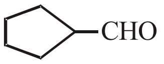
(b) HIO_4

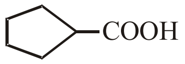
(c) PCC / CH_2Cl_2

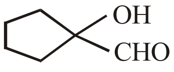
(d) $OsO_4, (CH_3)_3C.COOH, (CH_3)_3COH, OH^-$

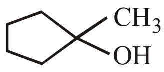
20. What is D in the following sequence of reactions ?



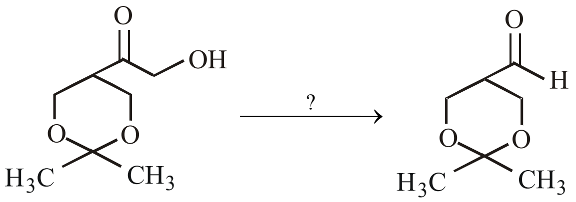
(a) 

(b) 

(c) 

(d) 

21. The reagents employed to carry the following transformation



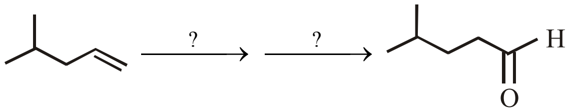
(a) $LiAlH_4, H_2SO_4$ / heat

(b) PCC / CH_2Cl_2 followed by HIO_4

(c) $NaBH_4 / CH_3OH$ followed by HIO_4

(d) O_3 followed by $(CH_3)_2S$

22. The suitable reaction steps to carryout the following transformation



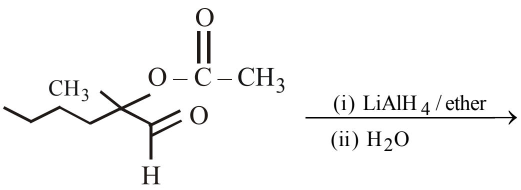
(a) $\xrightarrow[\text{(ii) } H_2O_2, NaOH]{\text{(i) } BH_3, THF} \xrightarrow[CH_2Cl_2]{PCC}$

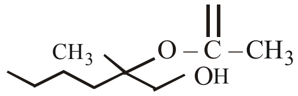
(b) $\xrightarrow[\text{(ii) } H_2O_2, NaOH]{\text{(i) } BH_3, THF} \xrightarrow{HIO_4}$

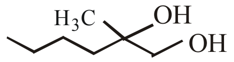
(c) $\xrightarrow{H_2O, H_2SO_4} \xrightarrow[CH_2Cl_2]{PCC}$

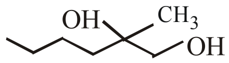
(d) $\xrightarrow[(CH_3)_3C.COOH, OH]{OsO_4} \xrightarrow[H_2O]{K_2Cr_2O_7, H_2SO_4}$

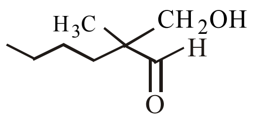
23. The suitable product of the reaction



(a) 

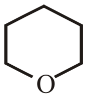
(b) 

(c) 

(d) 

24. Which of the following is not suitable solvent for Grignard's reagents ?

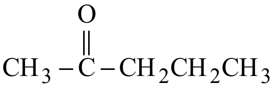
(a) $CH_3CH_2OCH_2CH_3$ (b)



(c) CH_3CH_2OH (d) All are suitable

25. The correct reagents to carry out the following conversion

$HC \equiv C.CH_2CH_2CH_3 \xrightarrow{?}$



$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2CH_3$

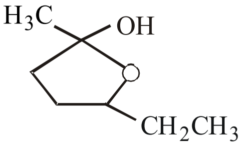
(a) H_2/Lindlar Pd followed by H_2SO_4/H_2O

(b) $H_2O, H_2SO_4/HgSO_4$

(c) $LiAlH_4$ followed by H_2O

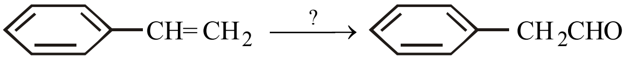
(d) O_3 followed by H_2O

26. The compound shown below is the cyclic hemiacetal of



(a) 5 - hydroxyheptanal
(b) 6 - hydroxy - 3- heptanone
(c) 5 - hydroxy - 2- heptanone
(d) 6 - hydroxy heptanal

27. The correct set of reagents to carry out the following conversion

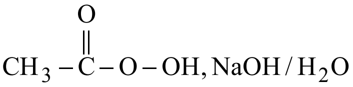


(a) C_2H_6/diglyme, H_2O_2/NaOH, PCC/CH_2Cl_2

(b) $Br_2, NaNH_2, HgSO_4/H_2SO_4$

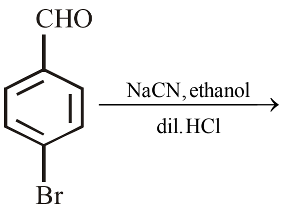
(c) $H_2O/H_2SO_4, CrO_3/H_2SO_4$

(d)

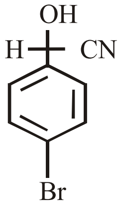


$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-OH, NaOH/H_2O$

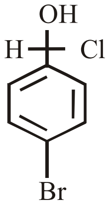
28. What is the product of the following reaction ?



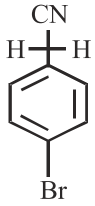
(a)



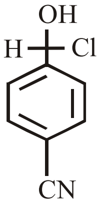
(b)



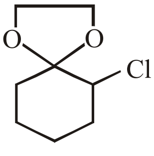
(c)



(d)

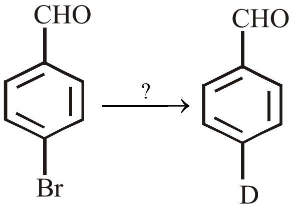


29. Acid catalysed hydrolysis of the cyclic acetal gives



(a) ethanal and 2-chlorocyclohexanol
(b) ethanol and 2-chlorocyclohexanol
(c) 1, 2-ethanediol and 2-chlorocyclohexanone
(d) 1, 2-ethanediol 2-chlorocyclohexanol

30. The following change can be brought about by



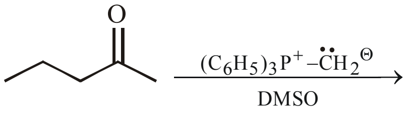
(a) Mg/ diethyl ether, D_2O

(b) $LiAlD_4$/diethyl ether, D_2O

(c) $HOCH_2CH_2OH/H^+$, Mg/diethyl ether, $D_2O, H_2O/H^+$

(d) $HOCH_2CH_2OH/H^+, DCl, H_2O/H^+$

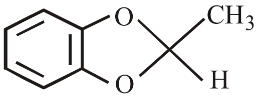
31. What is the product of the following reaction ?



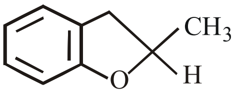
(a) 2 - methyl - 1- pentene
(b) 4 - methyl - 1- pentene
(c) 2 - methyl - 2- propyloxirane
(d) 1 - pentene

32. Which of the following gives ethanal CH_3CHO on acid hydrolysis?

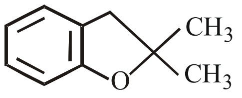
(a)



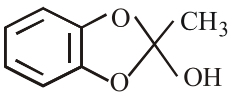
(b)



(c)



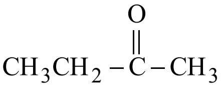
(d)

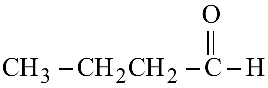


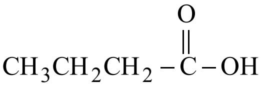
33. Which of the following reacts with $(CH_3CH_2)_2NH$ to give the compound ?

$CH_3CH_2CH = CHN(CH_2CH_3)_2$

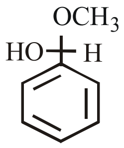
(a) $CH_3CH_2CH_2CH_2Br$

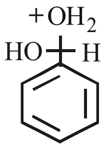
(b)

$CH_3CH_2-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$

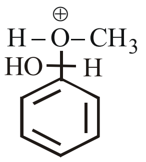
(c)

$CH_3-CH_2CH_2-\overset{\overset{\displaystyle O}{||}}{C}-H$

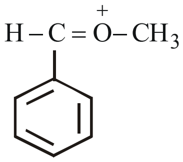
(d)

$CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{||}}{C}-OH$

34. Which of the following is not intermediate in the acid catalysed reaction of benzaldehyde with 2 equivalent of methanol to give acetal ?

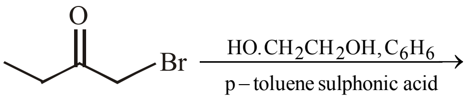
(a)


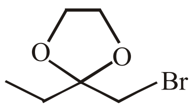
(b)


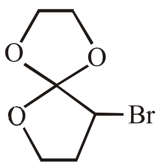
(c)


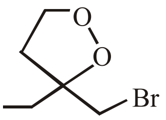
(d)


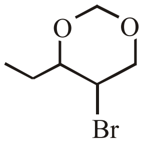
35. What is the product of the reaction shown below



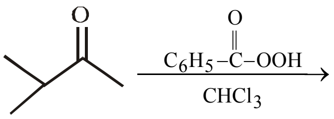
(a)


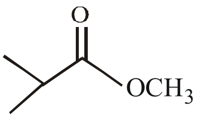
(b)


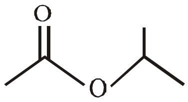
(c)


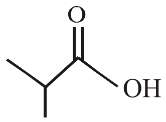
(d)


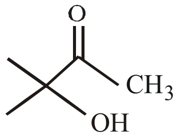
36. The product of the following oxidation reaction



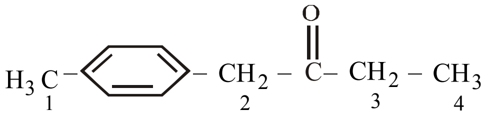
(a)


(b)


(c)


(d)


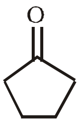
37. The most acidic hydrogen for the following compound

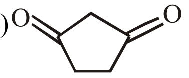


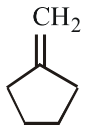
(a) 2 (b) 1

(c) 4 (d) 3

38. Arrange the following in order of decreasing acidity

(A)


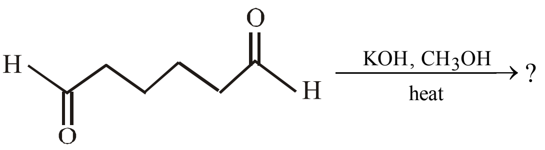
(B)


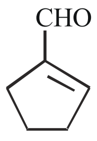
(C)


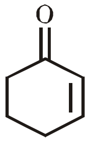
(a) C>A>B (b) C>B>A

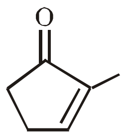
(c) A>C>B (d) A>B>C

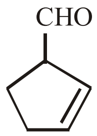
39. What is the product of the following reaction.



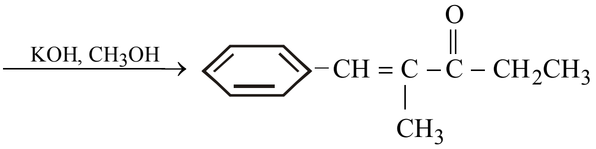
(a)


(b)


(c)


(d)


40. The starting compounds needed to make the following compound ?



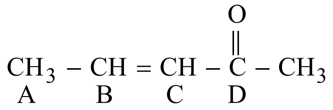
(a) benzaldehyde and 3-pentanone

(b) acetophenone and 2-butanone

(c) acetophenone and butanal

(d) benzaldehyde and 2-pentanone

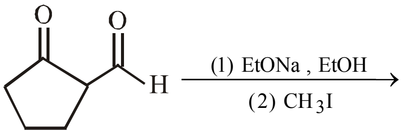
41. Which carbon atoms are most susceptible to nucleophilic attack ?

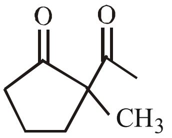


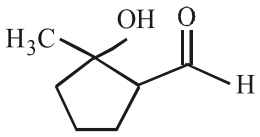
$$\underset{A}{CH_3} - \underset{B}{CH} = \underset{C}{CH} - \underset{D}{\overset{O}{\overset{\|}{C}}} - CH_3$$

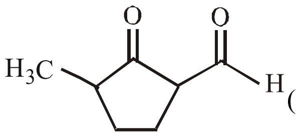
(a) A and B (b) B and C
(c) B and D (d) A and D

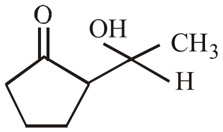
42. What is the product of the following reaction ?



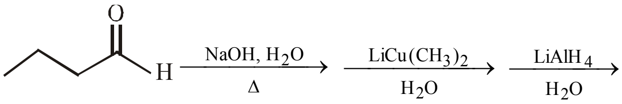
(a) 

(b) 

(c) 

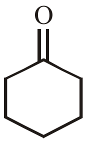
(d) 

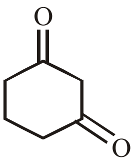
43. The final product of the following sequence of reactions

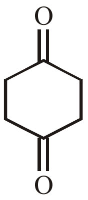


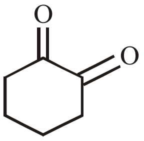
(a) 3-ethyl-2-methyl-1-hexanol
(b) 2, 3-dimethyl-1-pentanol
(c) 2-ethyl-3-methyl-1-hexanol
(d) 3, 3-dimethyl-1-pentanol

44. Which of the following has the largest value of dissociation constant K_a ?

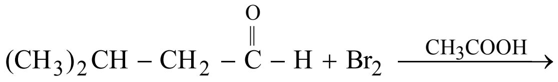
(a) 

(b) 

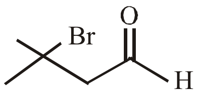
(c) 

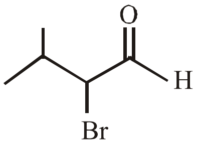
(d) 

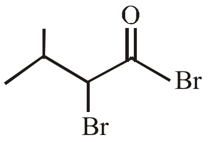
45. What is the product of the reaction given below ?

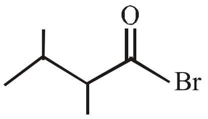


$$(CH_3)_2CH - CH_2 - \overset{O}{\overset{\|}{C}} - H + Br_2 \xrightarrow{CH_3COOH}$$

(a) 

(b) 

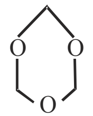
(c) 

(d) 

Hints & Solutions

EXERCISE 1

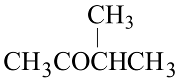
1. $CH_3CHO + HI \xrightarrow[\text{Reduction}]{\text{Red P, high pressure}} CH_3—CH_3 + 2I_2 + H_2O$
2. CH_3CHO does not give Cannizaro's reaction. It is because that it does not have α-hydrogen atom.
5. The compound (A) is 3-pentanone, *i.e.,* $CH_3CH_2COCH_2CH_3$.
6. This is because in aldehyde carbon hydrogen bond cleavage is involved whereas in ketones carbon-carbon bond cleavage is involved.
7. It forms a trimer (metaformaldehyde or trioxane).



Metaformaldehyde (Trioxane)

8. + 1 oxidation state.
10. Nucleophilic addition reactions.
14. Clemmensen reduction and Wolff's-Kishner reduction.
18. **(d)**
19. **(d)**
20 **(c)**
21. **(d)**
22. **(c)**
23. **(c)**
24. **(c)**
25. **(a)**
26. **(a)**
27. **(a)**
28. **(a)**

EXERCISE 2

1. **(b)** Aldehydes and ketones have C = O in which C is sp^2 hybridised.
2. **(d)** $CH_3COCH_2CH_2CH_3$ and  $CH_3CO\overset{CH_3}{CH}CH_3$

chain isomers

$CH_3COCH_2CH_2CH_3$ and $CH_3CH_2COCH_2CH_3$

position isomers or metamers

$CH_3COCH_2CH_2CH_3$ and $CH_3CH_2CH_2CH_2CHO$

functional isomers

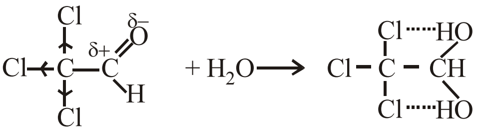
3. **(b)** It has 1° and 2° alcoholic group, but not 3°
4. **(d)**
5. **(c)** (a) $RCOOR' \xrightarrow{H_2O} RCOOH + R'OH$

(b) $RCH_2OH \xrightarrow{\text{Oxidation}} RCHO$

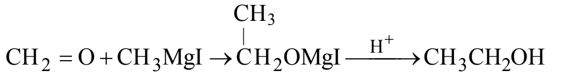
(c) $R_2CHOH \xrightarrow{\text{Oxidation}} R_2CO$

(d) $RX + HOR \rightarrow ROR' + HX$

6. **(b)** 7. **(a)**
8. **(c)** (See Rosenmund reduction)
9. **(b)** 10. **(d)** 11. **(d)** 12. **(c)**
13. **(a)** $C_6H_5CHCl_2 \xrightarrow{H^+/H_2O} [C_6H_5CH(OH)_2] \rightarrow C_6H_5CHO + H_2O$
14. **(a)** ArCOR' can be prepared by the combination of ArH + R'COCl and not by ArCOCl + RMgX because here the ArCOR formed will further react with RMgX to form 3° alcohol, $ArC(OH)R_2$ as the final products.
15. **(b)**
16. **(a)** Alkanenitriles (other than methanenitrile) and benzonitrile give ketones with Grignard reagents.
17. **(a)** 18. **(c)** 19. **(c)** 20. **(b)**
21. **(b)** In acetophenone ($C_6H_5COCH_3$) carbonyl carbon is sterically hindered.
22. **(b)** Three electron withdrawing chlorine atoms increase the positive charge on the carbonyl carbon with the result chloral readily adds weak nucleophile (H_2O) to form chloral hydrate



Further, once chloral hydrate is fomed intramolecular H-bonding between Cl and H atoms of the OH group stabilizes the chloral hydrate molecule

23. **(a)** 24. **(b)** 25. **(b)**
26. **(a)** $6CH_2O + 4NH_3 \rightarrow (CH_2)_6N_4 + 6H_2O$
27. **(d)** With ammonia formaldehyde gives urotroprine (hexamethylene tetramine) acetaldehyde give acetaldehyde ammonia followed by acetaldimine, while acetone gives diacetoneamine.
28. **(a)**  $CH_2 = O + CH_3MgI \rightarrow \overset{CH_3}{CH_2}OMgI \xrightarrow{H^+} CH_3CH_2OH$
29. **(a)** Aldehydes, other than formaldehyde, when treated with RMgX give 2° alcohols

30. (d) 1-Phenylethanol ($CH_3\overset{C_6H_5}{\overset{|}{C}}HOH$) is a 2° alcohol and can be prepared by the reaction of benzaldehyde with Grignard reagent CH_3MgI.

31. (c) *tert*- Alcohols are prepared by the action of Grignard reagent (CH_3MgI) with ketones (CH_3COCH_3)

32. (c) Aldehydes (CH_3CHO) reduce Fehling solution to give red precipitate of cuprous oxide (Cu_2O)

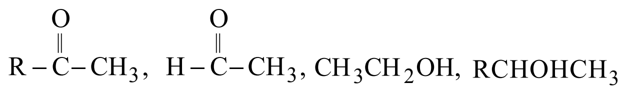
33. (a) Aldehydes (e.g. CH_3CHO) restore the pink colour of Schiff's reagent

34. (b) Schiff's reagent is rosaniline hydrochloride solution whose colour is discharged by passing SO_2 gas .

35. (c) Selenium dioxide oxidises aldehydes and ketones at α-position to carbonyl group.

$$CH_3CHO \rightarrow OHC.CHO$$

36. (b) Iodoform test (haloform test) is given by following types of compounds



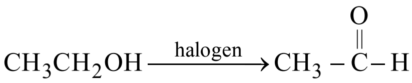
$$R-\overset{O}{\overset{||}{C}}-CH_3,\ H-\overset{O}{\overset{||}{C}}-CH_3,\ CH_3CH_2OH,\ RCHOHCH_3$$

methyl ketones acetaldehyde ethanol 2° alcohols having atleast one R as CH_3

when these are treated with NaOH or KOH and halogen or with sodium or potassium hypohalites (NaOX)

37. (b) $(CH_3)_2C=CHCOCH_3 \xrightarrow{NaOI} (CH_3)_2C=CHCOO^-Na^+ + CHI_3$

38. (b) Among 1° alcohols, only CH_3CH_2OH gives haloform test because only it can be converted into ethanal.

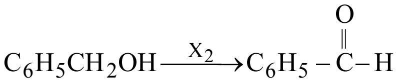


$$CH_3CH_2OH \xrightarrow{halogen} CH_3-\overset{O}{\overset{||}{C}}-H$$

Methanol on oxidation gives methanal (HCHO), having no - $COCH_3$ group.

39. (c) Benzophenone neither has $COCH_3$ group nor it can develop - $COCH_3$ group on oxidation, others either have - $COCH_3$ group or can develop - $COCH_3$ group on oxidation by halogen as $CH_3CH_2OH \rightarrow CH_3CHO$.

40. (d) Benzyl alcohol, $C_6H_5CH_2OH$, neither has - $COCH_3$ group nor can develop the same on oxidation



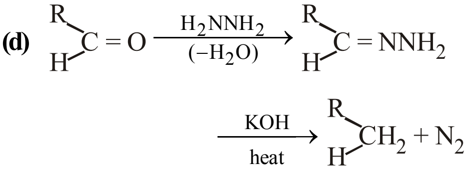
$$C_6H_5CH_2OH \xrightarrow{X_2} C_6H_5-\overset{O}{\overset{||}{C}}-H$$

(no - $COCH_3$ group)

41. (b) **42. (b)**

43. (c) Catalytic reduction, Na/C_2H_5OH and $LiAlH_4$ reduce $\rangle$C=O group to $\rangle$CHOH and not $\rangle CH_2$.

44. (d)

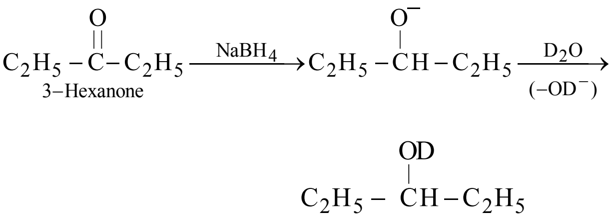


$$\begin{matrix}R\\H\end{matrix}\rangle C=O \xrightarrow[(-H_2O)]{H_2NNH_2} \begin{matrix}R\\H\end{matrix}\rangle C=NNH_2 \xrightarrow[heat]{KOH} \begin{matrix}R\\H\end{matrix}\rangle CH_2 + N_2$$

45. (a) Normally $NaBH_4$ as well as $LiAlH_4$ reduce only –CHO group without effecting carbon-carbon double bond, however when it is present in conjugation with benzene ring and aldehydic group it is also reduced along with the reduction of –CHO group.

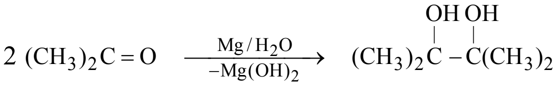
$$C_6H_5CH=CH\,CHO \xrightarrow{LiAlH_4} C_6H_5CH_2CH_2CH_2OH$$

46. (c) Remember that during reduction with $NaBH_4$, a hydride ion is transferred by $NaBH_4$ to carbonyl carbon and a proton (or deutron) is transferred from the solvent (in the second step) to carbonyl oxygen.



$$\underset{\text{3−Hexanone}}{C_2H_5-\overset{O}{\overset{||}{C}}-C_2H_5} \xrightarrow{NaBH_4} C_2H_5-\overset{O^-}{\overset{|}{C}}H-C_2H_5 \xrightarrow[(-OD^-)]{D_2O} C_2H_5-\overset{OD}{\overset{|}{C}}H-C_2H_5$$

47. (b)

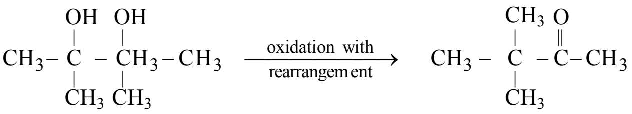


$$2\,(CH_3)_2C=O \xrightarrow[-Mg(OH)_2]{Mg/H_2O} (CH_3)_2\overset{OH}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}(CH_3)_2$$

Acetone 2, 3 -dimethylbutane -2, 3- diol (pinacol)

Since two molecules are reduced to form a single compound, it is known as bimolecular reduction.

48. (b) Pinacolone is oxidation product of pinacol.

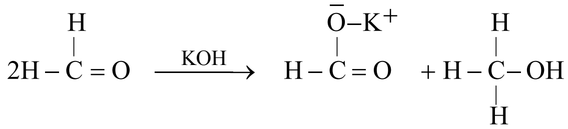


$$CH_3-\underset{CH_3}{\overset{OH}{\overset{|}{\underset{|}{C}}}}-\underset{CH_3}{\overset{OH}{\overset{|}{\underset{|}{C}}}}H_3-CH_3 \xrightarrow[\text{rearrangement}]{\text{oxidation with}} CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{O}{\overset{||}{C}}-CH_3$$

Pinacol Pinacolone

3, 3-dimethyl-2-butanone

49. (c) Cannizzaro reaction is given by aldehydes, not having any α- hydrogen atom. The reagent used is KOH or NaOH and the products formed are the potassium or sodium salt of a carboxylic acid and an aldehyde.



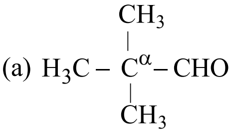
$$2H-\overset{H}{\overset{|}{C}}=O \xrightarrow{KOH} H-\overset{\bar{O}-K^+}{\overset{|}{C}}=O + H-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-OH$$

Formaldehyde Pot. formate Methyl alcohol

50. (c) $2C_6H_5CHO \xrightarrow{NaOH} C_6H_5COO^-Na^+ + C_6H_5CH_2OH$

Benzaldehyde Sod. benzoate Benzyl alcohol

51. (c) Recall that Cannizzaro reaction is given by aldehydes having no α- hydrogen atom, for example $(CH_3)_3CCHO$.

52. (a) (a)

$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^{\alpha}}}-CHO$
2,2 -dimethylpropanal
(not α-H)

(b) $H_3C^{\alpha}-CHO$
acetaldehyde
(α-H)

(c) $CH_3\overset{\alpha}{C}H_2CHO$
propionaldehyde
(α-H)

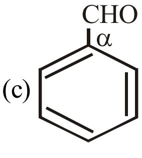
(d) $C_6H_5CH=\overset{\alpha}{C}HCHO$
cinnamaldehyde
(α-H)

53. (b)

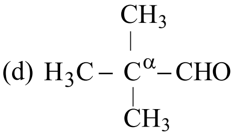
54. (a) Note that only acetaldehyde (CH_3CHO) has α- H atoms, so it will not undergo Cannizzaro reaction.

(a) $\overset{\alpha}{C}H_3CHO$
(α-H)

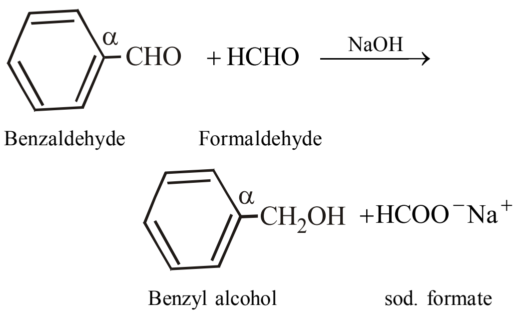
(b) HCHO
(no α- carbon hence no α-H)

(c)


(no α -H)

(d)

$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^{\alpha}}}-CHO$
(no α- H)

55. (a) Benzaldyde and formaldehyde, both do not have α - hydrogen atom, so both will undergo Cannizzaro reaction; here formaldehyde will always be oxidised to formate while the other aldehyde (C_6H_5CHO or any other aldehyde not having α-H, viz- Me_3CCHO) will always be reduced to corresponding alcohol *(crossed Cannizzaro reaction)*

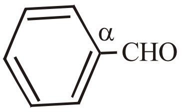


56. (c) Aldehydes having α- H atom, when treated with *aluminium ethoxide* (in place of NaOH or KOH), undergo Cannizzaro type of reaction with a difference that the product isolated is an ester rather than salt of acid or alcohol. Such reaction in called Tischenko reaction.

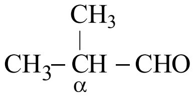
$$\underset{\text{Acetaldehyde}}{2CH_3CHO}\xrightarrow{Al(OC_2H_5)_3}$$

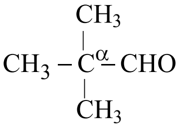
$$[CH_3COOH+CH_3CH_2OH]\to \underset{\text{Ethylacetate}}{CH_3COOC_2H_5}$$

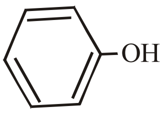
57. (d) Aldol condensation is given by only those aldehydes or ketones which have α-*hydrogen atom on a saturated carbon;* α-H present on unsaturated carbon atom cannot be easily removed by a base.

(a)


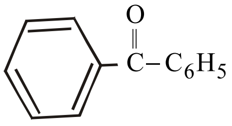
(not α - H)

(b)

$CH_3-\overset{\displaystyle CH_3}{\underset{\alpha}{CH}}-CHO$
(α - H)

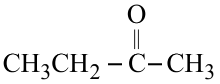
(c)

$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^{\alpha}}}-CHO$
(not α - H)

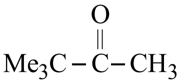
58. (a)


A phenol

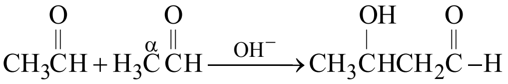
(b)


(no α- H)

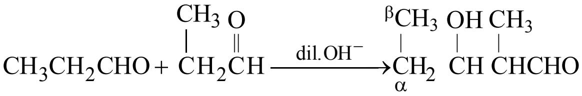
(c)

$CH_3CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$
(α-H)

(d)

$Me_3C-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$
(α-H)

Although (c) and (d) both have α-H, latter does not undergo aldol condensation because of steric hindrance.

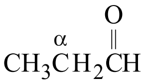
59. (b)

$$CH_3\overset{\displaystyle O}{\overset{\|}{C}}H+H_3\overset{\alpha}{C}\overset{\displaystyle O}{\overset{\|}{C}}H\xrightarrow{OH^-}\underset{\text{Aldol}}{CH_3\overset{\displaystyle OH}{\overset{|}{C}}HCH_2\overset{\displaystyle O}{\overset{\|}{C}}-H}$$

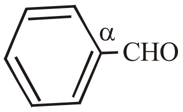
It is the α- H that adds on the carbonyl oxygen of the second carbonyl compound.

60. (d)

$$CH_3CH_2CHO+\overset{\displaystyle CH_3}{\overset{|}{C}}H_2\overset{\displaystyle O}{\overset{\|}{C}}H\xrightarrow{\text{dil.}OH^-}\underset{\alpha}{\overset{^{\beta}CH_3}{\overset{|}{C}H_2}}\ \overset{\displaystyle OH}{\overset{|}{CH}}\ \overset{\displaystyle CH_3}{\overset{|}{C}}HCHO$$

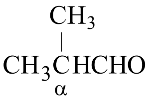
Propanal(2 molecules)

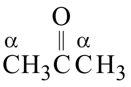
Note that it is the α - part - H (and not β–) that is adding on the carbonyl oxygen of the other propanal molecule.

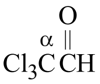
61. (b) (a)

$CH_3\overset{\alpha}{C}H_2\overset{\displaystyle O}{\overset{\|}{C}}H$
(α-H)

(b)


(no α-H)

(c)

$CH_3\overset{\displaystyle CH_3}{\underset{\alpha}{\overset{|}{C}}}HCHO$
(α-H)

(d)

$CH_3\overset{\alpha}{}\overset{\displaystyle O}{\overset{\|}{C}}\overset{\alpha}{C}H_3$
(α-H)

62. (a) (a)

$Cl_3\overset{\alpha}{C}\overset{\displaystyle O}{\overset{\|}{C}}H$
(not α-H)

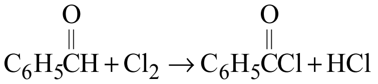
(b) $C_6H_5\overset{\alpha}{C}H_2CHO$
(α-H)

(c) $C_4H_9\overset{\alpha}{C}H_2CHO$
(α-H)

(d) $\overset{\alpha}{C}H_3NO_2$

63. (b) $CH_3CHO + PCl_5 \rightarrow CH_3CHCl_2 + POCl_3$

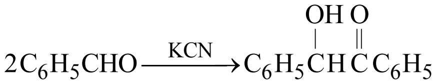
Ethylidene chloride

64. (c) 

$C_6H_5\overset{\overset{O}{\parallel}}{C}H + Cl_2 \rightarrow C_6H_5\overset{\overset{O}{\parallel}}{C}Cl + HCl$

Benzoyl chloride

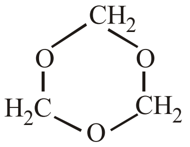
65. (b)

66. (c) 

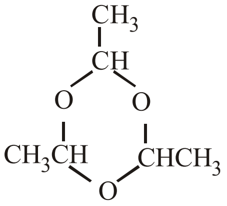
$2C_6H_5CHO \xrightarrow{KCN} C_6H_5\underset{}{\overset{\overset{OH}{|}}{C}H}\overset{\overset{O}{\parallel}}{C}C_6H_5$

Benzoin

67. (b)

68. (b) 

Trioxane

69. (a) 

Paraldehyde

70. (c) (a) Formalin is an aqueous solution of HCHO, hence gives formaldehyde on distillation, trioxane is a trimer and paraformaldehyde is polymer of HCHO and give back HCHO, on heating. *Paraldehyde* is a trimer of acetaldehyde and hence gives acetaldehyde on heating.

71. (a) $3CH_3COCH_3 \xrightarrow[\text{heat}]{\text{conc.} H_2SO_4} \text{Mesitylene}$

72. (b) Acetophenone ($C_6H_5COCH_3$) being a ketone, does not reduce Tollen's reagent.

73. (a)

$$C_6H_5COC_6H_5 + KOH \xrightarrow{\text{fusion}} C_6H_6 + C_6H_5COO^-K^+$$

74. (b) Lucas' test is used for differentiating 1°, 2° and 3° alcohols. Aldehydes and ketones do not respond to Lucas reagent.

75. (a) The complex formed by addition of sodium tartarate to copper sulphate solution is called Fehling solution which gives red precipitate of Cu_2O with aldehydes (CH_3CHO) and not ketones or carboxylic acids.

76. (d) Acetaldehyde and acetone, both (i) respond bromoform test, (ii) do not respond Molisch test (test for carbohydrates), (iii) are insoluble in water. However, acetaldehyde reduces Tollen's reagent to metallic silver while acetone does not.

77. (c) Unsaturation is not detected by Tollen's reagent, a reagent for differentiating between aldehydes and ketones.

78. (a) Sodium bisulphite forms crystalline addition product with acetone but not with acetophenone due to steric hindrance.

79. (b)

Test	$C_4H_9CH_2CHO$ (hexanal)	$CH_3COC_4H_9$ (2- hexanone)
Tollen's reagent	Positive	Negative
Br_2in CCl_4	Negative	Negative
I_2 in NaOH	Negative	Positive
Fehling sol.	Positive	Negative

80. (d) Sodium dihydrogen phosphate (NaH_2PO_4) does not have a lone pair of electrons on the P atom, hence it can't act as a nucleophile and thus does not react with aldehydes and ketones.

81. (c) Although maltose is a disaccharide, its one of glucose units has free –CHO group hence it reduces Fehling solution.

82. (d) Negative reaction with 2, 4- dinitrophenylhydrazine indicates absence of aldehydic (option *a*) and ketonic (option *c*) group, while negative reaction with metallic sodium indicates absence of an alcoholic group (option *b*), hence the organic compound, C_3H_6O is $CH_2 = CHOCH_3$ (option *d*).

83. (c) Reaction with hydroxylamine to form an oxime indicates the presence of a carbonyl group (aldehyde or ketone), but its negative reaction with Tollen's reagent indicates absence of an aldehydic group, hence the compound C_3H_6O should be a ketone, i.e., CH_3COCH_3

84. (c) $HC \equiv CH \xrightarrow[20\%H_2SO_4]{1\%HgSO_4} \underset{[A]}{CH_3CHO} \xrightarrow[H_2O]{CH_3MgX}$

$$\underset{[B]}{CH_3CHOHCH_3} \xrightarrow{[O]} \underset{\text{Acetone}[C]}{CH_3COCH_3}$$

85. (d)

$$CH \equiv CH \xrightarrow[HgSO_4]{30\%H_2SO_4} \underset{[A]}{CH_3CHO}$$

$$\xrightarrow{NaOH} \underset{[B]}{CH_3CHOHCH_2CHO}$$

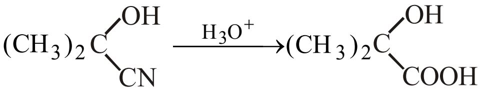
86. (c) $CH_3CHO \xrightarrow{HCN} CH_3CH(OH)CN$

$$\xrightarrow{H^+/H_2O} CH_3\overset{*}{C}H(OH)COOH$$

Lactic acid

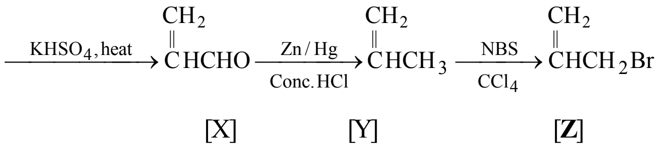
Since the product (lactic acid) has a chiral carbon atom, hence it shows enantiomerism.

87. (a) $(CH_3)_2CO \xrightarrow{NaCN/HCl}$



[A] [**B**]

88. (c) Glycerol



$$\xrightarrow{KHSO_4,\,heat} CH_2=CHCHO \xrightarrow[Conc.\,HCl]{Zn/Hg} CH_2=CHCH_3 \xrightarrow[CCl_4]{NBS} CH_2=CHCH_2Br$$

[X] [Y] [Z]

3-bromopropene

89. (b)

$$C_4H_8 \xleftarrow[(-H_2O)]{Conc.\,H_2SO_4} C_4H_{10}O \xrightarrow{Oxi} C_4H_8O\ (R-COCH_3)$$

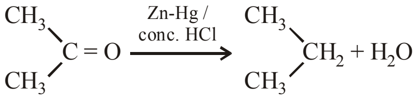
Thus C_4H_8O should be $CH_3CH_2COCH_3$, hence $C_4H_{10}O$ should be $CH_3CH_2CHOHCH_3$

EXERCISE 3

1. **(d)** $>C=O \xrightarrow{Zn\text{-}Hg\ /\ conc.\ HCl} >CH_2 + H_2O$

Clemmensen reduction

e.g.

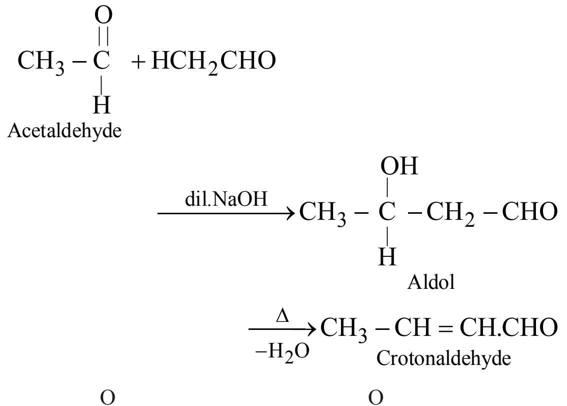


$$(CH_3)_2C=O \xrightarrow{Zn\text{-}Hg\ /\ conc.\ HCl} (CH_3)_2CH_2 + H_2O$$

2. **(a)** Aldehydes containing no α-hydrogen atom on warming with 50% NaOH or KOH undergo disproportionation i.e., self oxidation - reduction known as cannizzaro's reaction.

$$2C_6H_5CHO + NaOH \longrightarrow C_6H_5COONa + C_6H_5CH_2OH$$

3. **(a)** Aldehydes and ketones having at least one α-hydrogen atom in presence of dilute alkali give β-hydroxy aldehyde or β-hydroxy ketone



$$CH_3-\overset{O}{\overset{||}{C}}-H + HCH_2CHO$$

Acetaldehyde

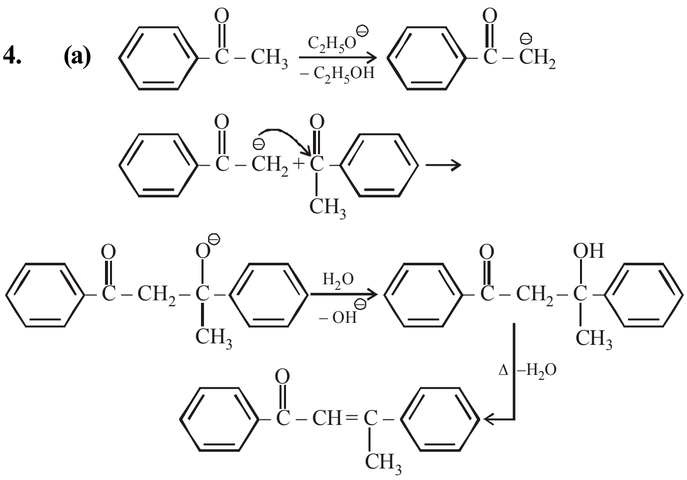
$$\xrightarrow{dil.\,NaOH} CH_3-\underset{H}{\overset{OH}{C}}-CH_2-CHO$$

Aldol

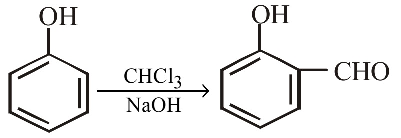
$$\xrightarrow[-H_2O]{\Delta} CH_3-CH=CH.CHO$$

Crotonaldehyde

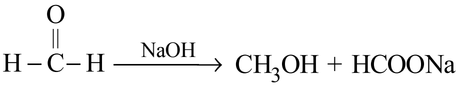
4. **(a)**



5. **(b)** (a)



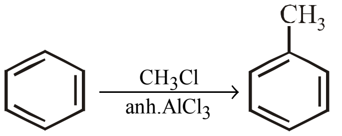
(b)



$$H-\overset{O}{\overset{||}{C}}-H \xrightarrow{NaOH} CH_3OH + HCOONa$$

(c) $2CH_3Cl \xrightarrow[dry\,ether]{Na} CH_3-CH_3$

(d)



Note that new C–C bond is formed in a, c and d.

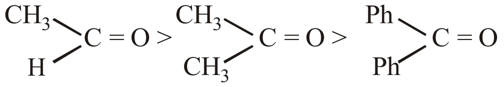
6. **(d)** Among the given compounds only CH_3OH does not give iodoform reaction.

7. **(d)** The intermediate is carbocation which is destabilised by C = O group in the first three cases. In (d), α–hydrogen is more acidic which can be removed as water. Moreover, the positive charge on the intermediate carbocation is relatively away from the C = O group.

8. **(b)** Clemmensen reduction is

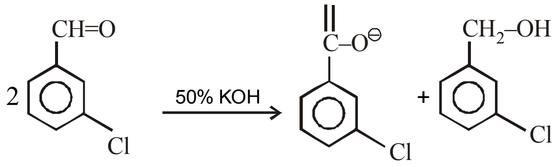
$$>C=O \xrightarrow{Zn\text{–}Hg/HCl} >CH_2$$

9. **(d)** The reactivity of the carbonyl group toward the nucleophilic addition reactions depend upon the magnitude of the positive charge on the carbonyl carbon atom (electronic factor) and also on the crowding around the carbonyl carbon atom in the transition state (steric factor). Both these factors predict the following order

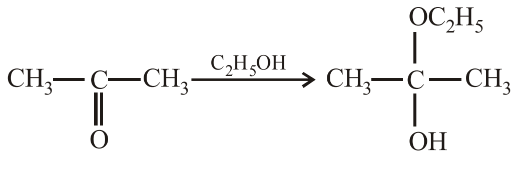


(due to steric crowding).

10. **(c)** Cannizzaro reaction - when an aldehyde containing no α – H undergo reaction in presence of 50% KOH. It disproportionates to form a molecule of carboxylic acid and a molecule of alcohol.

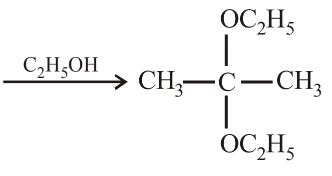


11 **(d)** Anhydrous alcohols add to the carbonyl group of aldehydes in the presence of anhydrous hydrogen chloride to form acetals via hemiacetals.



$$CH_3-\underset{O}{\underset{||}{C}}-CH_3 \xrightarrow{C_2H_5OH} CH_3-\underset{OH}{\overset{OC_2H_5}{C}}-CH_3$$

Hemiacetal



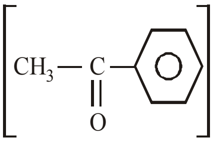
$$\xrightarrow{C_2H_5OH} CH_3-\underset{OC_2H_5}{\underset{|}{\overset{OC_2H_5}{\overset{|}{C}}}}-CH_3$$

Acetal

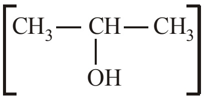
12. **(d)** $R-CH=O+H_2N-NH_2 \rightarrow R-CH=N-NH_2$

Such reactions take place in slightly acidic medium and involve nucleophilic addition of the ammonia derivative.

13. **(b)** It is iodoform reaction. Acetophenone



and 2-Hydroxypropane



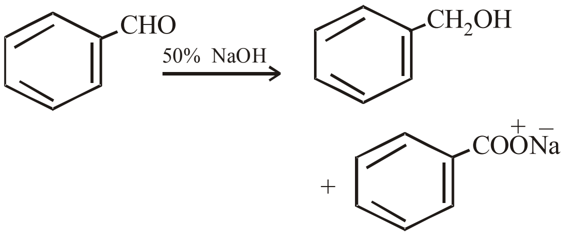
$$\left[CH_3-\underset{OH}{\underset{|}{CH}}-CH_3\right]$$

both give a yellow precipitate of CHI_3 (iodoform) with iodine and alkali.

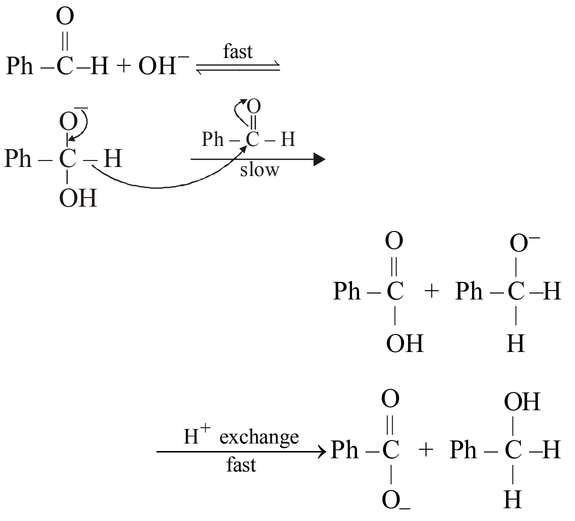
14. **(c)** Zn/Hg and HCl reduce carboxyl group to methylene group (Clemmensen reduction).

15. **(b)** Aldehydic group gets oxidised to carboxylic group. Double bond breaks and carbon gets oxidised to carboxylic group.

16. **(b)**



17. **(a)**

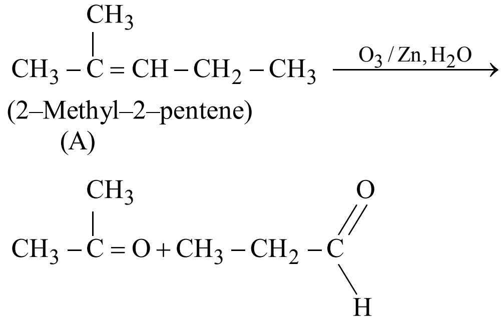


$$Ph-\overset{O}{\overset{||}{C}}-H+OH^- \xrightleftharpoons{fast}$$

$$Ph-\underset{OH}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-H \xrightarrow[slow]{Ph-\overset{O}{\overset{||}{C}}-H} Ph-\underset{OH}{\underset{|}{\overset{O}{\overset{||}{C}}}} + Ph-\underset{H}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-H$$

$$\xrightarrow[fast]{H^+\ exchange} Ph-\underset{O^-}{\underset{|}{\overset{O}{\overset{||}{C}}}} + Ph-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-H$$

18. **(c)** From the products formed it is clear that the compound has 5 carbon atoms with a double bond and methyl group on 2nd carbon atom.



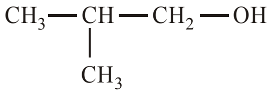
$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_3 \xrightarrow{O_3/Zn,H_2O}$$

(2–Methyl–2–pentene)
(A)

$$CH_3-\overset{CH_3}{\overset{|}{C}}=O+CH_3-CH_2-C\begin{matrix}\nearrow O\\ \searrow H\end{matrix}$$

Acetone Propionaldehyde

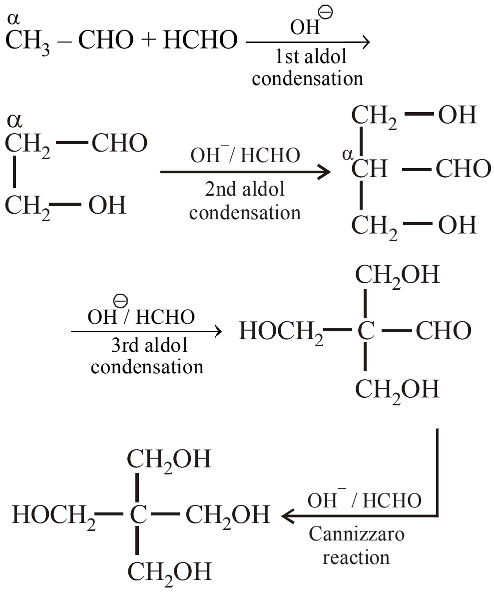
19. **(d)** Iodoform test is given by methyl ketones, acetaldehyde and secondary alcohols which contain – CH_3 groups at carbon containing – OH group.



$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-OH$$

isobutyl alcohol is a primary alcohol hence does'nt give positive iodoform test.

20. **(c)**



$$\overset{\alpha}{CH_3}-CHO+HCHO \xrightarrow[\text{1st aldol condensation}]{OH^{\ominus}} \begin{matrix}\overset{\alpha}{CH_2}-CHO\\ |\\ CH_2-OH\end{matrix} \xrightarrow[\text{2nd aldol condensation}]{OH^-/HCHO} \begin{matrix}CH_2-OH\\ |\\ \overset{\alpha}{CH}-CHO\\ |\\ CH_2-OH\end{matrix}$$

$$\xrightarrow[\text{3rd aldol condensation}]{OH^{\ominus}/HCHO} HOCH_2-\underset{CH_2OH}{\underset{|}{\overset{CH_2OH}{\overset{|}{C}}}}-CHO \xrightarrow[\text{Cannizzaro reaction}]{OH^-/HCHO} HOCH_2-\underset{CH_2OH}{\underset{|}{\overset{CH_2OH}{\overset{|}{C}}}}-CH_2OH$$

EXERCISE 4

1. **(a)** $C_6H_5CH_3 \xrightarrow{CrO_3} [C_6H_5CHO] \xrightarrow{(CH_3CO)_2O}$

$$C_6H_5CH(OCOCH)_3 \xrightarrow[H_2O]{OH^-} C_6H_5CHO+2CH_3COONa$$

2. **(b)**

$$C_6H_6+HCN+HCl \xrightarrow{\text{anhy. }ZnCl_2} [C_6H_5CH=NH] \rightarrow C_6H_5CHO$$

3. **(a)** Reactivity of carbonyl group toward nucleophilic addition reactions increases as the magnitude of positive charge on the carbonyl carbon decreases. Thus presence of electron withdrawing group on carbonyl carbon increases the reactivity while electron pushing group decreases the reactivity. Reactivity also decreases with increase in size of the group present on the carbonyl carbon.

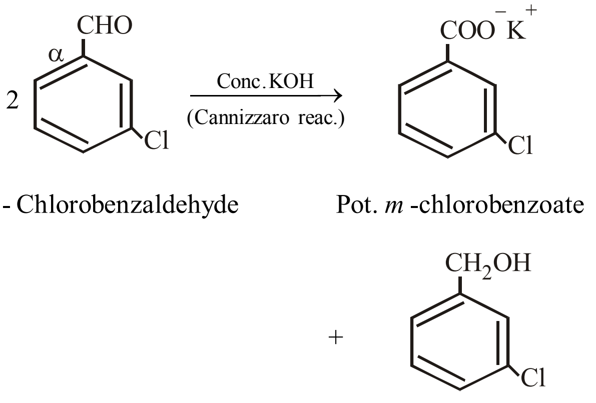
4. **(b)** $-NO_2$ group is electron withdrawing which enchances the addition of CN^- ion (a nucleophilic additon reaction).

5. **(a)** $CH_3COCH_3 \xrightarrow{SeO_2} CH_3COCHO$

6. **(c)** Wurtz reaction is the *condensation* of alkyl halides with metallic sodium in presence of dry ether to form *higher hydrocarbons.* Carbonyl compounds (aldehydes and ketones) can be converted into hydrocarbons by means of Clemensen reduction (Zn + Hg/HCl), Wolf-Kishner reduction (NH_2NH_2/OH^-) and heating with HI and red P at about 200° C.

7. **(b)** Like clemmensen reduction, Wolf-Kishner reduction involves reduction of $>C=O$ to $>CH_2$, of course by different reagent.

8. **(d)**



m - Chlorobenzaldehyde

Pot. *m* -chlorobenzoate

m- Chlorobenzyl alcohol

9. **(b)** This is intramolecular Cannizzaro's reaction.

10. **(c)** (I) $\underset{\text{1-phenylethanol}}{CH_3CHOHC_6H_5} \xrightarrow{Oxi} \underset{\text{Acetophenone}}{CH_3COC_6H_5}$

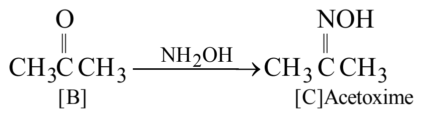
(II) $C_6H_5CHO + CH_3MgBr \rightarrow \underset{\text{1-phenylethanol}}{C_6H_5CHOHCH_3}$

(III) $C_6H_6 + CH_3COCl \xrightarrow{anh. AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3}$

(IV) $\underset{\text{Cal. benzoate}}{(C_6H_5COO)_2Ca} \xrightarrow{distil} \underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + CaCO_3$

11. **(c)** Acetophenone gives all the four given reactions thus statement III and IV are wrong, i.e., option *(c)* is correct.

12. **(d)** $CH_3COOH \xrightarrow{CaCO_3} \underset{[A]}{(CH_3COO)_2Ca} \xrightarrow{heat}$



$$\underset{[B]}{CH_3\overset{\overset{O}{\|}}{C}CH_3} \xrightarrow{NH_2OH} \underset{[C]\text{Acetoxime}}{CH_3\overset{\overset{NOH}{\|}}{C}CH_3}$$

13. **(c)** Since compound A (C_3H_6O) undergoes iodoform test, it must be CH_3COCH_3 (propanone). Further the compound B obtained from A has three times the number of carbon atoms in A (propanone), B must be phorone, i.e., 2, 6-dimethyl 2, 5- heptadien -4- one.

$$\underset{\text{A, propanone (3 molecules)}}{(CH_3)_2C = O + H_3CCOCH_3 + O = C(CH_3)_2}$$

$$\xrightarrow{HCl} \underset{\text{2, 6-dimethyl- 2,5 -heptadiene-4-one}}{(CH_3)_2C = CHCOCH = C(CH_3)_2}$$

14. **(a)** $\underset{A}{C_3H_8O} \xrightarrow{K_2Cr_2O_7/H^+} \underset{B(-CHO)}{C_3H_6O} \xrightarrow{H_2NCONHNH_2} C$

Since B reduces Tollen's reagent, it indicates that it has an –CHO group, so it must be CH_3CH_2CHO. Hence

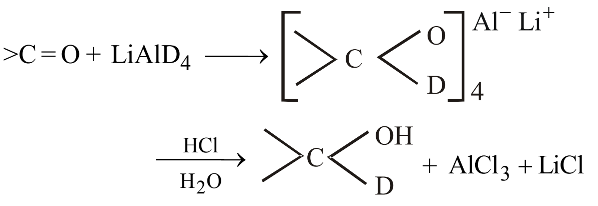
$$\underset{[A]}{CH_3CH_2CH_2OH} \rightarrow \underset{[B]}{CH_3CH_2CHO} \xrightarrow{H_2NNHCONH_2}$$

$$\underset{[C]}{CH_3CH_2CH = NNHCONH_2}$$

15. **(c)** 16. **(c)**

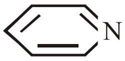
17. **(b)** $LiAlH_4$ reduces $>C = O \longrightarrow >CHOH$, group without affecting the double bond.

18. **(b)**



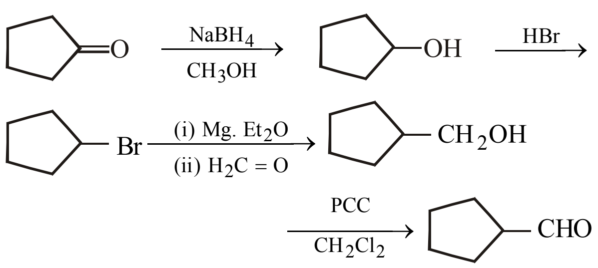
$$>C=O + LiAlD_4 \longrightarrow \left[>C<\begin{matrix}O\\D\end{matrix}\right]_4 Al^- Li^+$$

$$\xrightarrow[H_2O]{HCl} >C<\begin{matrix}OH\\D\end{matrix} + AlCl_3 + LiCl$$

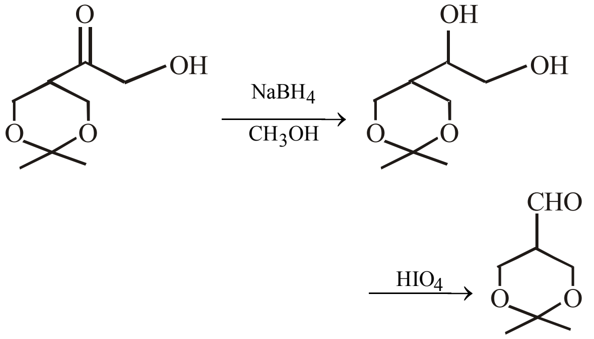
19. **(c)** Pyridinium chloro chromate selectively oxidises a primary alcohol to an aldehyde  N. CrO_3HCl e.g.

$$RCH_2OH \xrightarrow[CH_2Cl_2]{PCC} RCHO$$

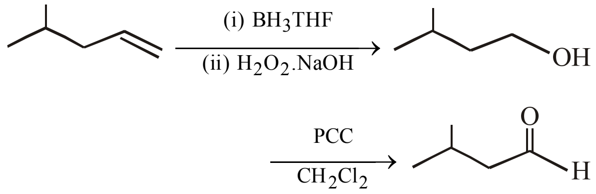
20. **(a)**



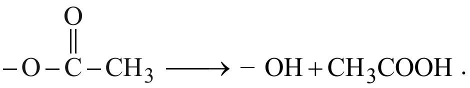
21. **(c)**



22. (a)



23. (b) $LiAlH_4$/ether will convert $-CHO \longrightarrow CH_2OH$ and hydrolysis will convert

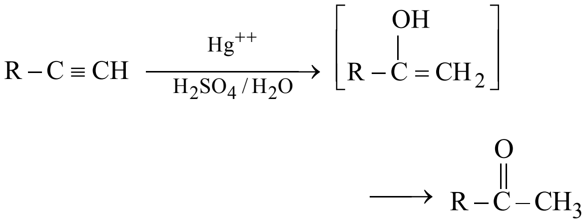


$$-O-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow -OH+CH_3COOH.$$

24. (c) CH_3CH_2OH contains active hydrogen and will react with Grignard's reagent.

$$CH_3CH_2OH + R\,MgX \longrightarrow CH_3CH_2OMgX + RH$$

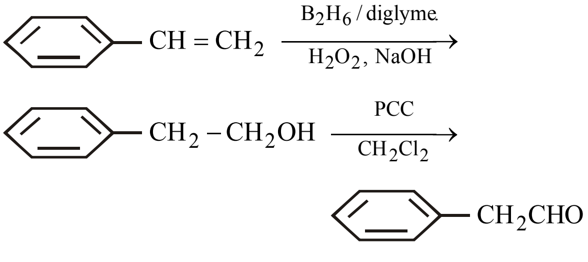
25. (b)



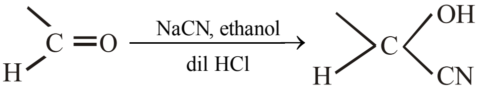
$$R-C\equiv CH \xrightarrow[H_2SO_4/H_2O]{Hg^{++}} \left[R-\overset{\overset{OH}{|}}{C}=CH_2\right] \longrightarrow R-\overset{\overset{O}{\|}}{C}-CH_3$$

26. (c) When you open the ring, you get 5-hydroxy-2-heptanone.

27. (a)



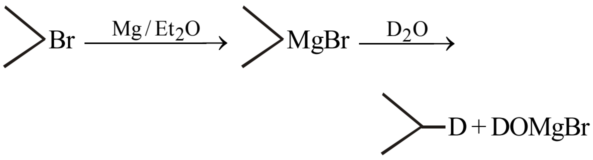
28. (a)



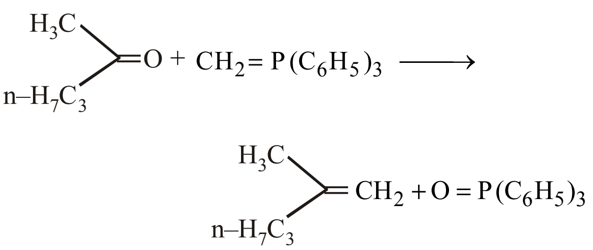
Cyanohydrin

29. (c) Open the ring containing oxygen atoms you will get the products.

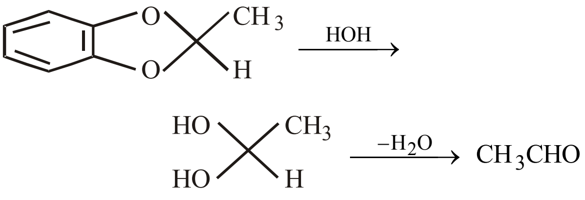
30. (a)



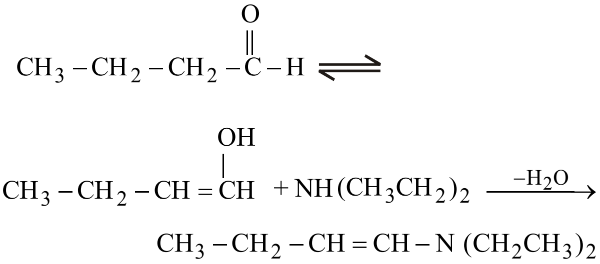
31. (a)



32. (a)

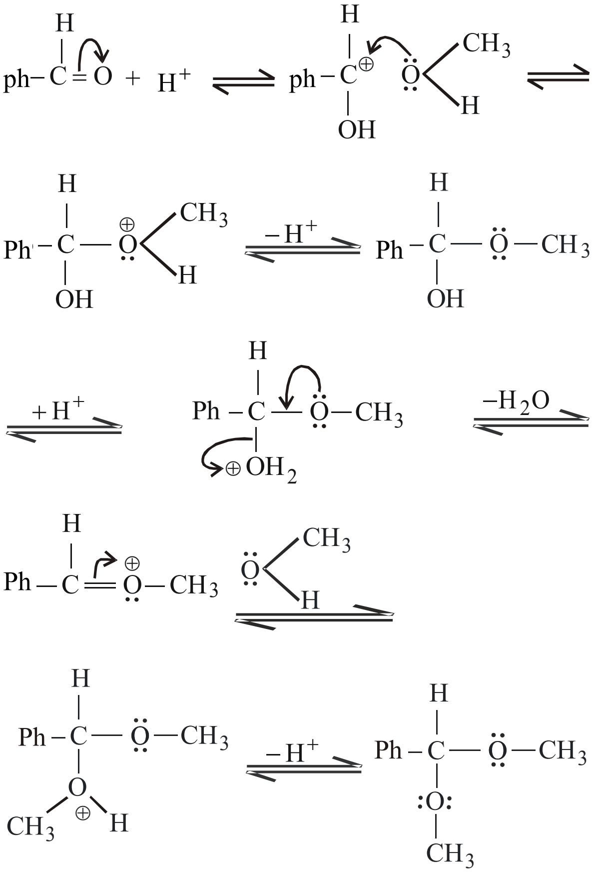


33. (c)

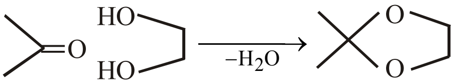


$$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H \rightleftharpoons CH_3-CH_2-CH=\overset{\overset{OH}{|}}{C}H + NH(CH_3CH_2)_2 \xrightarrow{-H_2O} CH_3-CH_2-CH=CH-N(CH_2CH_3)_2$$

34. (b)



35. (a) The product is cyclic Ketal

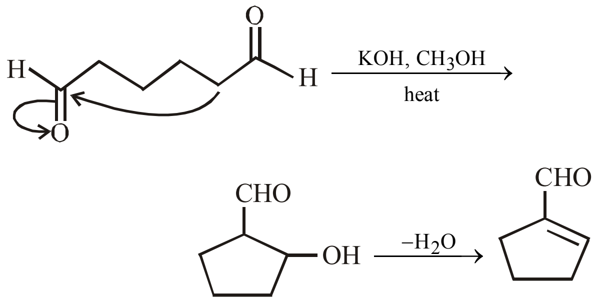


36. (b)

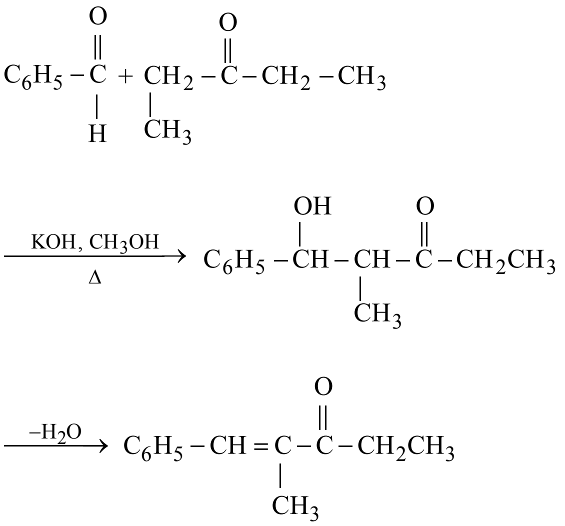
37. (a) Hydrogen atoms attached C_2 are most acidic due to presence of electrons withdrawing groups on both sides.

38. (a) (C) contains the most reactive methylene group followed by (A) then (B).

39. (a) It is an example of intramolecular aldol condensation



40. (a)

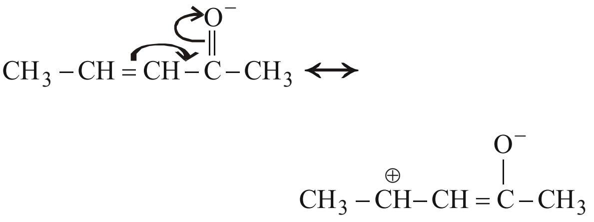


$$C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}} + \underset{\underset{CH_3}{|}}{CH_2}-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

$$\xrightarrow[\Delta]{KOH,\ CH_3OH} C_6H_5-\overset{\overset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-CH_2CH_3$$

$$\xrightarrow{-H_2O} C_6H_5-CH=\underset{\underset{CH_3}{|}}{C}-\overset{\overset{O}{\|}}{C}-CH_2CH_3$$

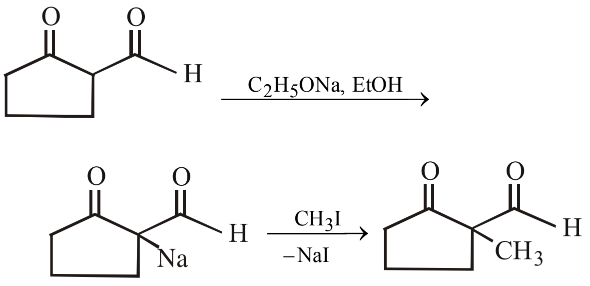
41. (c)



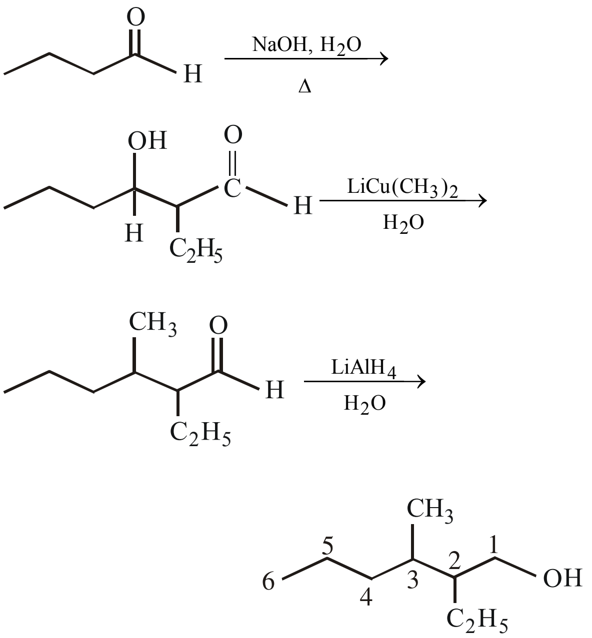
$$CH_3-CH=CH-\overset{\overset{O^-}{\|}}{C}-CH_3 \longleftrightarrow$$

$$CH_3-\overset{\oplus}{CH}-CH=\overset{\overset{O^-}{|}}{C}-CH_3$$

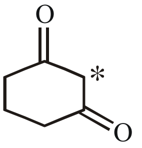
42. (a)



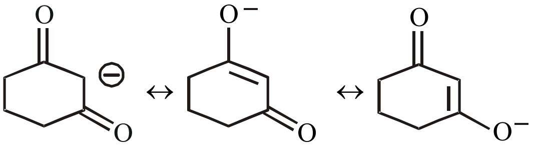
43. (c)



44. (b)

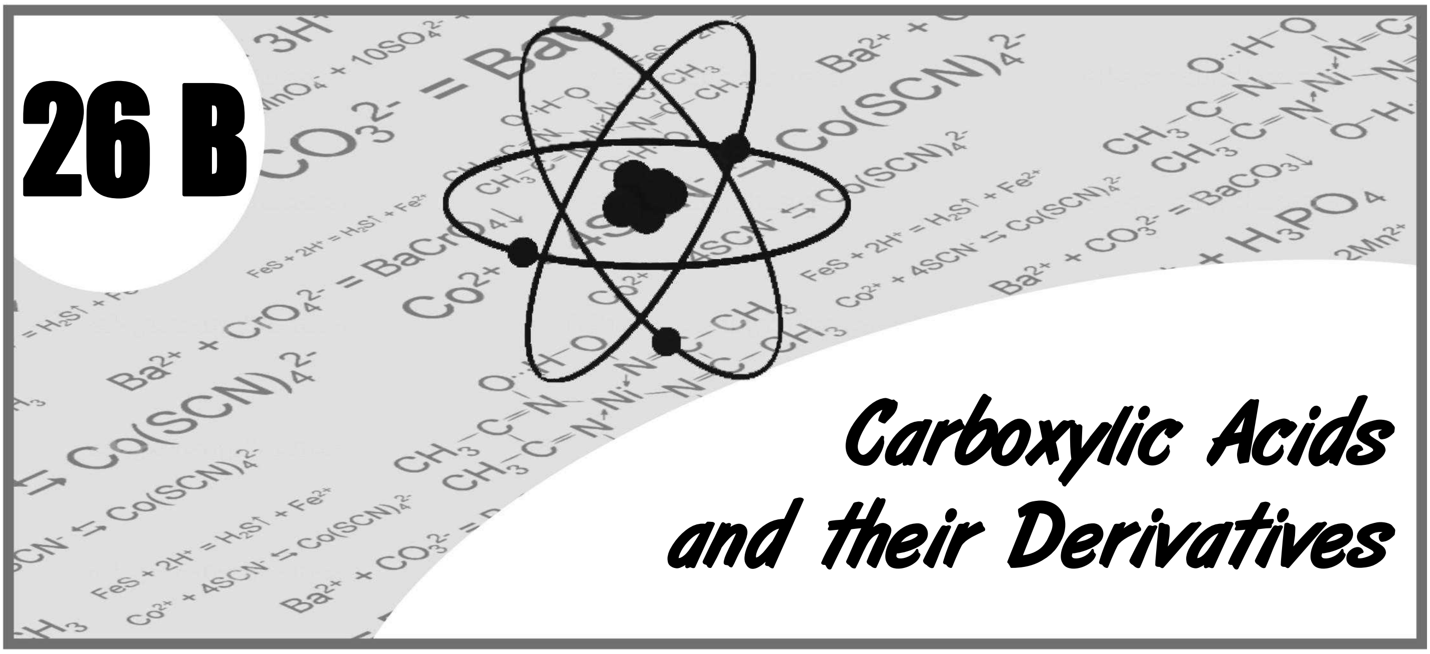


It contains the most reactive methylene group (*) and resulting anion is stabilised by resonance



45. (b) The reaction will give α – bromo substituted product.

❑❑❑



26 B

Carboxylic Acids and their Derivatives

The compounds containing the carboxyl functional group $-\overset{\overset{O}{||}}{C}-OH$ are called **Carboxylic** acids. The word carboxyl is a combination of two words carbonyl (>C=O) and hydroxyl (–OH).

CLASSIFICATION :

Depending upon the number of –COOH groups they are classified as (i) Manocarboxylic acids: containing one - COOH group (ii) dicarboxylic acids: containing two -COOH groups and so on

Fatty acids: Aliphatic monocarboxylic acids are commonly called fatty acids because higher members are obtained by the hydrolysis of oils and fats.

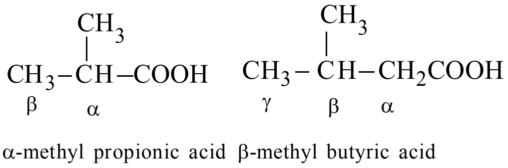
NOMENCLATURE :

There are three ways of naming carboxylic acids

(i) ***Common System:*** The common names are derived from the source of acids.

Formula	Common name	Source
HCOOH	Formic acid	Red ant (formica)
CH_3COOH	Acetic acid	Vineger (acetium)
C_3H_7COOH	Butyric acid	Butter (butyrum)

The position of substituents are indicated by Greek letters α, β, γ etc. The carbon atom adjascent to carboxyl group is assigned the letter α, the next β and so on

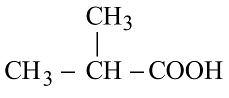


$$\underset{\beta}{CH_3}-\underset{\alpha}{\overset{\overset{CH_3}{|}}{CH}}-COOH \qquad \underset{\gamma}{CH_3}-\underset{\beta}{\overset{\overset{CH_3}{|}}{CH}}-\underset{\alpha}{CH_2}COOH$$

α-methyl propionic acid β-methyl butyric acid

(ii) ***Derived System:*** Acids are regarded as alkyl derivatives of acetic acid eg

$CH_3.CH_2COOH$	$C_6H_5CH_2.COOH$
methyl acetic acid	Phenyl acetic acid



$$CH_3-\overset{\overset{CH_3}{|}}{CH}-COOH$$

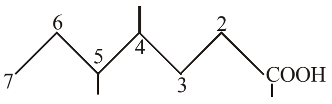
Dimethyl acetic acid

(iii) ***IUPAC System:*** they are named as Alkanoic acids eg.

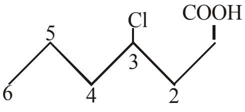
HCOOH Methanoic acid

C_3H_7COOH Butanoic acid

While naming the complex acids, the longest chain is picked up and the carbon atoms are numbered starting from carboxyl group which is given number 1.



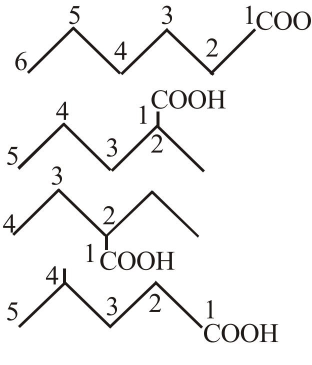
4, 5 - dimethyl heptanoic acid



3 - Chloro hexanoic acid

Isomerism: They exhibit

(i) Position and chain Isomerism eg. $C_6H_{12}O_2$ represent



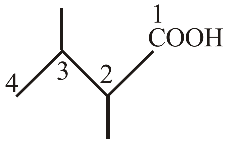
1-Hexanoic acid

2-methyl pentanoic acid

2-ethyl butanoic acid

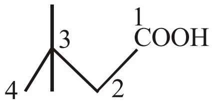
4-methyl pentanoic acid

Position isomers

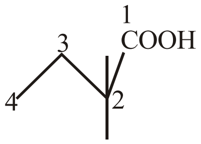


2, 3 - dimethyl butanoic acid

All the seven are chain Isomers

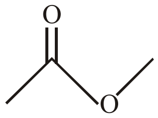
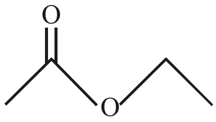
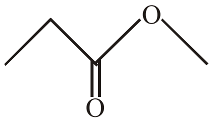


3, 3 - dimethyl butanoic acid



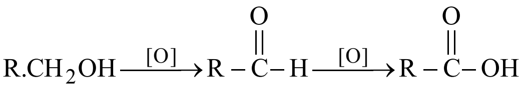
2, 2 - dimethyl butanoic acid

(ii) Functional Isomerism

Formula	Functional	Isomers	
$C_3H_6O_2$	 Propanoic acid	 methylacetate	
$C_4H_8O_2$	 butanoic acid	 ethyl ethanoate	 methyl propanoate

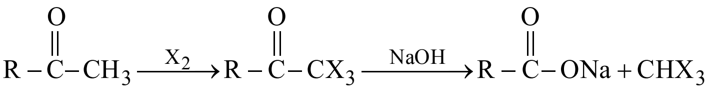
GENERAL METHODS OF PREPARATION:

(i) ***Oxidation*** of 1° alcohols and aldehydes with acid $K_2Cr_2O_7$ or $KMnO_4$



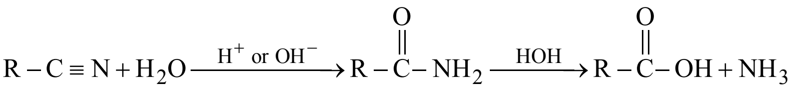
$$R.CH_2OH \xrightarrow{[O]} R-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{[O]} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

(ii) ***Oxidation of methyl ketones*** (Haloform reaction) with X_2/NaOH



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{X_2} R-\overset{\overset{\displaystyle O}{\|}}{C}-CX_3 \xrightarrow{NaOH} R-\overset{\overset{\displaystyle O}{\|}}{C}-ONa + CHX_3$$

(iii) ***Hydrolysis of cyanides :*** Hydrolysis may be effected by acid or alkali



$$R-C\equiv N + H_2O \xrightarrow{H^+ \text{ or } OH^-} R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow{HOH} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NH_3$$

(iv) ***Hydrolysis of an ester:*** with alkali or acid

Ester $RCOOR' + H_2O \xrightarrow{H^+ \text{ or } OH^-} RCOOH + R'OH$

Acid chloride $RCOCl + H_2O \xrightarrow{H^+ \text{or } OH^-} RCOOH + HCl$

Acid amide $RCONH_2 + H_2O \xrightarrow{H^+ \text{or } OH^-} RCOOH + NH_3$

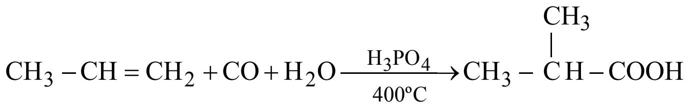
Anhydride $(RCO)_2O + H_2O \xrightarrow{H^+} 2RCOOH$

- Ease of hydrolysis $RCOCl > (RCO)_2O > RCOOR' > RCONH_2$
- Alkaline hydrolysis of an ester is known as **saponification**

(v) ***Hydrolysis of trihalogen derivative of alkanes***

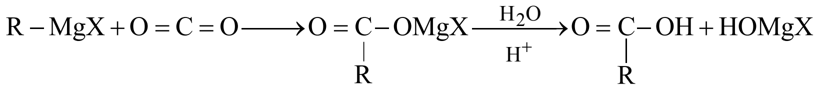
$$R.CCl_3 + 3NaOH \longrightarrow RC(OH)_3 \xrightarrow{-H_2O} R-\overset{\overset{\displaystyle O}{||}}{C}-OH$$

(vi) ***Carboxylation of alkenes (Koch reaction)***



$$CH_3-CH=CH_2+CO+H_2O \xrightarrow[400^\circ C]{H_3PO_4} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-COOH$$

(vii) ***Reaction of Grignard Reagents with CO_2***



$$R-MgX+O=C=O \longrightarrow O=\underset{\underset{\displaystyle R}{|}}{C}-OMgX \xrightarrow[H^+]{H_2O} O=\underset{\underset{\displaystyle R}{|}}{C}-OH+HOMgX$$

(viii) ***By heating sodium alkoxide with CO***

$$RONa+CO \xrightarrow[\text{pressure}]{160^\circ C} RCOONa \xrightarrow{HCl} RCOOH+NaCl$$

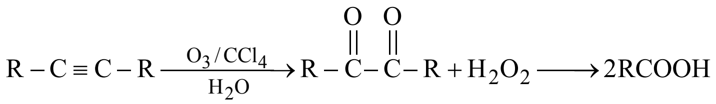
(ix) ***From Sodium alkyl and CO_2***

$$C_2H_5Na+CO_2 \longrightarrow C_2H_5COONa \xrightarrow{HCl} C_2H_5COOH+NaCl$$

(x) ***Catalytic oxidation of long chain hydrocarbons***

$$R.CH_3+O_2 \xrightarrow[(CH_3COO)_2\,Mn]{120^\circ C} RCOOH+H_2O$$

(xi) ***From alkynes***



$$R-C\equiv C-R \xrightarrow[H_2O]{O_3/CCl_4} R-\overset{\overset{\displaystyle O}{||}}{C}-\overset{\overset{\displaystyle O}{||}}{C}-R+H_2O_2 \longrightarrow 2RCOOH$$

(xii) ***By heating dicarboxylic acids eg oxalic acid or malonic acid***

$$(COOH)_2 \xrightarrow{\Delta} HCOOH+CO_2$$

(xiii) ***By acidic hydrolysis of Malonic or aceto acetic ester***

$$RCH(COOC_2H_5)_2 \xrightarrow{H^+} RCH(COOH)_2 \xrightarrow{\Delta} RCH_2.COOH$$

$$CH_3CO.CHR.COOC_2H_5 \xrightarrow{NaOH} CH_3COOH+RCH_2COOH+C_2H_5OH$$

MANUFACTURE OF METHANOIC ACID :

$$NaOH+CO \xrightarrow[\text{under 8 atm.}]{150^\circ C} HCOONa \xrightarrow{H_2SO_4} HCOOH+NaHSO_4$$

MANUFACTURE OF ACETIC ACID :

(i) ***By air oxidation of Acetaldehyde***

$$2CH_3CHO+O_2 \xrightarrow[50-70^\circ C]{(CH_3COO)_2\,Mg} 2CH_3COOH$$

(ii) ***By air oxidation of Butane***

$$CH_3CH_2\,CH_2.CH_3+O_2 \xrightarrow[200^\circ C]{(CH_3COO)_2\,Co} 2CH_3COOH$$

(iii) ***Quick vinegar process***

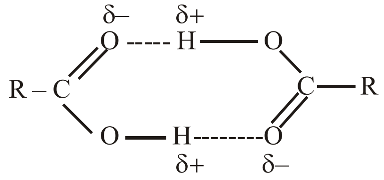
$$2CH_3CH_2OH+O_2 \xrightarrow{\text{aceti.Bacterium}} 2CH_3CHO+2H_2O \xrightarrow[\text{aceti.B}]{O_2} 2CH_3COOH$$

The production is limited to the production of vinegar only which is 5 to 7% acetic acid

Glacial acetic acid: Pure acetic acid when cooled forms ice like solid (glacier) hence it is called **glacial acetic** acid

GENERAL PROPERTIES :

Acids upto C_{10} are liquids with unpleasant odours. The higher members are colourless waxy solids. Boiling points of acids increase regularly with molecular weight and higher than alcohols (of comparable molecular mass) due to formation of dimer through H-bonding



Solubility :

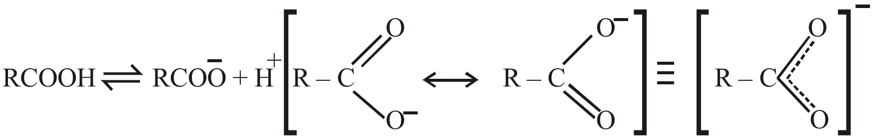
Acids upto C_4 are completely soluble in water due to H-bonding. Solubility regularly decreases rapidly due to increase in hydrophobic character of alkyl group.

Melting points :

The melting point of even number acid is always higher than the next lower and higher odd number acid (**alternation effect or oscillation effect**) due to effective crystal lattice being symmetrical in nature*

ACIDITY OF CARBOXYLIC ACIDS :

The carboxylic acids on ionisation produce carboxylate ion which is stabilised by resonance

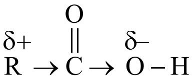


Carboxylate ion

Resonance hybrid

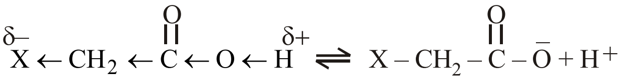
- Electrons releasing alkyl groups decrease the acidity. Hence lower members are more acidic than higher members eg $HCOOH > CH_3COOH > C_2H_5COOH > C_3H_7COOH$

As the size of alkyl group increases the ionic character of O-H bond decreases



$$\overset{\delta+}{R} \rightarrow \overset{\overset{O}{\|}}{C} \rightarrow \overset{\delta-}{O} - H$$

Electrons withdrawing substituents increase the acidity by increasing the ionic character of – O – H bond by inductive effect and dispersing the negative charge of anion formed



$$\overset{\delta-}{X} \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow \overset{\delta+}{H} \rightleftharpoons X - CH_2 - \overset{\overset{O}{\|}}{C} - \bar{O} + H^+$$

Acid	pK_a	Acid	pK_a
Formic acid	3.75	Trifluoro acetic acid	0.23
Acetic acid	4.76	Bromo acetic acid	2.9
Propionic acid	4.87	lodo acetic acid	3.16
n-Butyric acid	4.82	α-chloropropionic acid	2.80
Isobutyric acid	4.86	β-Chloropropionic acid	4.08
Chloro acetic acid	2.85	Nitro acetic acid	1.68
Dichloro acetic acid	1.25	Hydroxy acetic acid	3.83
Trichloro acetic acid	0.66	Hydro chloric acid	–7.00

The smaller the value of pK_a, the stronger is the acid

CHEMICAL PROPERTIES :

R.COOH ⟶

$$\xrightarrow{Na} RCOONa + 1/2\ H_2$$
$$\xrightarrow{NaOH} RCOONa + H_2O$$
$$\xrightarrow{NaHCO_3} RCOONa + H_2O + CO_2 \text{ (Test for acids also)}$$

Salt formation

$$\xrightarrow{PCl_5} RCOCl + POCl_3 + HCl$$
$$\xrightarrow{PCl_3} RCOCl + H_3PO_3$$
$$\xrightarrow{SOCl_2} RCOCl + SO_2 + HCl$$

Acid chloride

$$\xrightarrow{NH_3} RCOONH_4 \xrightarrow{\Delta} RCONH_2 \underset{\text{amide}}{\xrightarrow{P_2O_5}} RCN$$
$$\xrightarrow{P_2O_5} (RCO)_2O + H_2O \text{ (Anhydride)}$$
$$\xrightarrow{R'OH/H_2SO_4} RCOOR' + H_2O \text{ (Ester formation)}$$
$$\xrightarrow{NaOH+CaO} RH + CO_2 \text{ (Decarboxylation)}$$
$$\xrightarrow{LiAlH_4} R.CH_2OH \text{ (Reduction)}$$
$$\xrightarrow{HI/Red\,P} RCH_3 \text{ (Reduction)}$$
$$\xrightarrow{Cl_2/P \text{ or } Br_2/P} RCHCl.COOH \text{ or } RCHBrCOOH \text{ (HVZ reaction)}$$

α – halogenated acid (**Hell volhard zelinsky** reaction)

$$\xrightarrow{\text{Ca Salt distillation.}} RCOR \text{ (Ketone)}$$
$$\xrightarrow{\text{K or Na Salt Electrolysed}} R-R \text{ (at anode)}$$

Kolbe's electrolytic method

$$\xrightarrow{Ag\ Salt/Br_2\ a\ Cl_2/CCl_4} RBr \text{ or } RCl$$ (**Hunsdiecker's** reaction)

REDUCING CHARACTER OF FORMIC ACID :

(1) $$\underset{\text{Fehling Solution}}{HCOO^- + 2Cu^{2+}} + 5OH^- \longrightarrow \underset{\text{Red ppt.}}{Cu_2O} + CO_3^{2-} + 3H_2O$$

$$\underset{\text{Tollen's reagent}}{HCOO^- + 2Ag^+ + 3OH^-} \longrightarrow \underset{\text{Silver mirror}}{2Ag} + CO_3^{2-} + 2H_2O$$

$$2KMnO_4 + 3H_2SO_4 + 5HCOOH \longrightarrow K_2SO_4 + MnSO_4 + 8H_2O + 5CO_2$$

$$2HgCl_2 + HCOOH \longrightarrow Hg_2Cl_2 + 2HCl + CO_2$$

ACTION OF HEAT ON FORMATES:

Sodium formate $2HCOONa \xrightarrow{\Delta} \begin{array}{l} COONa \\ | \\ COONa \end{array} + H_2$

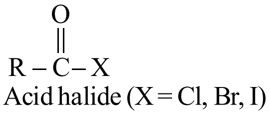
Sod. oxalate

Calcium formate $(HCOO)_2Ca \xrightarrow{\Delta} HCHO + CaCO_3$

Ammonium formate $HCOONH_4 \xrightarrow{\Delta} HCONH_2 + H_2O$

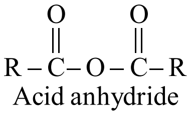
ACID DERIVATIVES

The compounds obtained by replacing –OH group of $-\overset{\overset{O}{||}}{C}-OH$ in acid by –X, –OCOR, –OR or –NH_2 are called acid derivatives. They are



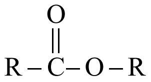
$R-\overset{\overset{O}{||}}{C}-X$

Acid halide (X = Cl, Br, I)



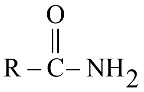
$R-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-R$

Acid anhydride



$R-\overset{\overset{O}{||}}{C}-O-R$

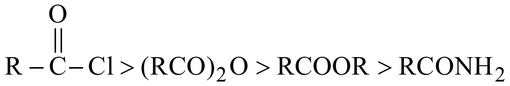
Ester



$R-\overset{\overset{O}{||}}{C}-NH_2$

Acid amide

The order of reactivity for nucleophilic substitution reactions (known as acyl substitution reactions) is as follows



$$R-\overset{\overset{O}{||}}{C}-Cl > (RCO)_2O > RCOOR > RCONH_2$$

The factors affecting the above order are (i) **Inductive effect** (ii) **Resonance** and (iii) **Nature of leaving group**. The more the basic character of the leaving group, the lesser is the reactivity and basic character follows the order

$$NH_2^- > \bar{O}R > RCOO^- > Cl^-$$

ACID CHLORIDES :

IUPAC name Alkanoyl Chloride

Formula	Comon name	IUPAC name
$HCOCl$	Formyl Chloride	Methanoyl Chloride
CH_3COCl	Acetyl Chloride	Ethanoyl Chloride
C_6H_5COCl	Benzoyl Chloride	Benzoyl chloride

HCOCl is unstable and combination of $(CO + HCl) \rightarrow$ HCOCl act as formyl chloride

Methods of preparation

(i) ***From acids***

$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2\uparrow + HCl\uparrow$

$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$

(ii) ***From Salts (Industrial method)***

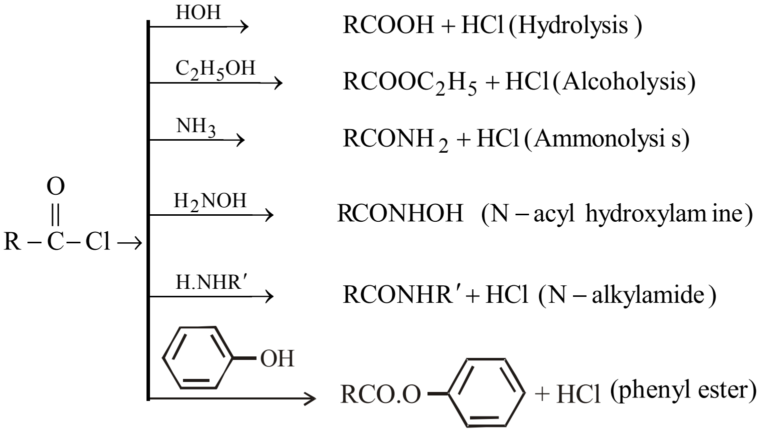
$3RCOONa + PCl_3 \longrightarrow 3RCOCl + Na_3PO_3$

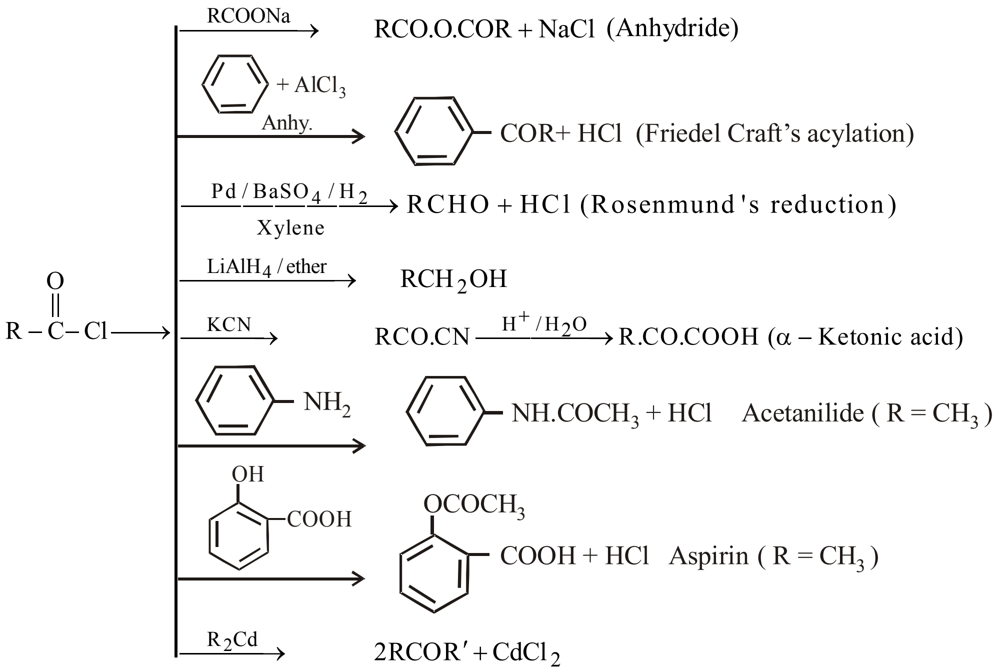
$2RCOONa + PCl_3 \longrightarrow 2RCOCl + NaPO_2 + NaCl$

$(RCOO)_2Ca + SO_2Cl_2 \longrightarrow 2RCOCl + CaSO_4$

Properties : Acid Chlorides are polar in nature, still insoluble in water due to absence of hydrogen bonding which is also the reason of their having low b.p. than acids.

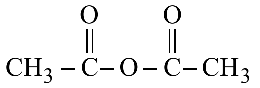
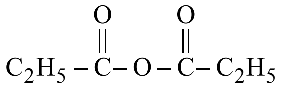
Chemical properties:





Uses (i) As acylating agent (ii) Determination of $-NH_2$ and OH group in a molecule

ACID ANHYDRIDE $(RCO)_2O$: IUPAC name Alkanoic anhydride

Formula	Common name	IUPAC name
 $CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$	Acetic anhydride	Ethanoic anhydride
 $C_2H_5-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-C_2H_5$	Propionic anhydride	Propanoic anhydride

Methods of preparation :

(i) $2RCOOH \xrightarrow[\Delta]{P_2O_5} (RCO)_2O + H_2O$

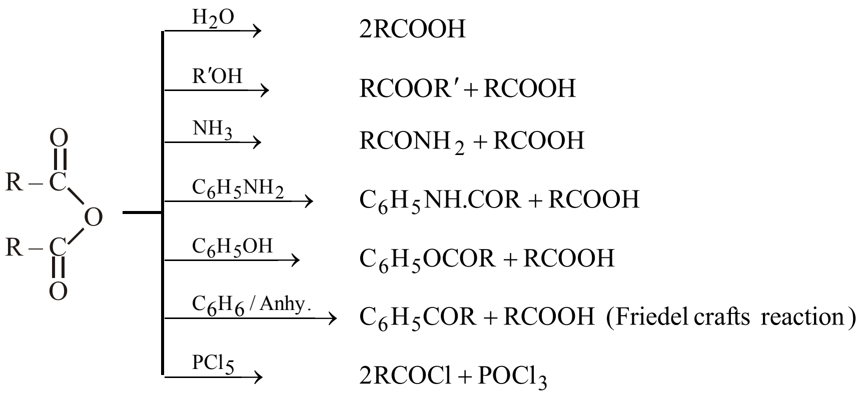
(ii) $RCOONa + RCOCl \longrightarrow (RCO)_2O + NaCl$

$RCOONa + R'COCl \longrightarrow RCO.O.COR' + NaCl$ (mixed anhydride)

(iii) $\underset{\text{Ketene}}{CH_2=C=O} + CH_3COOH \longrightarrow \underset{\text{acetic anhydride}}{(CH_3CO)_2O}$ (Industrial method)

Properties: The anhydrides are colourless liquids with irritating smell. Insoluble in water but soluble in organic solvents.

Chemical properties:



$\xrightarrow{HCl} RCOCl + RCOOH$

$\xrightarrow{CH_3CHO} CH_3CH(OCOR)_2$ ethylidene derivative

$\xrightarrow{[O]} RCO-O-O-COR$ acyl peroxide

$\xrightarrow{LiAlH_4/ether} 2R.CH_2OH$

$\xrightarrow{N_2O_5} RCO.ONO_2$ acyl nitrate

Uses: Acetic anhydride is used as acetylating agent in the manufacture of plastics, cellulose acetate and polyvinyl acetate.

ESTERS :

IUPAC name alkyl alkanoate

Formula	Common name	IUPAC name
$CH_3COOC_2H_5$	ethyl acetate	ethyl ethanoate
CH_3COOCH_3	methyl acetate	methyl ethanoate

Methods of preparation

1. $RCOCl + R'OH \longrightarrow RCOOR' + HCl$
2. $(RCO)_2O + R'OH \longrightarrow RCOOR' + RCOOH$
3. $RCOOH + R'OH \xrightarrow{H^+} RCOOR' + H_2O$
4. $RCOOH + CH_2N_2 \longrightarrow RCOOCH_3 + N_2$

Properties: Esters are pleasant smelling liquids sparingly soluble in water soluble in alcohol and ether.

Chemical properties

$R-\overset{\overset{O}{||}}{C}-OR \longrightarrow$

$\xrightarrow{H^+/H_2O} RCOOH + ROH$ (Hydrolysis)

$\xrightarrow{NaOH/H_2O} RCOONa + ROH$ (Saponification)

$\xrightarrow[pyridine]{PCl_5 \text{ or } SOCl_2} RCOCl + RCl$

$\xrightarrow{NH_3} RCONH_2 + ROH$ (Ammonolysis)

$\xrightarrow{Na/Alcohol} RCH_2OH + ROH$ (Bouveault – Blanc reduction)

$\xrightarrow{R'OH/R'ONa \text{ or } \overset{+}{H}} RCOOR' + ROH$ (Trans esterification or Alcoholysis)

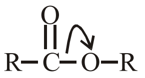
$\xrightarrow{H_2N\ NH_2 \text{ Hydrazine}} RCONH.NH_2 + ROH$ (Acid hydrazide)

$\xrightarrow{R'COOH} R'COOR + RCOOH$ (Acidolysis)

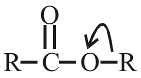
Note. Alcoholysis is usually effective in replacing a higher alcohol by lower one eg.

$$CH_3COOC_4H_9 + C_2H_5OH \xrightleftharpoons{C_2H_5ONa} CH_3COOC_2H_5 + C_4H_9OH$$

Hydrolysis of carboxylic esters may be formulated in two ways



acyl-oxygen heterolysis



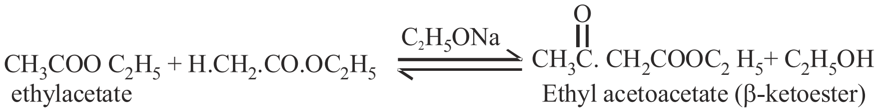
alkyl-oxygen heterolysis

B_{AC^2} and A_{AC^2} Base or acid catalysed bimolecular involving acyl-oxygen heterolysis are very common

A_{Al^1} Acid catalysed unimolecular involving alkyl-oxygen heterolysis is very common for t-alcohols

B_{Al^1} occurs in solvent having high ionizing power and alcohol forms stable carbonium ion.

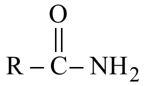
Claisen condensation: Intermolecular condensation of esters containing α-hydrogen atom in presence of strong base to form β-keto ester



$$\underset{\text{ethylacetate}}{CH_3COO\,C_2H_5 + H.CH_2.CO.OC_2H_5} \xrightleftharpoons{C_2H_5ONa} \underset{\text{Ethyl acetoacetate (β-ketoester)}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}.\,CH_2COOC_2\,H_5 + C_2H_5OH}$$

Uses of esters. In making artificial essences and flavours.

AMIDES :



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

IUPAC Name Alkanamide

Formula	**Common name**	**IUPAC name**
$HCONH_2$	Formamide	Methanamide
CH_3CONH_2	Acetamide	Ethanamide

Methods of preparation:

i. $RCOOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow{\Delta} RCONH_2 + H_2O$ (lab method)

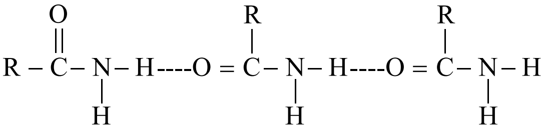
ii. $RCOCl + NH_3 \longrightarrow RCONH_2 + HCl$

iii. $(RCO)_2O + NH_3 \longrightarrow RCONH_2 + RCOOH$

iv. $RCOOR + NH_3 \longrightarrow RCONH_2 + ROH$

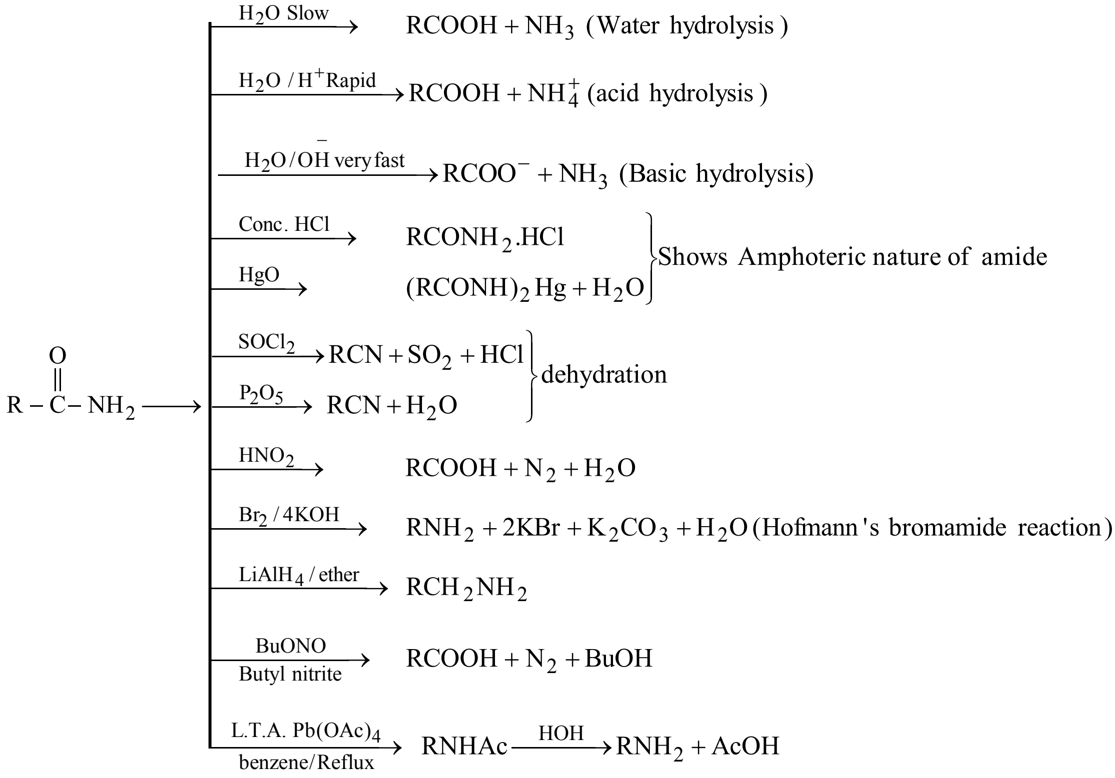
v. $RCN + H_2O \xrightarrow[H_2O_2]{\text{Alkaline}} RCONH_2$ (by partial hydrolysis)

Properties: Except formamide, amides are colourless, crystalline solids, lower members are soluble in water and alcohol. Their m.p.are higher due to hydrogen bonding



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-H\text{----}O=\overset{\overset{\displaystyle R}{|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-H\text{----}O=\overset{\overset{\displaystyle R}{|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-H$$

Chemical properties:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \longrightarrow$$

$$\xrightarrow{H_2O\ \text{Slow}} RCOOH + NH_3 \text{ (Water hydrolysis)}$$

$$\xrightarrow{H_2O\,/H^+\text{Rapid}} RCOOH + NH_4^+ \text{ (acid hydrolysis)}$$

$$\xrightarrow{H_2O/\overset{-}{O}H\ \text{very fast}} RCOO^- + NH_3 \text{ (Basic hydrolysis)}$$

$$\left.\begin{array}{l} \xrightarrow{\text{Conc. HCl}} RCONH_2.HCl \\ \xrightarrow{HgO} (RCONH)_2Hg + H_2O \end{array}\right\}\text{Shows Amphoteric nature of amide}$$

$$\left.\begin{array}{l} \xrightarrow{SOCl_2} RCN + SO_2 + HCl \\ \xrightarrow{P_2O_5} RCN + H_2O \end{array}\right\}\text{dehydration}$$

$$\xrightarrow{HNO_2} RCOOH + N_2 + H_2O$$

$$\xrightarrow{Br_2\,/4KOH} RNH_2 + 2KBr + K_2CO_3 + H_2O \text{ (Hofmann's bromamide reaction)}$$

$$\xrightarrow{LiAlH_4\,/\,\text{ether}} RCH_2NH_2$$

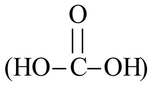
$$\xrightarrow[\text{Butyl nitrite}]{BuONO} RCOOH + N_2 + BuOH$$

$$\xrightarrow[\text{benzene/Reflux}]{\text{L.T.A. }Pb(OAc)_4} RNHAc \xrightarrow{HOH} RNH_2 + AcOH$$

Uses: In leather tanning and paper industry, preparation of nitrogen compounds.

UREA, CARBAMIDE ($H_2N.CO.NH_2$) :

It is diamide of carbonic acid

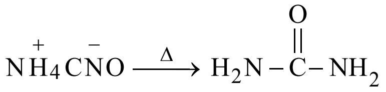


$$(HO-\overset{\overset{\large O}{||}}{C}-OH)$$

Urea is the normal end product of protein metabolism and excreted in urine about 30 gm in 24 hours by an adult person.

Preparation:

(i) Wohler synthesised in 1828, urea the first organic compound by heating ammonium cyanate

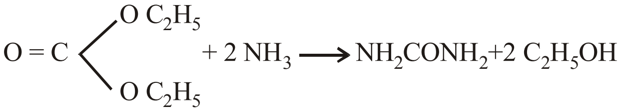


$$\overset{+}{N}H_4\overset{-}{CNO} \xrightarrow{\Delta} H_2N-\overset{\overset{\large O}{||}}{C}-NH_2$$

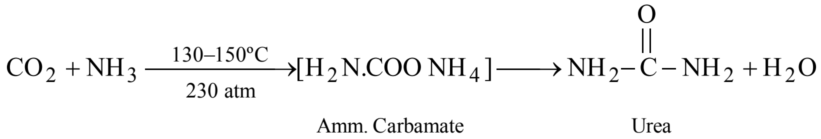
Ammonium Cyanate Urea

(ii) By the action of ammonia on phosgene, ethyl carbonate, chloroformate or Urethanes.

$$COCl_2 + 2NH_3 \longrightarrow H_2N.CONH_2 + 2HCl$$



(iii) ***Manufacture:***

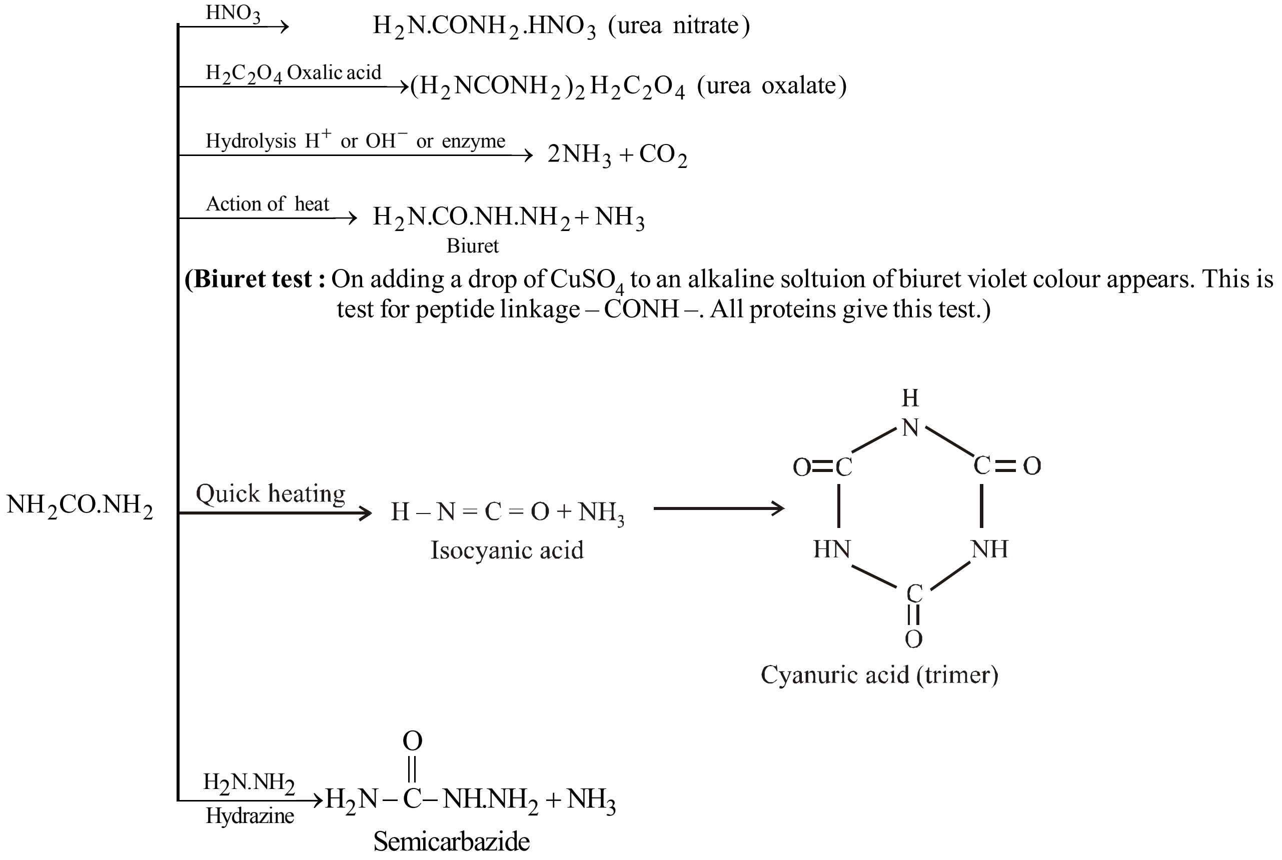


$$CO_2 + NH_3 \xrightarrow[230 \text{ atm}]{130\text{–}150°C} \underset{\text{Amm. Carbamate}}{[H_2N.COO\,NH_4]} \longrightarrow \underset{\text{Urea}}{NH_2-\overset{\overset{\large O}{||}}{C}-NH_2} + H_2O$$

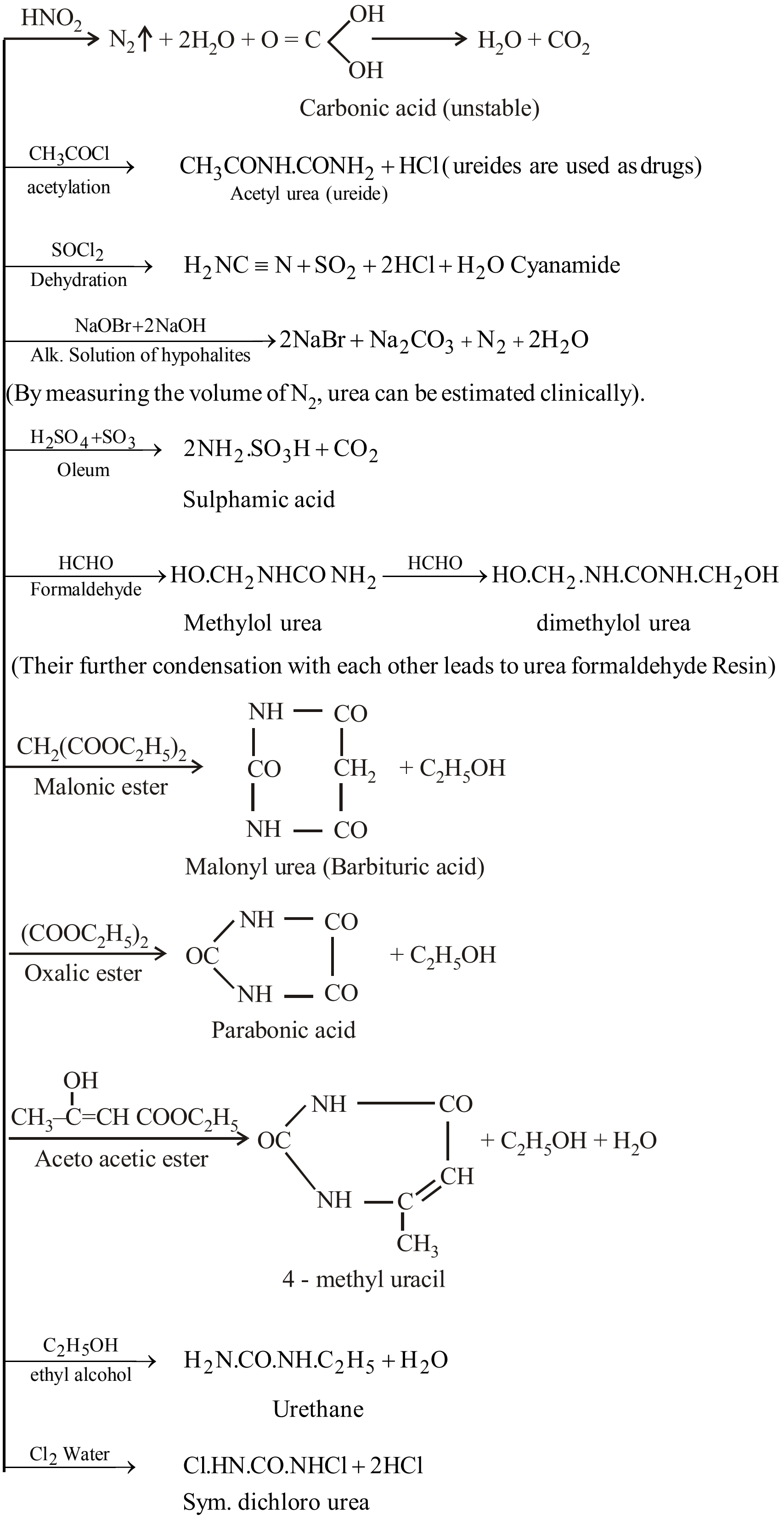
$$\text{or, } \underset{\text{Cal. Carbide}}{CaC_2} \xrightarrow{N_2} \underset{\text{Cal. Cyanamide}}{CaCN_2} \xrightarrow{H_2SO_4} \underset{\text{Cyanamide}}{H_2N.C \equiv N} \xrightarrow{H_2O} \underset{\text{Urea}}{H_2N.CONH_2}$$

Properties: White crystalline solid mpt 132°C soluble in water, alcohol, insoluble in ether. It is mono acidic base.

Chemical properties:



(**Biuret test :** On adding a drop of $CuSO_4$ to an alkaline soltuion of biuret violet colour appears. This is test for peptide linkage – CONH –. All proteins give this test.)



$$\xrightarrow{HNO_2} N_2\uparrow + 2H_2O + O=C(OH)_2 \longrightarrow H_2O + CO_2$$

Carbonic acid (unstable)

$$\xrightarrow[\text{acetylation}]{CH_3COCl} \underset{\text{Acetyl urea (ureide)}}{CH_3CONH.CONH_2} + HCl \text{ (ureides are used as drugs)}$$

$$\xrightarrow[\text{Dehydration}]{SOCl_2} H_2NC\equiv N + SO_2 + 2HCl + H_2O \text{ Cyanamide}$$

$$\xrightarrow[\text{Alk. Solution of hypohalites}]{NaOBr+2NaOH} 2NaBr + Na_2CO_3 + N_2 + 2H_2O$$

(By measuring the volume of N_2, urea can be estimated clinically).

$$\xrightarrow[\text{Oleum}]{H_2SO_4+SO_3} 2NH_2.SO_3H + CO_2$$

Sulphamic acid

$$\xrightarrow[\text{Formaldehyde}]{HCHO} HO.CH_2NHCO\,NH_2 \xrightarrow{HCHO} HO.CH_2.NH.CONH.CH_2OH$$

Methylol urea dimethylol urea

(Their further condensation with each other leads to urea formaldehyde Resin)

$$\xrightarrow[\text{Malonic ester}]{CH_2(COOC_2H_5)_2} \text{Malonyl urea} + C_2H_5OH$$

Malonyl urea (Barbituric acid)

$$\xrightarrow[\text{Oxalic ester}]{(COOC_2H_5)_2} \text{Parabonic acid} + C_2H_5OH$$

Parabonic acid

$$\xrightarrow[\text{Aceto acetic ester}]{CH_3-C(OH)=CH\,COOC_2H_5} \text{4 - methyl uracil} + C_2H_5OH + H_2O$$

4 - methyl uracil

$$\xrightarrow[\text{ethyl alcohol}]{C_2H_5OH} H_2N.CO.NH.C_2H_5 + H_2O$$

Urethane

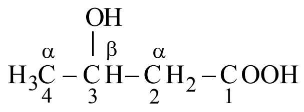
$$\xrightarrow{Cl_2 \text{ Water}} Cl.HN.CO.NHCl + 2HCl$$

Sym. dichloro urea

Uses: (i) It is used as fertilizer (ii) making barbiturates (iii) urea formaldehyde resin (iii) To improve octane number (v) Stabilizer for explosives.

SUBSTITUTED ACIDS

The acids obtained by replacing one or more hydrogen atoms from the alkyl group of the acid by groups such as Cl, OH, CN, NH_2 etc are known as substituted acids. The position of the latter is indicated by Greek letters like α, β, γ, δ etc (common system) or by numbers like 1, 2, 3 etc (IUPAC System) eg.

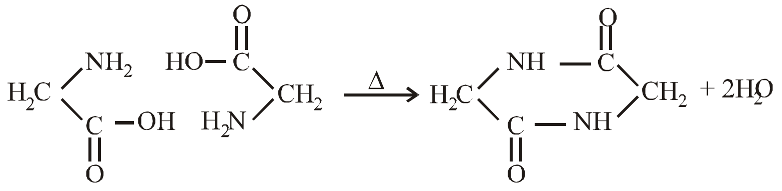


$$\overset{4}{H_3C}-\overset{3}{CH}(OH)-\overset{2}{CH_2}-\overset{1}{COOH}$$

β - hydroxybutyric acid (common)
3 - hydroxy butanoic acid (IUPAC)

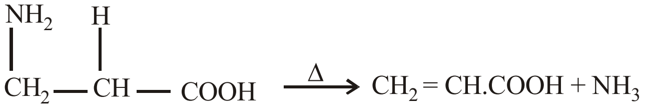
Distinction between different substituted acids can be made by the application of heat

(i) ***α-Amino acids***



Glycine Diketopiperazine

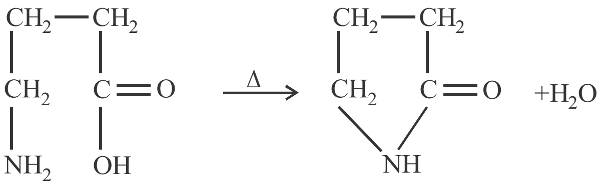
(ii) ***β–Amino acids***



$$CH_2(NH_2)-CH_2-COOH \xrightarrow{\Delta} CH_2=CH.COOH + NH_3$$

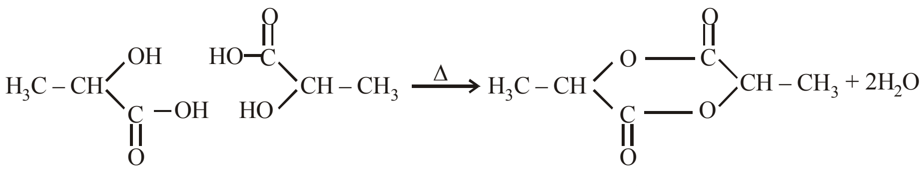
β-amino propionic acid Acrylic acid

(iii) ***γ-Amino acids***



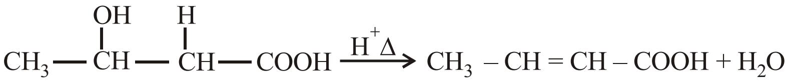
γ-amino butyric acid γ-butyrolactam

(iv) ***α-Hydroxy acids***



lactic acid lactide

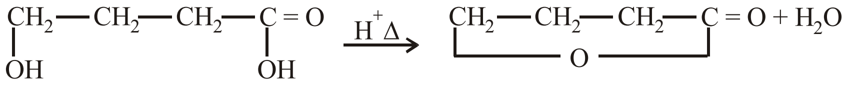
(v) ***β-hydroxy acids***



$$CH_3-CH(OH)-CH_2-COOH \xrightarrow{H^+\Delta} CH_3-CH=CH-COOH + H_2O$$

β-hydroxy butyric acid Crotonic acid

(vi) γ and δ–hydroxy acids



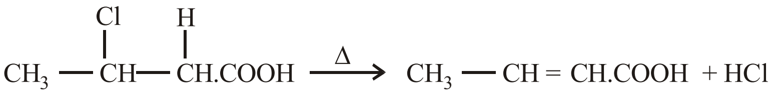
γ-hydroxy butyric acid γ-lactone

(vii) ***α-Halogeno acids.*** They yield α-hydroxy acids

$$CH_3CH_2.CHCl.COOH + H_2O \longrightarrow CH_3CH_2.CH(OH).COOH + HCl$$

α-chlorobutyric acid α-hydroxy butyric acid

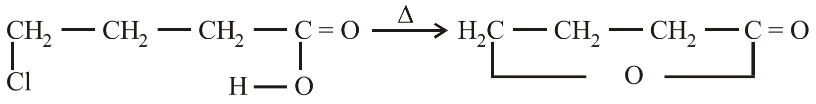
(viii) ***β-Halogeno acids***



$$CH_3-\overset{Cl}{\overset{|}{CH}}-\overset{H}{\overset{|}{CH}}.COOH \xrightarrow{\Delta} CH_3-CH=CH.COOH + HCl$$

Crotonic acid

(ix) ***γ-Halogeno acids***



γ-chlorobutyric acid γ-butyro lactone

SATURATED DICARBOXYLIC ACIDS :

The compounds containing two carboxyl groups are known as dicarboxylic acids. They have the general formula $C_nH_{2n}(COOH)_2$

Nomenclature: Their IUPAC group name is Alkanedioic acid

Value of n	Formula	Common name	IUPAC name
0	HOOC.COOH	Oxalic acid	Ethane - 1, 2-dioic acid
1	$HOOC.CH_2.COOH$	Malonic acid	Propane - 1, 3-dioic acid
2	$HOOC.(CH_2)_2COOH$	Succinic acid	Butane - 1, 4-dioic acid
3	$HOOC.(CH_2)_3.COOH$	Glutaric acid	Pentane - 1, 5-dioic acid
4	$HOOC(CH_2)_4COOH$	Adipic acid	Hexane - 1, 6-dioic acid

General properties: All are colourless crystalline solids, soluble in water. Solubility with increase in molecular weight, the odd acids are more soluble than even due to lower symmetry and poor packing.

Their melting points follow the **Oscillation** or **alternation** rule which states that the melting point of an "even" acid is higher than that of the "odd" acid immediately below and above it in the series. It is also known as "**saw-tooth**" rule.

Acid Strength: The strength of acids decreases from lower to higher member of the series as shown by the pk_a values

Acid	**Oxalic acid**	**Malonic acid**	**Succinic acid**	**Glutaric acid**	**Adipic acid**
pk_a	1.271	2.86	4.21	4.34	4.41

This is due to –I effect of the carboxylic group which decreases with the length of the carbon atom chain

Action of heat

$$(COOH)_2.2H_2O \xrightarrow{100-105°C} (COOH)_2 \xrightarrow{200°C} CO_2 + HCOOH \rightarrow CO + H_2O$$

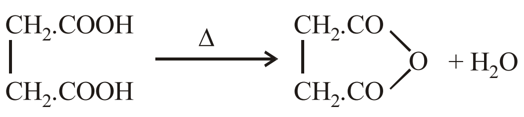
Oxalic acid

$$CH_2(COOH)_2 \xrightarrow{150°C} CH_3.COOH + CO_2$$

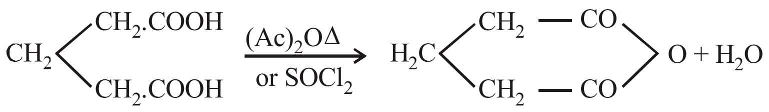
Malonic acid

$$\xrightarrow{P_2O_5} O=C=C=C=O + 2H_2O$$

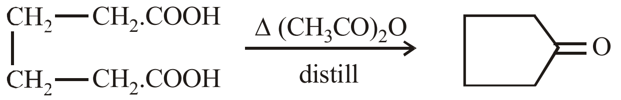
Carbon Suboxide



Succinic acid Succinic anhydride



Glutaric acid Glutaric anhydride



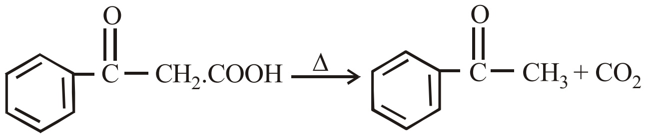
$$\begin{array}{l}CH_2-CH_2.COOH\\|\\CH_2-CH_2.COOH\end{array}\xrightarrow[\text{distill}]{\Delta\,(CH_3CO)_2O}$$

Adipic acid Cyclopentanone

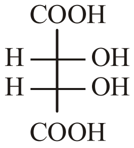
Blanc's rule: On heating the acid with acetic anhydride and then distilling the product at 300°C, 1, 4 and 1, 5 - dicarboxylic acid give cyclic anhydrides and 1, 6 and 1, 7-dicarboxylic acid give cyclic ketones provided the acids are unsubstituted. If no change the acid is 1, 8 or more.

The rule helps to determine the size of rings.

Note A β keto acid is easily decarboxylated by heating



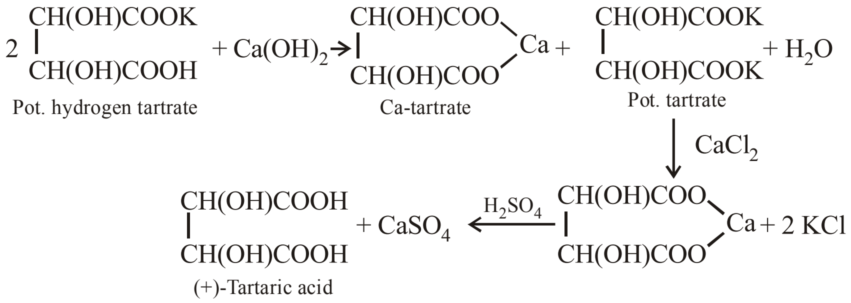
TARTARIC ACID



It occurs in free state in tamarind and as potassium salt in various fruits such as grapes, plums, etc.

Preparation : ***(i) From Argol or Tartar*** - A brown coloured crystalline mass formed during the fermentation of grape juice known as argol is crystallised from hot water to get **cream of tartar** which contains impure (+) potassium hydrogen tartrate. Tartaric acid is obtained as follows :

(i)



$$2\begin{array}{l}CH(OH)COOK\\|\\CH(OH)COOH\end{array}+Ca(OH)_2\rightarrow\begin{array}{l}CH(OH)COO\\|\\CH(OH)COO\end{array}\!\!>Ca+\begin{array}{l}CH(OH)COOK\\|\\CH(OH)COOK\end{array}+H_2O$$

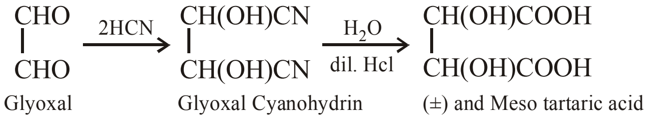
Pot. hydrogen tartrate Ca-tartrate Pot. tartrate

$$\downarrow CaCl_2$$

$$\begin{array}{l}CH(OH)COOH\\|\\CH(OH)COOH\end{array}+CaSO_4\xleftarrow{H_2SO_4}\begin{array}{l}CH(OH)COO\\|\\CH(OH)COO\end{array}\!\!>Ca+2\,KCl$$

(+)-Tartaric acid

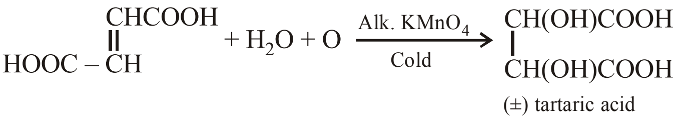
(ii) ***From Glyoxal***



$$\begin{array}{l}CHO\\|\\CHO\end{array}\xrightarrow{2HCN}\begin{array}{l}CH(OH)CN\\|\\CH(OH)CN\end{array}\xrightarrow[\text{dil. Hcl}]{H_2O}\begin{array}{l}CH(OH)COOH\\|\\CH(OH)COOH\end{array}$$

Glyoxal Glyoxal Cyanohydrin (±) and Meso tartaric acid

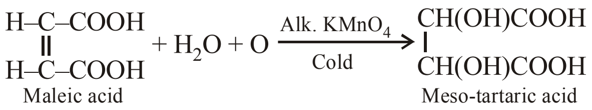
(iii) ***From Fumaric acid***



$$\begin{array}{r}CHCOOH\\\|\;\;\;\;\;\;\;\;\\HOOC-CH\;\;\;\;\;\;\end{array}+H_2O+O\xrightarrow[\text{Cold}]{\text{Alk. }KMnO_4}\begin{array}{l}CH(OH)COOH\\|\\CH(OH)COOH\end{array}$$

(±) tartaric acid

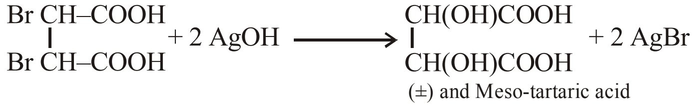
(iv) ***From Maleic acid***



$$\begin{array}{l}H-C-COOH\\\;\;\;\;\|\\H-C-COOH\end{array}+H_2O+O\xrightarrow[\text{Cold}]{\text{Alk. }KMnO_4}\begin{array}{l}CH(OH)COOH\\|\\CH(OH)COOH\end{array}$$

Maleic acid Meso-tartaric acid

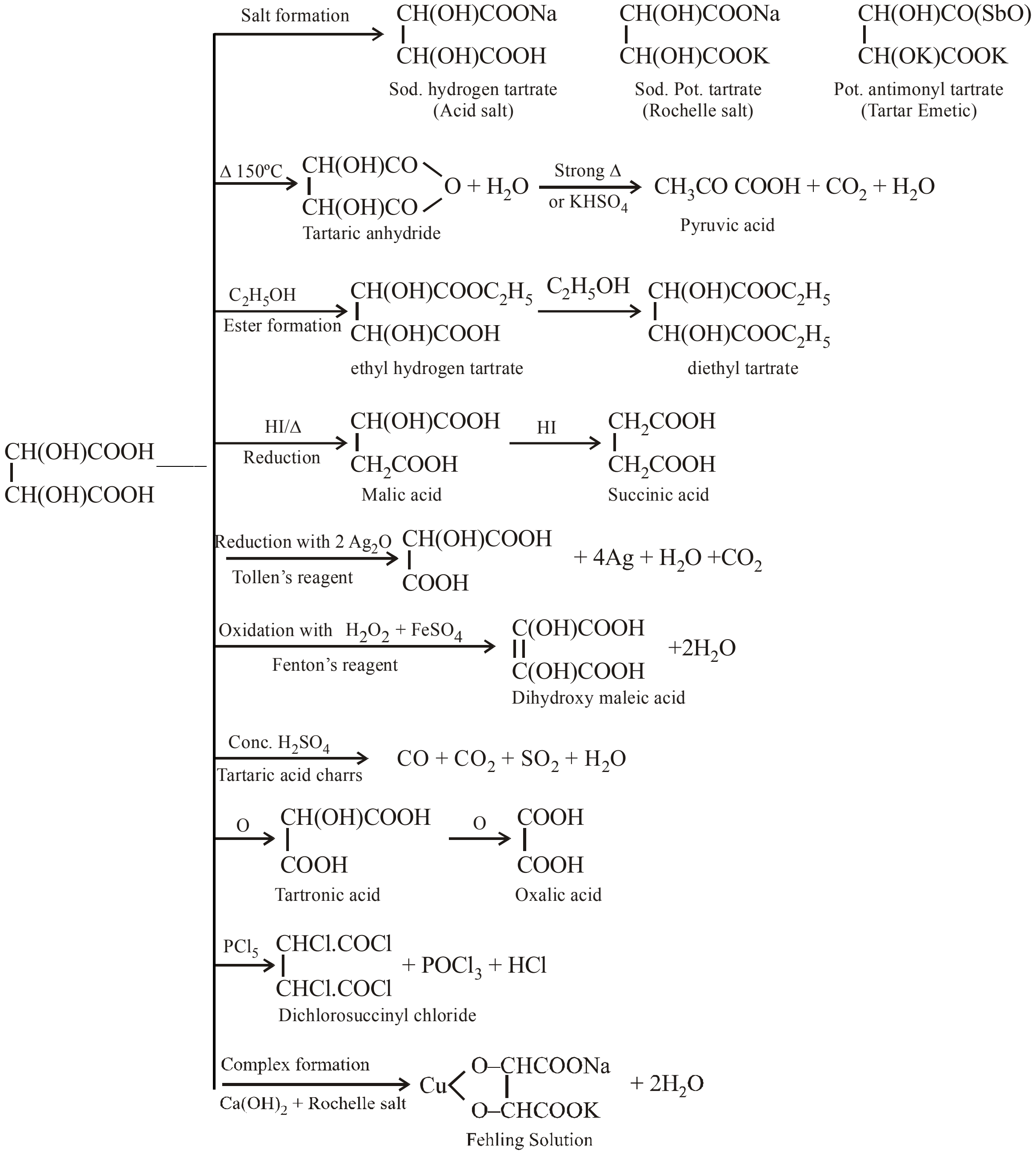
(v) ***From dibromo succinic acid***



$$\begin{array}{l}Br\,CH-COOH\\\;\;\;\;|\\Br\,CH-COOH\end{array}+2\,AgOH\longrightarrow\begin{array}{l}CH(OH)COOH\\|\\CH(OH)COOH\end{array}+2\,AgBr$$

(±) and Meso-tartaric acid

Properties : It is colourless crystalline solid m.p. 171°C soluble in water, alcohol, insoluble in ether. Natural tartaric acid is d-tartaric acid.



$\begin{array}{l}CH(OH)COOH\\ |\\ CH(OH)COOH\end{array}$

$\xrightarrow{\text{Salt formation}}$ $\begin{array}{l}CH(OH)COONa\\ |\\ CH(OH)COOH\end{array}$ Sod. hydrogen tartrate (Acid salt); $\begin{array}{l}CH(OH)COONa\\ |\\ CH(OH)COOK\end{array}$ Sod. Pot. tartrate (Rochelle salt); $\begin{array}{l}CH(OH)CO(SbO)\\ |\\ CH(OK)COOK\end{array}$ Pot. antimony tartrate (Tartar Emetic)

$\xrightarrow{\Delta\ 150^\circ C}$ $\begin{array}{l}CH(OH)CO\diagdown\\ |\qquad\qquad\quad O\\ CH(OH)CO\diagup\end{array} + H_2O$ Tartaric anhydride $\xrightarrow[\text{or } KHSO_4]{\text{Strong }\Delta}$ $CH_3CO\ COOH + CO_2 + H_2O$ Pyruvic acid

$\xrightarrow[\text{Ester formation}]{C_2H_5OH}$ $\begin{array}{l}CH(OH)COOC_2H_5\\ |\\ CH(OH)COOH\end{array}$ ethyl hydrogen tartrate $\xrightarrow{C_2H_5OH}$ $\begin{array}{l}CH(OH)COOC_2H_5\\ |\\ CH(OH)COOC_2H_5\end{array}$ diethyl tartrate

$\xrightarrow[\text{Reduction}]{HI/\Delta}$ $\begin{array}{l}CH(OH)COOH\\ |\\ CH_2COOH\end{array}$ Malic acid $\xrightarrow{HI}$ $\begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array}$ Succinic acid

$\xrightarrow[\text{Tollen's reagent}]{\text{Reduction with } 2\,Ag_2O}$ $\begin{array}{l}CH(OH)COOH\\ |\\ COOH\end{array} + 4Ag + H_2O + CO_2$

$\xrightarrow[\text{Fenton's reagent}]{\text{Oxidation with } H_2O_2 + FeSO_4}$ $\begin{array}{l}C(OH)COOH\\ ||\\ C(OH)COOH\end{array} + 2H_2O$ Dihydroxy maleic acid

$\xrightarrow[\text{Tartaric acid charrs}]{\text{Conc. } H_2SO_4}$ $CO + CO_2 + SO_2 + H_2O$

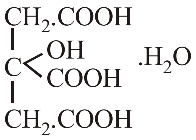
$\xrightarrow{O}$ $\begin{array}{l}CH(OH)COOH\\ |\\ COOH\end{array}$ Tartronic acid $\xrightarrow{O}$ $\begin{array}{l}COOH\\ |\\ COOH\end{array}$ Oxalic acid

$\xrightarrow{PCl_5}$ $\begin{array}{l}CHCl.COCl\\ |\\ CHCl.COCl\end{array} + POCl_3 + HCl$ Dichlorosuccinyl chloride

$\xrightarrow[Ca(OH)_2 + \text{Rochelle salt}]{\text{Complex formation}}$ $Cu\begin{array}{l}\diagup O{-}CHCOONa\\ \qquad\ |\\ \diagdown O{-}CHCOOK\end{array} + 2H_2O$ Fehling Solution

Uses : (i) It is used in silvering mirror (ii) Tartar emetic is used to cause nausea and vomitting in case of poisoning (iii) Pot. acid tartrate is used in Baking powder (iv) Rochelle salt is used in preparing Fehling solution.

CITRIC ACID :



$$\begin{array}{l}CH_2.COOH\\ |\\ C\begin{array}{l}\diagup OH\\ \diagdown COOH\end{array}\\ |\\ CH_2.COOH\end{array} .H_2O$$

It occurs in free state in citrus fruits eg.: lemon, orange lime etc. Lemon juice contains about 7% citric acid.

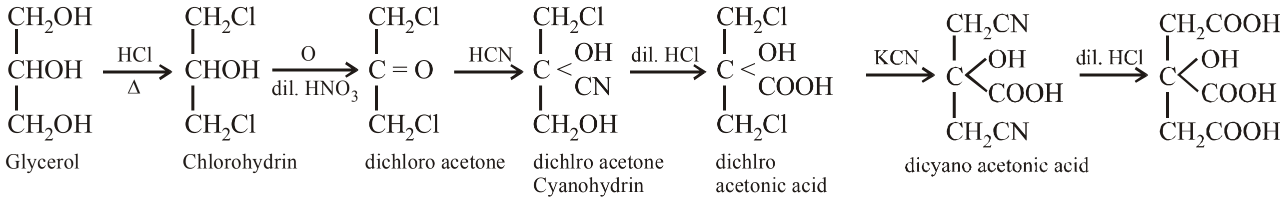
(i) **From lemon juice**

$$\text{Lemon juice}\xrightarrow[\text{Filter}]{\text{Boil}}\text{Clear Soln.}\xrightarrow{CaCO_3}\underset{\text{Ca-citrate}}{Ca_3(C_6H_5O_7)_2}\downarrow\xrightarrow[H_2SO_4]{\text{dil.}}CaSO_4\downarrow + C_6H_8O_7.H_2O$$

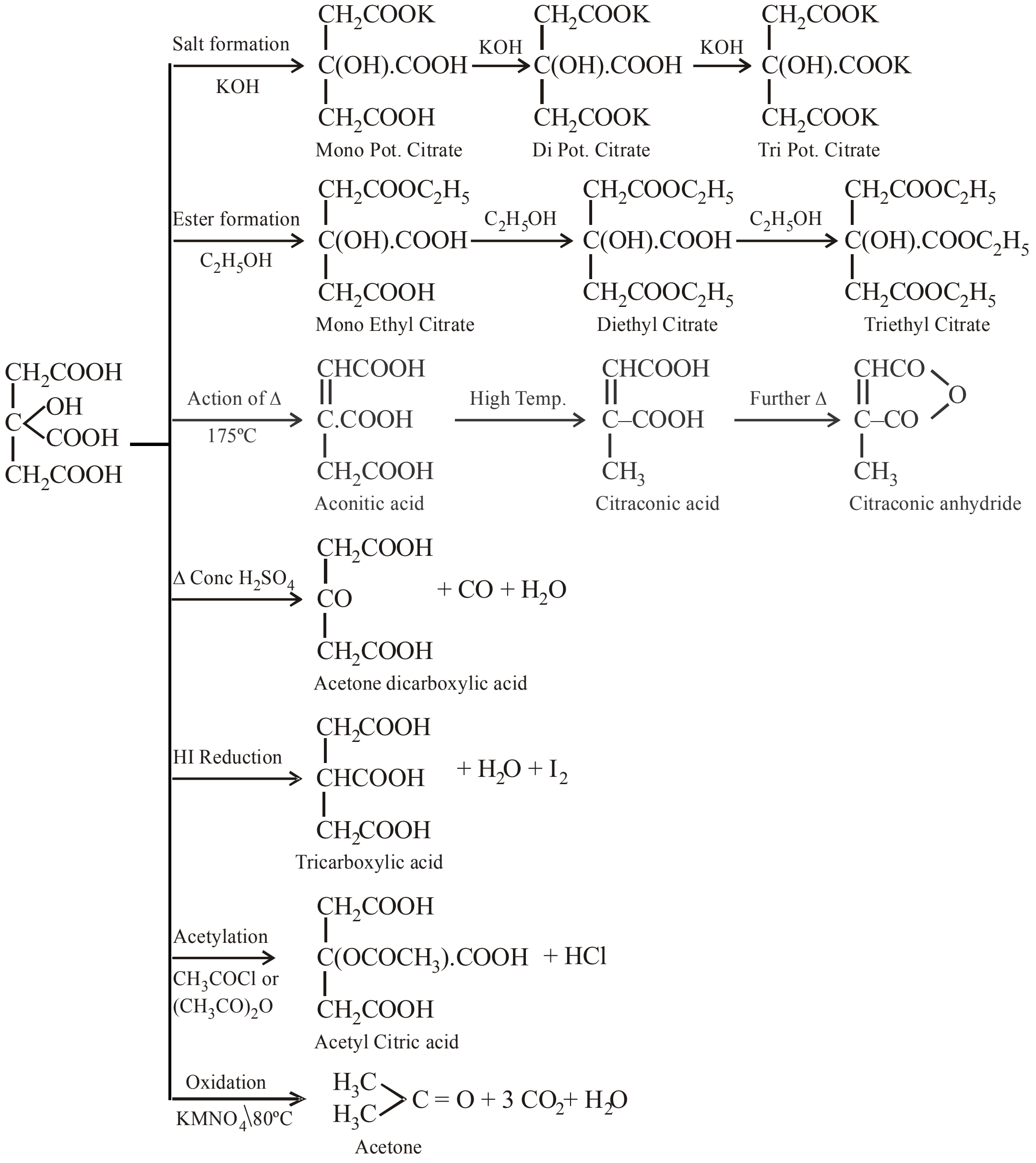
(ii) **From Sugar** - Fermentation of molasses in presence of aspergillus niger or citromyces pfeferianus and inorganic salts. eg.: $(NH_4)_2CO_3$, $MgSO_4$ etc.

$$C_{12}H_{22}O_{11} + 3O_2 \xrightarrow[30^\circ C\ pH\ 2.5]{Bacteria} 2C_6H_8O_7 + 3H_2O$$

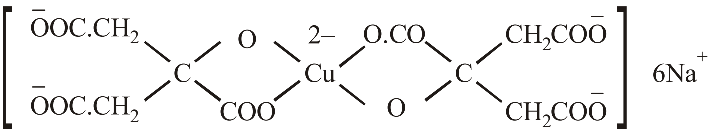
(iii) **From glycerol**



Properties : It is colourless crystalline substance. Its m. pt. is 100°C soluble in water and alcohol. Insoluble in ether. Optically inactive.



Complex formation : Benedict Solution. It contain Copper Sulphate, Sodium Carbonate and Sodium Citrate. The structure of complex is



It is more stable than Fehling solution

Uses : i) Mg Citrate is used as laxative in medicine. ii) As mordant in dyeing and printing. iii) Ferric ammonitran citrate as Iron tonic. iv) It is used in preparing acidulated soft drinks, jams, jellies, etc.

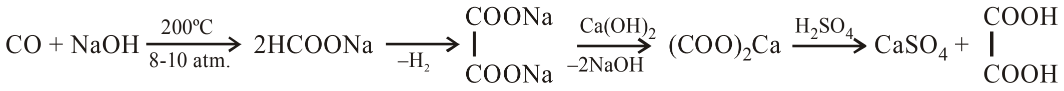
OXALIC ACID, ETHANEDIOIC ACID $(COOH)_2.2H_2O$

Preparation

(i) Lab method - Oxidation of Sucrose

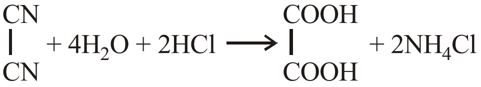
$$C_{12}H_{22}O_{11} + 18O \xrightarrow[\text{Con.}HNO_3]{V_2O_5} 6.(COOH)_2 + 5H_2O$$

(ii) ***Manufacture***



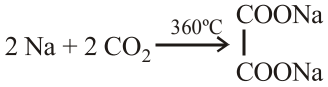
$$CO + NaOH \xrightarrow[\text{8-10 atm.}]{200^\circ C} 2HCOONa \xrightarrow[-H_2]{} \begin{matrix} COONa \\ | \\ COONa \end{matrix} \xrightarrow[-2NaOH]{Ca(OH)_2} (COO)_2Ca \xrightarrow{H_2SO_4} CaSO_4 + \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

(iii) ***Hydrolysis of Cyanogen***



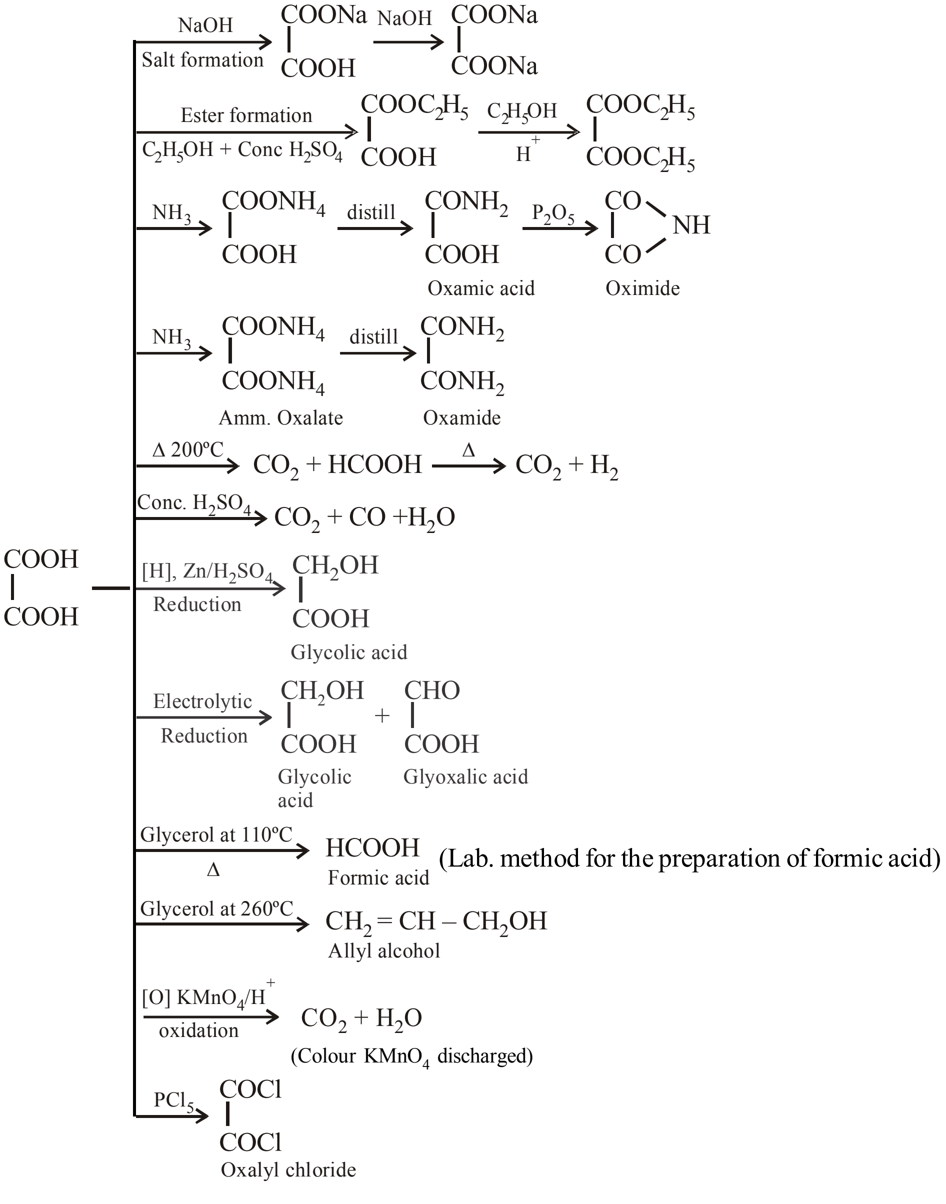
$$\begin{matrix} CN \\ | \\ CN \end{matrix} + 4H_2O + 2HCl \longrightarrow \begin{matrix} COOH \\ | \\ COOH \end{matrix} + 2NH_4Cl$$

(iv)



$$2\,Na + 2\,CO_2 \xrightarrow{360^\circ C} \begin{matrix} COONa \\ | \\ COONa \end{matrix}$$

Properties : Colourless crystalline compound. Soluble in water & alcohol, insoluble in ether. m.p. 101.2ºC (hydrated) & 189.5ºC (anhydrous)



(Lab. method for the preparation of formic acid)

Uses : (i) As a mordant in dyeing. (ii) Volumetric analysis. (iii) removing ink stains. (iv) In photography.

BENZOIC ACID :

C_6H_5COOH

General methods of preparation

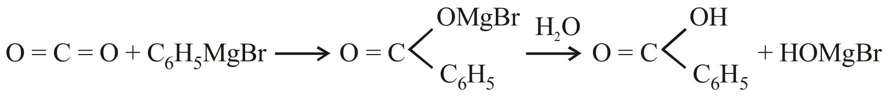
(i) By oxidation of alcohol or aldehyde

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} \xrightarrow[KMnO_4]{[O]} \underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{[O]} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

(ii) By Oxidation of homologues of benzene : Oxidising agents dil. HNO_3, alk. $KMnO_4$, $K_2Cr_2O_7 + H_2SO_4$

$$C_6H_5CH_3 \xrightarrow{Cl_2} C_6H_5CH_2Cl \xrightarrow{Na_2CO_3} C_6H_5CH_2OH \xrightarrow{[O]} C_6H_5COOH$$

(iii) ***By use of Grignard's reagent***



$$O=C=O + C_6H_5MgBr \longrightarrow O=C\begin{matrix}OMgBr\\C_6H_5\end{matrix} \xrightarrow{H_2O} O=C\begin{matrix}OH\\C_6H_5\end{matrix} + HOMgBr$$

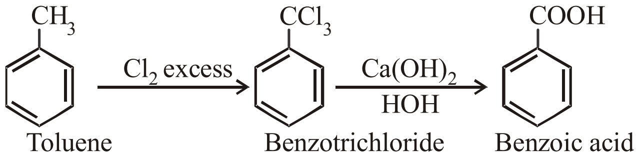
(iv) ***Hydrolysis of Cyanides***

$$C_6H_5CN + 2H_2O \xrightarrow{H_2SO_4} C_6H_5COOH + NH_3$$

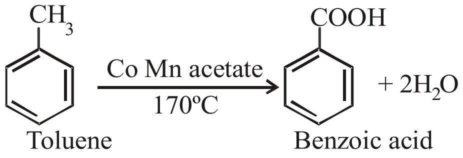
+

Manufacture of benzoic acid

(i)



(ii)



Properties : It is colourless crystalline compound. Stronger than aliphatic acids and sparingly soluble in water.

Acid Character : Ortho, para directing groups with activation decrease the acid character, while meta directing groups increase the acid character of benzoic acid.

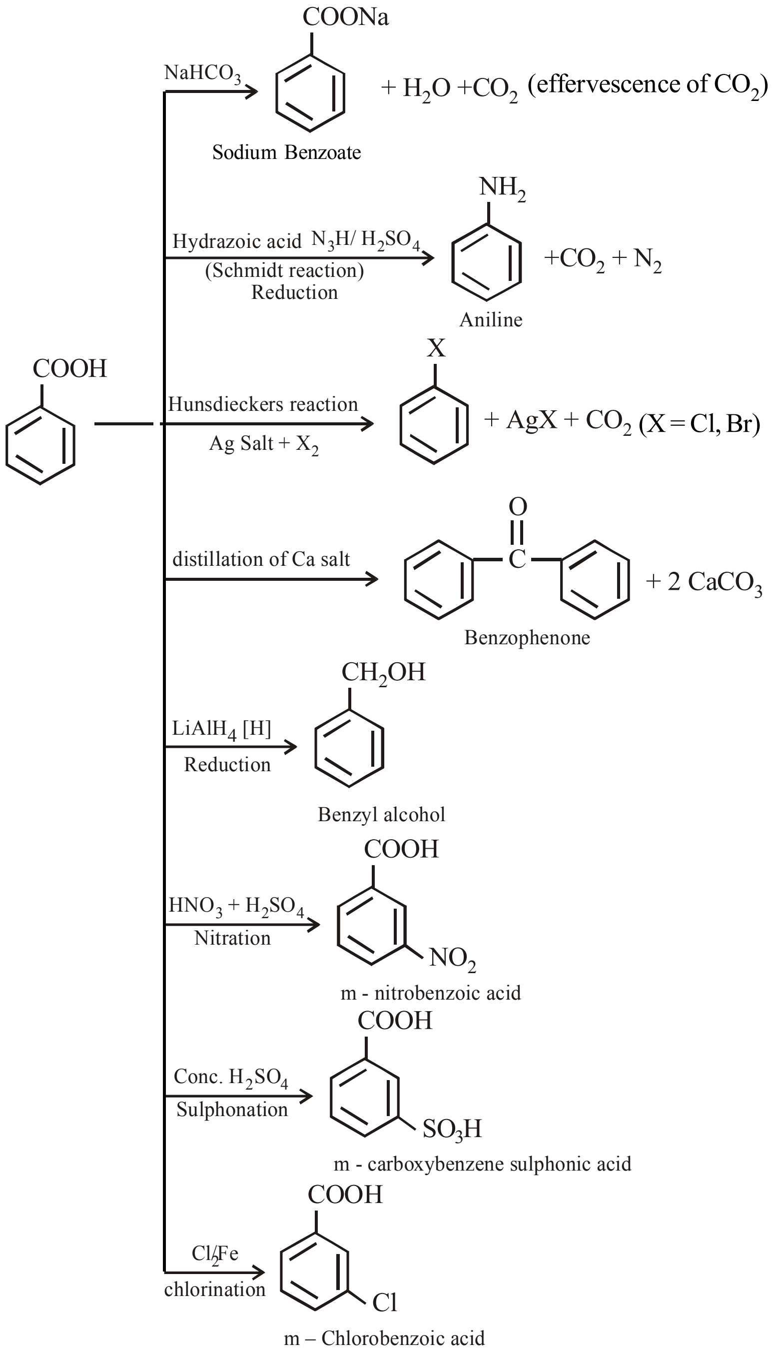
Ortho effect: Ortho substituted benzoic acids are more stronger than benzoic acid regardless of the nature of the substituent K_a of benzoic acid is 6.3×10^{-5}

Acidity constants of substituted benzoic acids and order of acid strength ($K_a = X \times 10^{-5}$)

$o-NO_2$	>	$o-Cl$	>	$o-OH$	>	$p-NO_2$	>	$m-NO_2$	>	$m-Cl$
X= 670		120		105		36		32		15.1
$o-CH_3$	>	$p-Cl$	>	$m-OH$	>	$o-OCH$	=	$m-OCH_3$	>	$m-CH_3$
X= 12.4		10.3		8.3		8.2		8.2		5.4
$p-CH_3$	>	$p-OCH_3$	>	$p-OH$	>	$m-NH_2$	>	$o-NH_2$	>	$p-NH_2$
X= 4.2		3.3		2.6		1.9		1.6		1.4

(multiply the numerical figures by 10^{-5} to have value of K_a)

Chemical properties :



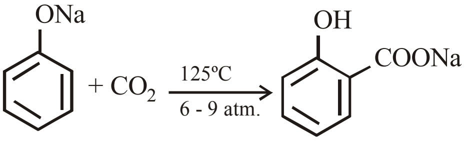
Uses : Sodium benzoate is used as food preservative.

SALICYCLIC ACID :

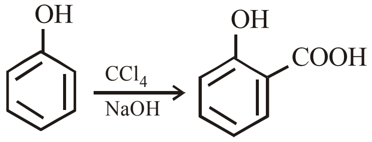
o-hydroxy benzoic acid

Preparation :

(i) Kolbe - Schmidt reaction

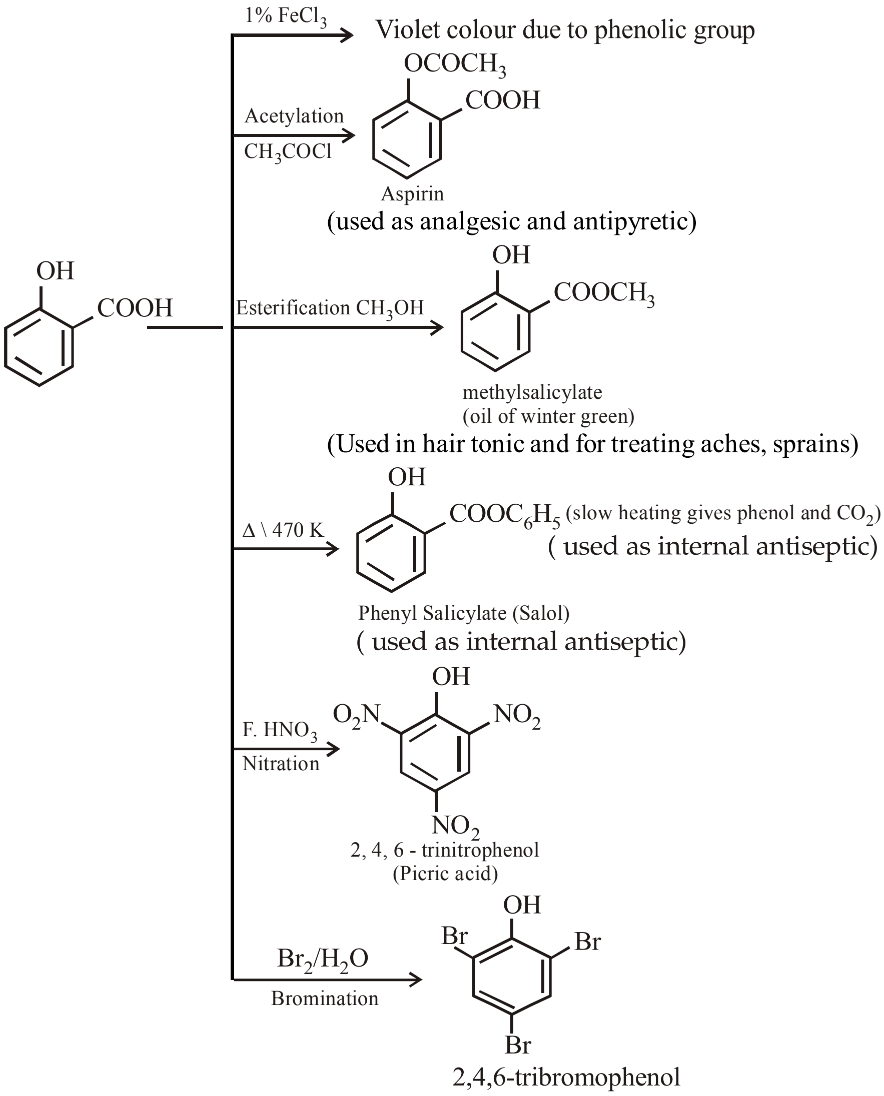


(ii) Reimer - Tiemann Reaction



Properties : Colourless crystalline substance m. pt. 429 K. Sublimes on heating.

Chemical properties :



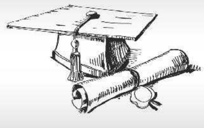
(used as analgesic and antipyretic)

(Used in hair tonic and for treating aches, sprains)

(used as internal antiseptic)

(used as internal antiseptic)

Exercise-1 | NCERT Based Questions



Very Short/ Short Answer Questions

1. Arrange the following in order of increasing acid strengths C_6H_5OH, C_2H_5OH, HCOOH, CH_3COOH.

2. How does acetyl chloride react with phenol?

3. How will you account in the preparation of an ester by the reaction of a carboxylic acid and an alcohol, the ester is distilled as fast as it is formed?

4. Arrange the following compounds in increasing ease of hydrolysis:

$$CH_3CONH_2, CH_3COCl, CH_3COOC_2H_5, (CH_3CO)_2O.$$

5. What makes ethanoic acid a stronger acid than ethanol?

6. Why is benzoic acid less soluble in water than acetic acid?

7. What is vinegar?

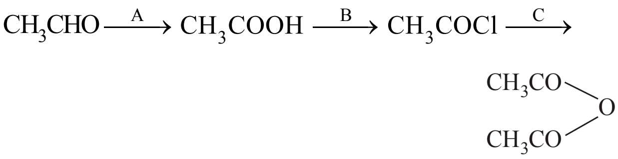
8. Why HCOOH does not give HVZ reaction but CH_3COOH does?

9. Chloroacetic acid has lower pK_a value than acetic acid. Why ?

10. Identify X, Y and Z in the following sequence of reactions.

$$CH_3COOC_2H_5 \xrightarrow{NH_3} X \xrightarrow{P_2O_5} Y \xrightarrow{H^+/H_2O} Z$$

11. Name the reagents A, B and C in the following sequence of reactions:



$$CH_3CHO \xrightarrow{A} CH_3COOH \xrightarrow{B} CH_3COCl \xrightarrow{C} \begin{matrix} CH_3CO \\ CH_3CO \end{matrix} \!\!>\! O$$

12. Carboxylic acids do not give reactions of aldehydes and ketones, although contain carbonyl group. Why?

Long Answer Questions

13. How can ethanoic acid be converted into propanoic acid and vice versa?

14. Discuss the mechanism of acid-catalysed esterification of carboxylic acid.

15. Explain why benzamide is less easily hydrolysed than methyl benzoate.

Multiple Choice Questions

16. The compound formed when malonic ester is heated with urea is

(a) Cinnamic acid (b) Bytyric acid

(c) Barbituric acid (d) Crotonic acid.

17. Benzoic acid gives benzene on being heated with X and phenol gives benzene on being heated with Y. Therefore X and Y are respectively

(a) Soda-lime and copper

(b) Zn dust and NaOH

(c) Zn dust and soda-lime

(d) Soda-lime and zinc dust.

18. Among acetic acid, phenol and n-hexanol, which of the following compounds well react with $NaHCO_3$ solution to give sodium salt and carbon dioxide ?

(a) Acetic acid

(b) n-Hexanol

(c) acetic acid and phenol

(d) Phenol.

19. An ester is boiled with KOH. The product is cooled and acidified with concentrated HCl. A white crystalline acid separates. The ester is

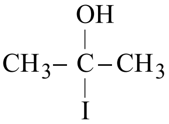
(a) Methyl acetate (b) Ethyl acetate

(c) Ethyl formate (d) Ethyl benzoate

20. Consider the following transformations :

$$CH_3COOH \xrightarrow{CaCO_3} \boxed{A} \xrightarrow{heat} \boxed{B} \xrightarrow[NaOH]{I_2} \boxed{C}$$

The molecular formula of $\boxed{C}$ is

(a) 

$$CH_3-\overset{\overset{\large OH}{|}}{\underset{\underset{\large I}{|}}{C}}-CH_3$$

(b) ICH_2-COCH_3

(c) CHI_3 (d) CH_3I

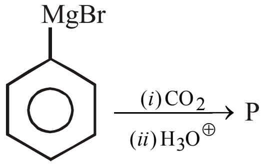
21. An ester (A) with molecular fomula, $C_9H_{10}O_2$ was treated with excess of CH_3MgBr and the complex so formed was treated with H_2SO_4 to give an olefin (B). Ozonolysis of (B) gave a ketone with molecular formula C_8H_8O which shows +ve iodoform test. The structure of (A) is

(a) $C_6H_5COOC_2H_5$

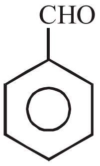
(b) $C_2H_5COOC_6H_5$

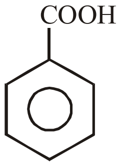
(c) $H_3COCH_2COC_6H_5$

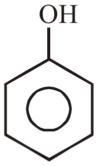
(d) $p-H_3CO-C_6H_4-COCH_3$

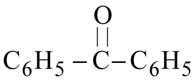
22. 

In the above reaction product 'P' is

(a) 

(b) 

(c) 

(d) 

$C_6H_5-\overset{O}{\overset{||}{C}}-C_6H_5$

Exercise-2 | CONCEPTUAL MCQs

1. The systematic name of $(CH_3)_2CH–COOH$ is
(a) 2-propanoic acid (b) isobutyric acid
(c) 2-methylpropanoic acid (d) 2-methylbutanoic acid

2. In presence of acid, hydrolysis of methyl cyanide gives
(a) acetic acid (b) methylamine
(c) methyl alcohol (d) formic acid

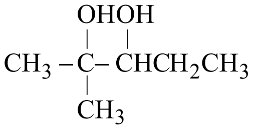
3. Hydrolysis of benzonitrile by dilute HCl yields
(a) aniline (b) benzoic acid
(c) benzamide (d) benzaldehyde

4. $R–CH_2–CH_2OH$ can be converted into RCH_2CH_2COOH. The correct sequence of reagents is
(a) PBr_3,KCN,H^+ (b) PBr_3, KCN, H_2
(c) KCN,H^+ (d) HCN,PBr_3,H^+

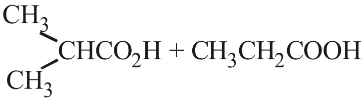
5. The general formula $C_nH_{2n}O_2$ could be for open chain
(a) diketones (b) carboxylic acids
(c) diols (d) dialdehydes

6. Methylmagnesium bromide reacts with carbon dioxide. The product formed is
(a) CH_3COCH_3 (b) CH_3CH_2OH
(c) CH_3CHO (d) CH_3COOH

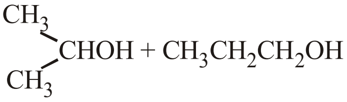
7. On vigorous oxidation by permanganate solution, $(CH_3)_2C=CH–CH_2–CH_3$ gives

(a) 

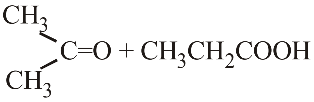
$CH_3-\overset{OH}{\underset{CH_3}{C}}-\overset{OH}{C}HCH_2CH_3$

(b) 

${CH_3 \atop CH_3}\!>CHCO_2H + CH_3CH_2COOH$

(c) 

${CH_3 \atop CH_3}\!>CHOH + CH_3CH_2CH_2OH$

(d) 

${CH_3 \atop CH_3}\!>C=O + CH_3CH_2COOH$

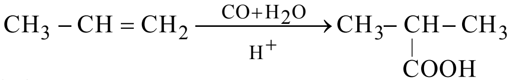
8. By aerial oxidation, which one of the following gives phthalic acid ?
(a) Naphthalene (b) Benzene
(c) Mesitylene (d) Toluene

9. Lactic acid on oxidation by alkaline potassium permanganate gives
(a) tartaric acid (b) pyruvic acid
(c) cinnamic acid (d) propionic acid

10. Which of the following on oxidation followed by hydrolysis gives pyruvic acid ?
(a) Acetaldehyde cyanohydrin
(b) Acetone cyanohydrin
(c) Formaldehyde cyanohydrin
(d) None of these

11. When 2-hydroxybenzoic acid is distilled with zinc dust, it gives
(a) phenol (b) benzoic acid
(c) benzaldehyde (d) a polymeric compound

12. The reaction,



$CH_3-CH=CH_2 \xrightarrow[H^+]{CO+H_2O} CH_3-\underset{COOH}{\underset{|}{C}}H-CH_3$

is known as
(a) Wurtz's reaction (b) Koch's reaction
(c) Clemmensen's reduction (d) Kolbe's reaction

13. Formic acid is obtained when
(a) calcium acetate is heated with conc. H_2SO_4
(b) calcium formate is heated with calcuim acetate
(c) glycerol is heated with oxalic acid at 373 K
(d) acetaldehyde is oxidised with $K_2Cr_2O_7$ and H_2SO_4

14. Lower carboxylic acids are soluble in water due to
(a) low molecular weight (b) hydrogen bonding
(c) dissociation into ions (d) easy hydrolysis

15. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to :
(a) ionization of benzoic acid
(b) dimerization of benzoic acid
(c) trimerization of benzoic acid
(d) solution of benzoic acid

16. Dimerisation of carboxylic acids is due to
(a) ionic bond
(b) covalent bond
(c) coordinate bond
(d) intermolecular hydrogen bond

17. Identify the correct order of boiling points of the following compounds :
$CH_3CH_2CH_2CH_2OH$ (1) $CH_3CH_2CH_2CHO$ (2)
$CH_3CH_2CH_2COOH$ (3)
(a) $1 > 2 > 3$ (b) $3 > 1 > 2$
(c) $1 > 3 > 2$ (d) $3 > 2 > 1$

18. Glacial acetic acid is
(a) pure acetic acid at 100° C
(b) pure acetic acid at 0° C
(c) acetic acid mixed with methanol
(d) pure acetic acid at 16.6° C

19. Glacial acetic acid is obtained by
(a) distilling vinegar
(b) crystallizing, separating and melting acetic acid
(c) treating vinegar with dehydrating agents
(d) chemically separating acetic acid

20. In the anion $HCOO^-$ the two carbon-oxygen bonds are found to be equal length. What is the reason for it?
(a) Electronic orbitals of carbon atom are hybridised
(b) The C=O bond is weaker than the C–C bond
(c) The anion $HCOO^-$ has two reasonating structures
(d) The anion is obtained by removal of a proton from the acid molecule.

21. Carboxylic acids are more acidic than phenol and alcohol because of
(a) intermolecular hydrogen bonding
(b) formation of dimers
(c) highly acidic hydrogen
(d) resonance stabilization of their conjugate base

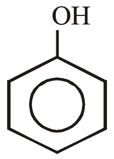
22. Which of the following compounds will react with $NaHCO_3$ solution to give sodium salt and carbon dioxide ?
(a) Acetic acid (b) n-Hexanol
(c) Phenol (d) Both (b) and (c)

23. Which of the following does not contain a carboxyl group ?
(a) picric acid (b) aspirin
(c) benzoic acid (d) ethanoic acid

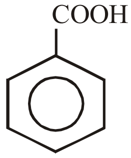
24. Which of the following is the strongest acid ?
(a) CH_3OH (b) CH_3CH_2OH
(c) $C_6H_5SO_3H$ (d) C_6H_5COOH

25. Which of the following has the maximum acidic strength ?
(a) o- nitrobenzoic acid (b) m-nitrobenzoic acid
(c) p-nitrobenzoic acid (d) p-nitrophenol

26. Which of the following is the weakest acid ?
(a)



(b) CH_3COOH
(c) HCOOH
(d)



27. Which of the following acids has the smallest dissociation constant ?
(a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH
(c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$

28. Which of the following is correct order of acidity?
(a) $HCOOH > CH_3COOH > ClCH_2COOH > C_2H_5COOH$
(b) $ClCH_2COOH > HCOOH > CH_3COOH > C_2H_5COOH$
(c) $CH_3COOH > HCOOH > ClCH_2COOH > C_2H_5COOH$
(d) $C_2H_5COOH > CH_3COOH > HCOOH > ClCH_2COOH$

29. Which of the following orders of relative strengths of acids is correct ?
(a) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH$
(b) $ClCH_2COOH > BrCH_2COOH > FCH_2COOH$
(c) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH$
(d) $ClCH_2CO_2H > FCH_2COOH > BrCH_2COOH$

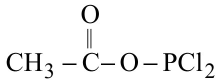
30. Which reagent will bring about the conversion of carboxylic acids into esters ?
(a) C_2H_5OH (b) dry $HCl + C_2H_5OH$
(c) $LiAlH_4$ (d) $Al(OC_2H_5)_3$

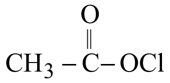
31. Which one of the following esters is obtained by the esterification of propan-2-ol with ethanoic acid ?
(a) $(CH_3)_2CHCOOCH_3$ (b) $CH_3COOCH_2CH_3$
(c) $CH_3COOCH(CH_3)_2$ (d) $(CH_3)_2CHCOOCH_2CH_3$

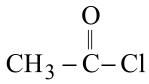
32. A fruity smell is produced by the reaction of C_2H_5OH with
(a) PCl_5 (b) CH_3COCH_3
(c) CH_3COOH (d) None of these

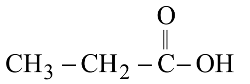
33. Acetic acid on heating in presence of P_2O_5 gives
(a) acetic anhydride (b) acetylene
(c) peracid (d) No reaction

34. The product obtained when acetic acid is treated with phosphorus trichloride, is

(a)

$CH_3-\overset{\overset{O}{\|}}{C}-O-PCl_2$

(b)

$CH_3-\overset{\overset{O}{\|}}{C}-OCl$

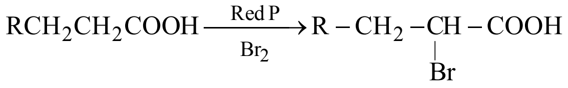
(c)

$CH_3-\overset{\overset{O}{\|}}{C}-Cl$

(d)

$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH$

35. Heating mixture of sodium benzoate and soda-lime gives
(a) benzene (b) methane
(c) sodium phenoxide (d) calcium benzoate

36. Benzoic acid gives benzene on being heated with X and phenol gives benzene on being heated with Y. Therefore X and Y are respectively
(a) soda-lime and copper (b) Zn dust and NaOH
(c) Zn dust and soda-lime (d) soda-lime and zinc dust

37. The reaction


$$RCH_2CH_2COOH \xrightarrow[Br_2]{Red\,P} R-CH_2-\underset{\underset{Br}{|}}{CH}-COOH$$

is called as
(a) Reimer- Tiemann reaction
(b) Hell-volhard Zelinsky reaction
(c) Cannizzaro reaction
(d) Sandmeyer reaction

38. $CH_3CH_2COOH \xrightarrow[\text{Red P}]{Br_2} X \xrightarrow{NH_3\text{(alc.)}} Y$

Y in the above reactions is
(a) lactic acid (b) ethylamine
(c) propylamine (d) alanine

39. For preparing an alkane, a concentrated aqueous solution of sodium or potassium salt of a saturated acid is subjected to
(a) hydrolysis (b) oxidation
(c) hydrogenation (d) electrolysis

40. The major product of nitration of benzoic acid is
(a) 3- Nitrobenzoic acid (b) 4- Nitrobenzoic acid
(c) 2- Nitrobenzoic acid (d) 2, 4- dinitrobenzoic acid

41. Which of the following cannot reduce Fehling solution?
(a) Formic acid (b) Acetic acid
(c) Formaldehyde (d) Acetaldehyde

42. Formic acid and acetic acid may be distinguised by reaction with
(a) sodium
(b) mercuric chloride
(c) ammonical silver nitrate solution
(d) Both (b) and (c)

43. Sodium formate on heating yields
(a) oxalic acid and H_2 (b) sodium oxalate and H_2
(c) CO_2 and NaOH (d) sodium oxalate

44. HCOOH reacts with conc. H_2SO_4 to produce
(a) CO (b) CO_2
(c) NO (d) NO_2

45. Oxalic acid when reduced with zinc and H_2SO_4 gives
(a) glyoxalic acid (b) nitrene
(c) glycollic acid (d) glycol

46. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is
(a) MeCOCl (b) MeCHO
(c) MeCOOMe (d) MeCOOCOMe

47. CH_3COCl cannot be obtained directly by reacting PCl_5 with
(a) CH_3COOH (b) $(CH_3CO)_2O$
(c) CH_3CONH_2 (d) CH_3COOR

48. The order of decreasing ease of reaction with ammonia is
(a) anhydrides, esters, ethers
(b) anhydrides, ethers, esters
(c) ethers, anhydrides, esters
(d) esters, ethers, anhydrides

49. Benzoyl chloride is prepared from benzoic acid by
(a) $Cl_2, h\nu$ (b) SO_2Cl_2
(c) $SOCl_2$ (d) Cl_2, H_2O

50. Which of the following cannot convert caboxylic acid into its acyl chloride ?
(a) PCl_3 (b) $SOCl_2$
(c) PCl_5 (d) NaCl

51. Methyl acetate will be obtained by reacting CH_3OH with
(a) CH_3COOH (b) CH_3COCl
(c) $(CH_3CO)_2O$ (d) All the three above

52. Ethyl acetate is obtained when methylmagnesium iodide reacts with
(a) ethyl formate (b) ethyl chloroformate
(c) acetyl chloride (d) carbon dioxide

53. The reduction of benzoyl chloride with Pd and $BaSO_4$ produces.
(a) benzyl chloride (b) benzaldehyde
(c) benzoic acid (d) None of these

54. Schotten-Baumann reaction is a reaction of phenols with
(a) benzoyl chloride and sodium hydroxide
(b) acetyl chloride and sodium hydroxide
(c) salicylic acid and conc. H_2SO_4
(d) acetyl chloride and conc. H_2SO_4

55. Hydrolytic reaction of fats with caustic soda is known as
(a) acetylation (b) carboxylation
(c) esterification (d) saponfication

56. Saponification of ethyl benzoate with caustic soda as alkali gives
(a) benzyl alcohol and ethanoic acid
(b) sodium benzoate and ethanol
(c) benzoic acid and sodium ethoxide
(d) phenol and ethanoic acid

57. Rancidity of butter is due to the formation of
(a) butanoic acid (b) butene -1
(c) lactic acid (d) lactose

58. Reaction of ethyl formate with excess of CH_3MgI followed by hydrolysis gives
(a) n- propyl alcohol (b) ethanal
(c) tert-Butyl alcohol (d) isopropyl alcohol

59. In $C_6H_5COOCH_3 \xrightarrow{LiAlH_4}$ X will be
(a) $C_6H_5COOH + CH_3OH$
(b) $C_6H_5CH_2OH + CH_3OH$
(c) $C_6H_5CHO + CH_3COOH$
(d) All of these

60. What will happen if $LiAlH_4$ is added to an ester?
(a) Two units of alcohols are obtained
(b) One unit of alcohol and one unit of acid is obtained
(c) Two units of acids are obtained
(d) None of these

61. The following reaction is called

$2CH_3COOC_2H_5 \rightarrow CH_3COCH_2COOC_2H_5$

(a) Perkin reaction
(b) Tischenko reaction
(c) Claisen condensation
(d) Schotten-Baumann's reaction

62. An ester is boiled with KOH. The product is cooled and acidified with concentrated HCl. A white crystalline acid separates. The ester is
(a) methyl acetate (b) ethyl acetate
(c) ethyl formate (d) ethyl benzoate

63. Hydrolsis of an ester gives a carboxylic acid which on Kolbe's electrolysis yields ethane. The ester is
(a) ethyl methanoate (b) methyl ethanoate
(c) methyl methanoate (d) methyl propanoate

64. The refluxing of $(CH_3)_2NCOCH_3$ with acid gives
(a) $2\,CH_3NH_2 + CH_3COOH$
(b) $2\,CH_3OH + CH_3CONH_2$
(c) $(CH_3)_2NH + CH_3COOH$
(d) $(CH_3)_2NCOOH + CH_4$

65. An aqueous solution of urea
(a) is neutral (b) is acidic
(c) is basic (d) can act as an acid as well as a base

66. When urea is heated slowly then NH_3 and one other substance is formed, that substance is
(a) biuret (b) carbonic acid
(c) cyanic acid (d) $NH_2CONHNO_2$

67. Amides may be converted into amines by a reaction named
(a) Perkin (b) Claisen
(c) Hofmann (d) Kekule

68. Which of the following compounds is formed when benzamide is warmed with bromine and alkali?
(a) Benzenediazonium chloride
(b) Aniline
(c) Benzene
(d) Bromobenzene

69. When acetamide is treated with NaOBr, the product formed is
(a) CH_3CN (b) $CH_3CH_2NH_2$
(c) CH_3NH_2 (d) None of these

70. In the mechanism of Hoffmann reaction, which intermediate rearranges to alkyl isocyanate ?
(a) Bromamide (b) Nitrene
(c) Nitroso (d) Amide

71. The acid amide is converted into acid with evolution of nitrogen gas by
(a) HCl (b) NaOH
(c) HNO_2 (d) P_2O_5

72. A colourless liquid, at room temperature, reacts with soda-lime to form sodium salt of a carboxylic acid and ammonia gas. The liquid is
(a) propanoic acid (b) formamide
(c) propanamide (d) methyl enthanoate

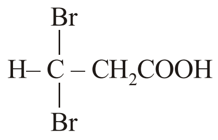
73. 59 g of an amide obtained from a carboxylic acid, RCOOH, upon heating with alkali liberates 17 g NH_3. The acid is
(a) formic acid (b) acetic acid
(c) propionic acid (d) benzoic acid

74. Identify the wrong statement from the following
(a) Salicyclic acid is a monobasic acid
(b) Methyl salicylate is an ester
(c) Salicylic acid gives violet colour with neutral ferric chloride as well as brisk effervescence with sodium bicarbonate
(d) Methyl salicylate does not occur in natural oils

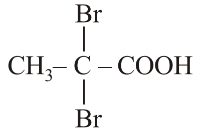
Exercise-3 | PAST COMPETITION MCQs

1. Which of the following represents the correct order of the acidity in the given compounds? **[CBSE-PMT 2007]**
(a) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$
(b) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$
(c) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$
(d) $CH_3COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$

2. Propionic acid with Br_2/P yields a dibromo product. Its structure would be: **[CBSE-PMT 2009]**

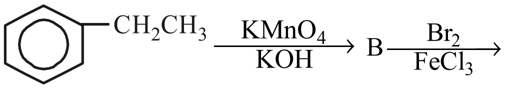
(a) 
$H-CBr_2-CH_2COOH$

(b) CH_2Br-CH_2-COBr

(c) 
CH_3-CBr_2-COOH

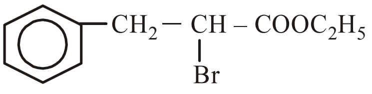
(d) $CH_2Br-CHBr-COOH$

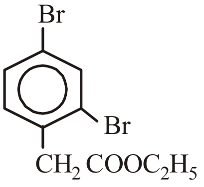
3. In a set of reactions, ethylbenzene yield a product D.

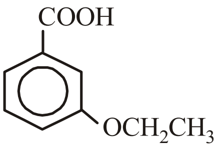


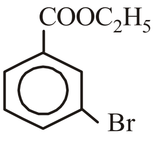
$$C \xrightarrow[H^+]{C_2H_5OH} D$$ **[CBSE-PMT 2010]**

Identify D :

(a) 

(b) 

(c) 

(d) 

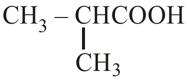
4. Match the compounds given in List-I with List-II and select the suitable option using the code given below : **[CBSE-PMT 2011 M]**

List I	**List-II**
(A) Benzaldehyde	(i) Phenolphthalein
(B) Phthalic anhydride	(ii) Benzoin condensation
(C) Phenyl benzoate	(iii) Oil of wintergreen
(D) Methyl salicylate	(iv) Fries rearrangement

Code :

	(A)	(B)	(C)	(D)
(a)	(iv)	(i)	(iii)	(ii)
(b)	(iv)	(ii)	(iii)	(i)
(c)	(ii)	(iii)	(iv)	(i)
(d)	(ii)	(i)	(iv)	(iii)

5. An organic compound ‘A’ on treatment with NH_3 gives ‘B’ which on heating gives ‘C’, ‘C’ when treated with Br_2 in the presence of KOH produces ethylamine. Compound ‘A’ is: **[CBSE-PMT 2011 M]**

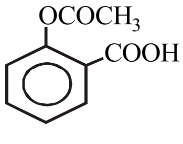
(a) CH_3COOH
(b) $CH_3\,CH_2\,CH_2\,COOH$
(c) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}COOH$
(d) CH_3CH_2COOH

6. The correct order of decreasing acid strength of trichloroacetic acid (*A*), trifluoroacetic acid (*A*), acetic acid (*C*) and formic acid (*D*) is : **[CBSE-PMT 2012]**

(a) $B > A > D > C$
(b) $B > D > C > A$
(c) $A > B > C > D$
(d) $A > C > B > D$

7. $CH_3CH_2COOH \xrightarrow[\text{red P}]{Cl_2} A \xrightarrow{\text{alc. KOH}} B.$ What is *B*? **[AIEEE 2002]**

(a) CH_3CH_2COCl
(b) CH_3CH_2CHO
(c) $CH_2{=}CHCOOH$
(d) $ClCH_2CH_2COOH.$

8. The compound  is used as **[AIEEE 2002]**

(a) antiseptic
(b) antibiotic
(c) analgesic
(d) pesticide.

9. When $CH_2 = CH — COOH$ is reduced with $LiAlH_4$, the compound obtained will be **[AIEEE 2003]**

(a) $CH_2{=}CH—CH_2OH$
(b) $CH_3—CH_2—CH_2OH$
(c) $CH_3—CH_2—CHO$
(d) $CH_3—CH_2—COOH$

10. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is **[AIEEE 2004]**

(a) $CH_3COCl + C_2H_5OH + NaOH$
(b) $CH_3COONa + C_2H_5OH$
(c) $CH_3COOC_2H_5 + NaCl$
(d) $CH_3Cl + C_2H_5COONa$

11. Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon? **[AIEEE 2004]**

(a) Acetamide
(b) Acetic acid
(c) Ethyl acetate
(d) Butan-2-one

12. Among the following acids which has the lowest pK_a value? **[AIEEE 2005]**

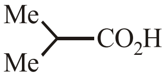
(a) CH_3CH_2COOH
(b) $(CH_3)_2CH-COOH$
(c) HCOOH
(d) CH_3COOH

13. The increasing order of the rate of HCN addition to compound A – D is **[AIEEE 2006]**

(A) HCHO
(B) CH_3COCH_3
(C) $PhCOCH_3$
(D) PhCOPh

(a) $D < C < B < A$
(b) $C < D < B < A$
(c) $A < B < C < D$
(d) $D < B < C < A$

14. The correct order of increasing acid strength of the compounds **[AIEEE 2006]**

(A) CH_3CO_2H
(B) $MeOCH_2CO_2H$
(C) CF_3CO_2H
(D)  is

(a) $D < A < B < C$
(b) $A < D < B < C$
(c) $B < D < A < C$
(d) $D < A < C < B$

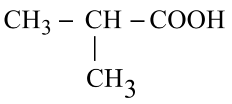
15. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was : **[AIEEE 2009]**

(a) HCHO
(b) CH_3COCH_3
(c) CH_3COOH
(d) CH_3OH

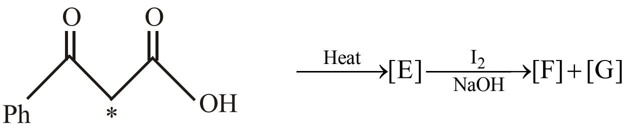
16. Aspirin is known as : **[AIEEE 2012]**

(a) Acetyl salicylic acid
(b) Phenyl salicylate
(c) Acetyl salicylate
(d) Methyl salicylic acid

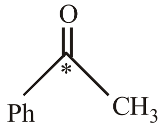
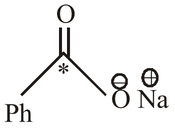
17. An organic compound A upon reacting with NH_3 gives B. On heating B gives C. C in presence of KOH reacts with Br_2 to given $CH_3CH_2NH_2$. A is : **[JEE M 2013]**

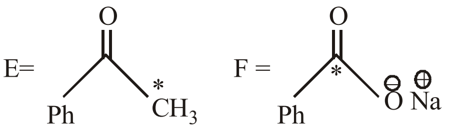
(a) CH_3COOH
(b) $CH_3CH_2CH_2COOH$
(c) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$
(d) CH_3CH_2COOH

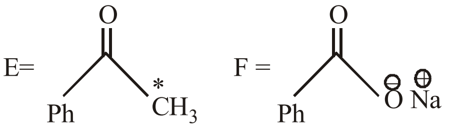
18. In the following reaction sequence, the correct structures of E, F and G are **[IIT-JEE 2007]**

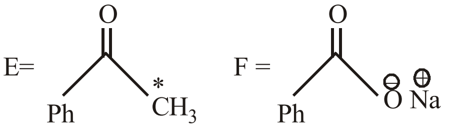


[* implies ^{13}C labelled carbon)

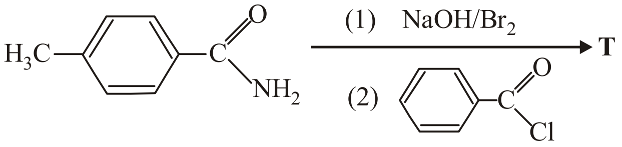
(a) E=  F =  $G = CHI_3$

(b)  $G = CHI_3$

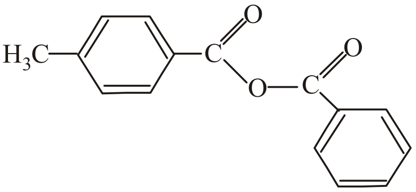
(c)  $G = \overset{*}{C}HI_3$

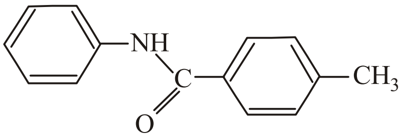
(d)  $G \overset{*}{=} CH_3I$

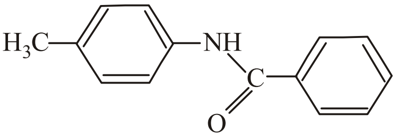
19. In the reaction

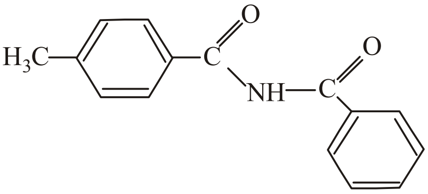


the structure of the product **T** is : **[IIT-JEE 2010]**

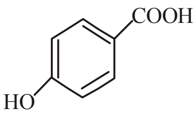
(a) 

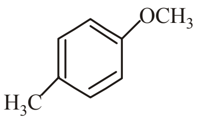
(b) 

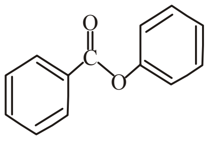
(c) 

(d) 

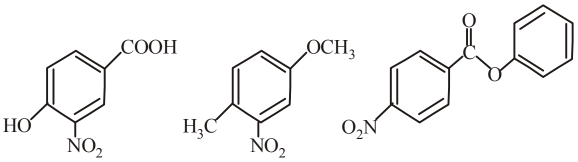
20. The compounds P, Q and S

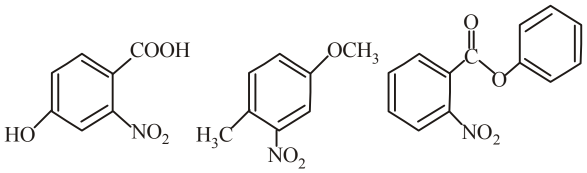

P

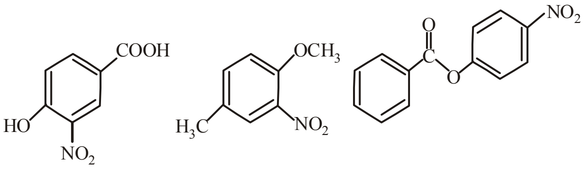

Q

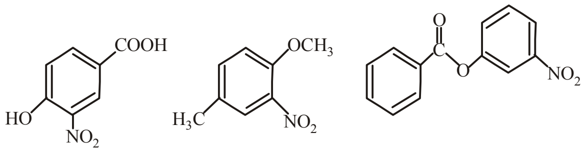

S

were separately subjected to nitration using HNO_3/H_2SO_4 mixture. The major product formed in each case respectively, is : **[IIT-JEE 2010]**

(a) 

(b) 

(c) 

(d) 

21. The carboxyl functional group (– COOH) is present in **[IIT-JEE 2012]**

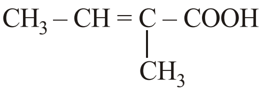
(a) picric acid (b) barbituric acid

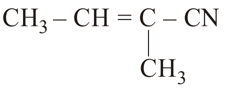
(c) ascorbic acid (d) aspirin

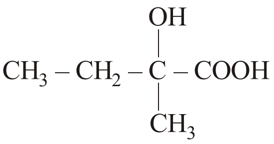
22. The major product **H** of the given reaction sequence is

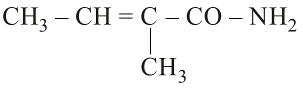
$$CH_3-CH_2-CO-CH_3 \xrightarrow{CN^{\ominus}} G \xrightarrow[\text{Heat}]{95\%\ H_2SO_4} H$$

[IIT-JEE 2012]

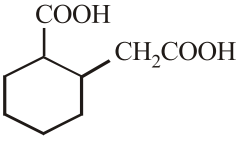
(a) 
$CH_3-CH=\underset{CH_3}{\underset{|}{C}}-COOH$

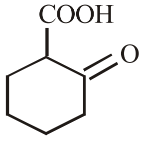
(b) 
$CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CN$

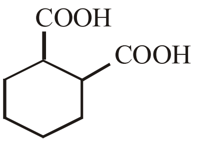
(c) 
$CH_3-CH_2-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-COOH$

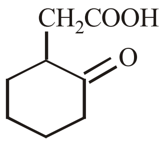
(d) 
$CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CO-NH_2$

23. The compound that undergoes decarboxylation most readily under mild condition is **[IIT-JEE 2012]**

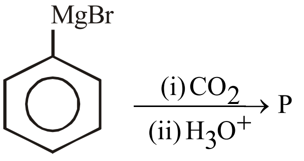
(a) 

(b) 

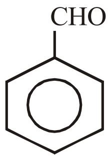
(c) 

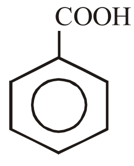
(d) 

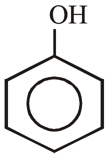
Exercise-4 | Applied MCQs

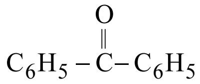
1. 

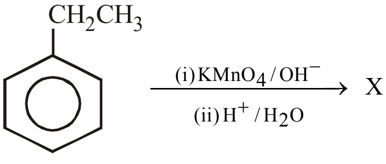
In the above reaction, product 'P' is

(a) 

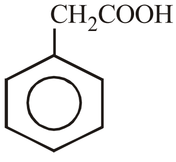
(b) 

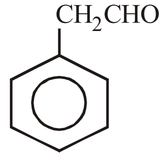
(c) 

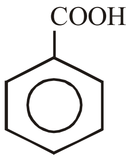
(d) 
$C_6H_5-\overset{O}{\overset{\|}{C}}-C_6H_5$

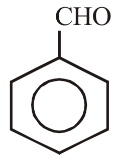
2. 

Predict 'X' in the above reaction

(a) 

(b) 

(c) 

(d) 

3. Carboxylic acid group does not give the usual addition and elimination reactions of aldehydes and ketones because

(a) O–H bond is more polar than $>C=O$ group
(b) carboxylate ion gets ionised
(c) carboxylate ion gets stabilised by resonance
(d) it exists as – COOH and there is no carbonyl group

4. When propanoic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The 'C' of CO_2 comes from

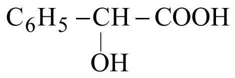
(a) methyl group (b) caboxylic acid group
(c) methylene group (d) bicarbonate

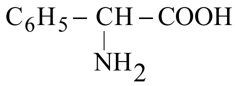
5. Which one of the following orders of acid strength is correct?

(a) $RCOOH > HOH > ROH > HC\equiv CH$
(b) $RCOOH > HOH > HC\equiv CH > ROH$
(c) $RCOOH > HC\equiv CH > HOH > ROH$
(d) $RCOOH > ROH > HOH > HC\equiv CH$

6. Which of the following carboxylic acids undergoes decarboxylation easily ?

(a) $C_6H_5–CO–CH_2–COOH$ (b) $C_6H_5–CO–COOH$

(c) 
$C_6H_5-\underset{OH}{\underset{|}{CH}}-COOH$

(d) 
$C_6H_5-\underset{NH_2}{\underset{|}{CH}}-COOH$

7. On bromination, propionic acid gives two isomeric 2-bromopropionic acids. This pair will be an example of

(a) optical isomers (b) cis-trans isomers
(c) chain isomers (d) position isomers

8. Predict the nature of C in the following series of reactions

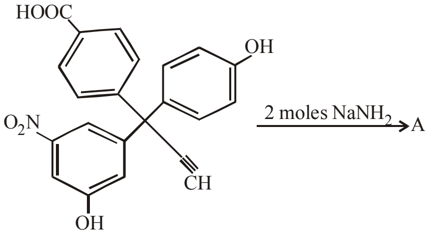
$$CH_3COOH \xrightarrow{PCl_5} [A] \xrightarrow[\text{anhy } AlCl_3]{C_6H_6} [B] \xrightarrow{CH_3MgBr} [C]$$

(a) CH_3COCH_5 (b) $CH_3CH(OH)C_6H_5$
(c) $CH_3C(C_2H_5)(OH)C_6H_5$ (d) $CH_3CH(OH)C_2H_5$

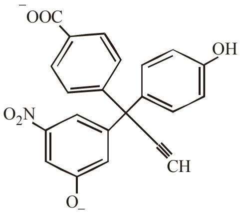
9. What is Z in the following sequence of reactions?

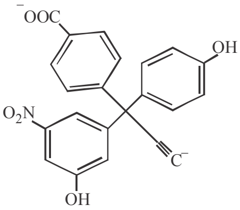
$$\text{Phenol} \xrightarrow[\text{dust}]{Zn} X \xrightarrow[\text{Anhyd. } AlCl_3]{CH_3Cl} Y \xrightarrow[KMnO_4]{\text{Alkaline}} Z$$

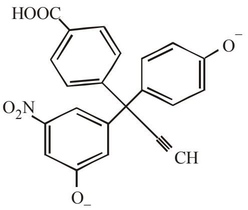
(a) Benzene (b) Toluene
(c) Benzaldehyde (d) Benzoic acid

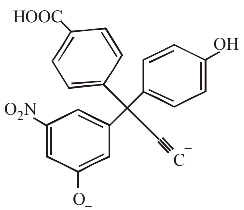
10. 

The product A will be

(a) 

(b) 

(c) 

(d) 

11. Identify Z in the following reaction sequence.

$$CH_3CHO \xrightarrow[\text{Dil.} H_2SO_4]{MnO_4^-} X \xrightarrow{SOCl_2} Y \xrightarrow[\Delta]{CH_3COONa} Z$$

(a) CH_3COCH_2COONa (b) $(CH_3CO)_2O$
(c) $CH_3CO–O–COCH_2Cl$ (d) $CH_3CO–OCOCHCl_2$

12. Which of the following esters cannot undergo Claisen self condensation ?
(a) $CH_3CH_2CH_2CH_2COOC_2H_5$
(b) $C_6H_5–COOC_2H_5$
(c) $C_6H_{11}CH_2COOC_2H_5$
(d) $C_6H_5CH_2COOC_2H_5$

13. Identify Z in the sequence

$$CH_3COONH_4 \xrightarrow{\Delta} X \xrightarrow[\Delta]{P_2O_5} Y \xrightarrow{H_2O/H^+} Z$$

(a) $CH_3CH_2CONH_2$ (b) CH_3CN
(c) CH_3COOH (d) $(CH_3CO)_2O$

14. Identify X in the following sequence of reactions?

$$\underset{(X)}{C_4H_7OCl} \xrightarrow{NH_3} C_4H_9ON \xrightarrow{Br_2,\ KOH} CH_3CH_2CH_2NH_2$$

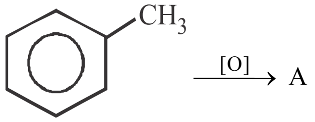
(a) $(CH_3)_2CHCOCl$
(b) $CH_3CH_2CH(OH)CH_2Cl$
(c) $CH_3CH_2CH_2COCl$
(d) $ClCH_2CH_2CH_2CHO$

15. The product (D) of the reaction

$$CH_3Cl \xrightarrow{KCN} (A) \xrightarrow{H_2O/H^+} (B) \xrightarrow{NH_3} (C) \xrightarrow{\Delta} (D) \text{ is}$$

(a) $CH_3CH_2NH_2$ (b) CH_3CN
(c) $HCONH_2$ (d) CH_3CONH_2

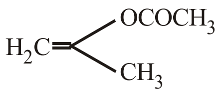
16. In the following sequence of reactions, what is D?



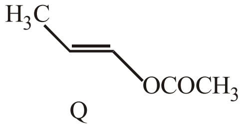
$$A \xrightarrow{SOCl_2} B \xrightarrow{NaN_3} C \xrightarrow{heat} D$$

(a) Primary amine (b) An amide
(c) Phenyl isocyanate (d) A higher hydrocarbon

17. The product of acid hydrolysis of P and Q can be distinguished by



P



Q

(a) Lucas reagent (b) 2, 4- DNP
(c) Fehling's solution (d) $NaHSO_3$

18. When a mixture of 1-hexanol and hexanoic acid in diethyl ether is shaken with an aqueous $NaHCO_3$ solution, then which of the following is correct distribution ?

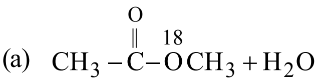
	Ether	Sodium bicarbonate solution
(a)	Hexanoic acids	1- Hexanol
(b)	1-hexanol	Sodium hexanoate
(c)	1-hexanol	Hexanoic acid
(d)	Sodium hexanoate	1-hexanol

19. The correct product of the following sequence of reactions

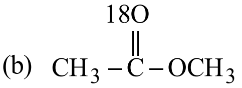
$$(CH_3)_2CHCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} \xrightarrow{PBr_3} \xrightarrow[DMSO]{KCN} \xrightarrow[\Delta]{H_2O,\ H^+}$$

(a) $(CH_3)_2CHCHBr.COOH$
(b) $(CH_3)_2CHCH_2COOH$
(c) $(CH_3)_2CHCH_2CH_2NH_2$
(d) $(CH_3)_2C = CHCOOH$

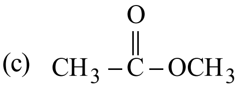
20. When CH_3COOH reacts with labeled $CH_3\overset{18}{O}H$ and catalytic H_2SO_4, it gives

(a) 

$CH_3-\overset{\overset{O}{\|}}{C}-\overset{18}{O}CH_3 + H_2O$

(b) 

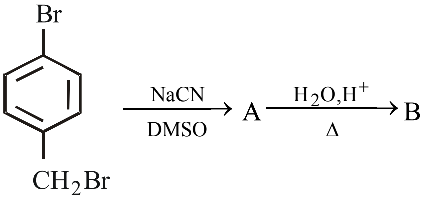
$CH_3-\overset{\overset{18O}{\|}}{C}-OCH_3$

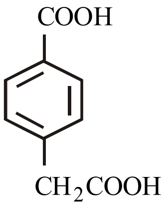
(c) 

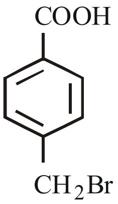
$CH_3-\overset{\overset{O}{\|}}{C}-OCH_3$

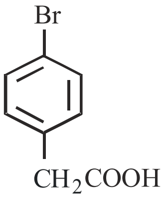
(d) Equal amounts of (a) and (b)

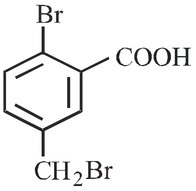
21. What is B in the sequence of reactions shown below ?



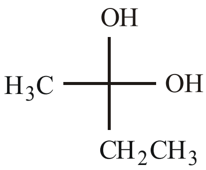
(a) 

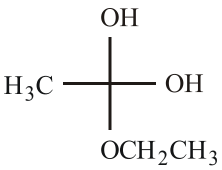
(b) 

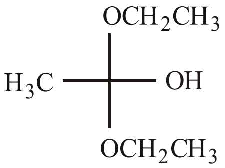
(c) 

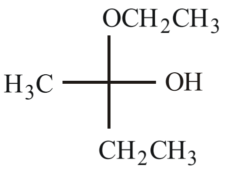
(d) 

22. The intermediate formed when CH_3COOH react with CH_3CH_2OH

(a) 

(b) 

(c) 

(d) 

23. Which of the following is not a good method to make 2, 2- dimethyl propanoic acid ?

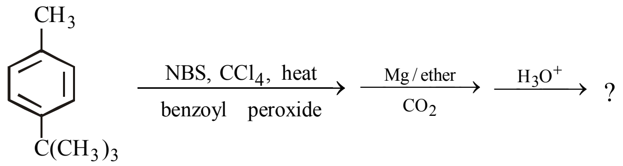
(a) $(CH_3)_3CBr \xrightarrow[Et.OEt]{Mg} \xrightarrow[H_2O,H^+]{CO_2}$

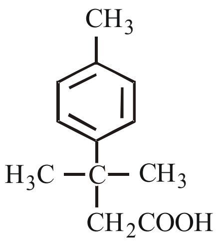
(b) $(CH_3)_3CBr \xrightarrow{NaCN} \xrightarrow[\Delta]{H_2O,H^+}$

(c) $(CH_3)_3C-C\equiv CH \xrightarrow{O_3} \xrightarrow{H_2O}$

(d) $(CH_3)_3CCH_2OH \xrightarrow[H_2O\ \Delta]{K_2Cr_2O_7,H_2SO_4}$

24. The final product of the following sequence of reactions is



(a)


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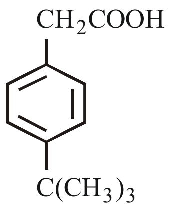

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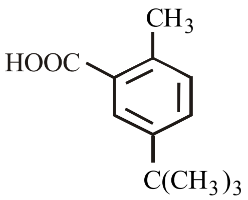
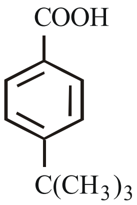
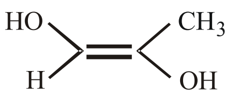
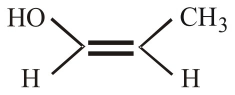
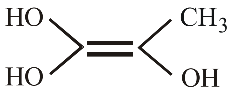


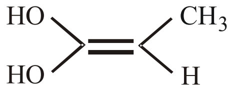
(d)


25. Which of the following is the enol/intermediate in the thermal decarboxylation of methyl propanedioic acid $CH_3CH(COOH)_2$

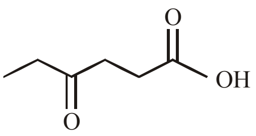
(a)


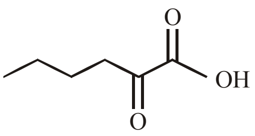
(b)


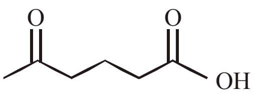
(c)


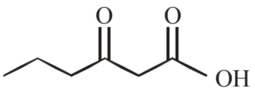
(d)


26. Which one of the following compounds undergoes decarboxylation upon heating ?

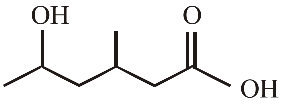
(a)


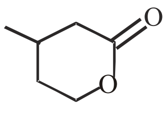
(b)


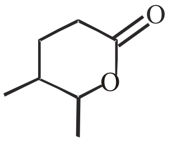
(c)


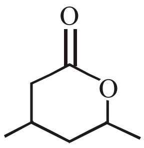
(d)


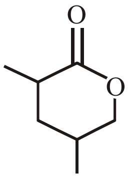
27. Which lactone is formed by heating the following hydroxy acid ?



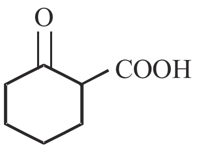
(a)


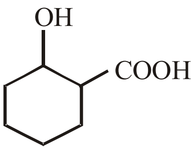
(b)


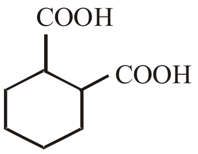
(c)


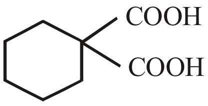
(d)


28. Which of the following undergoes decarboxylation upon heating ?

A


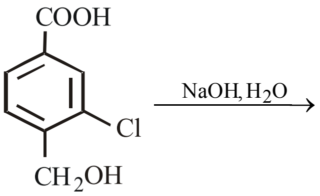
B


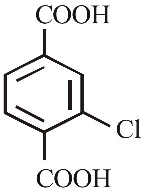
C


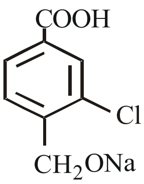
D


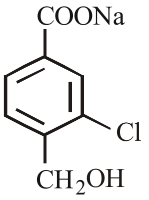
(a) C and D (b) A and D
(c) A and C (d) B and C

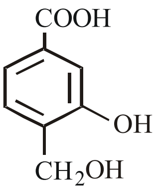
29. The product of the reaction shown below is



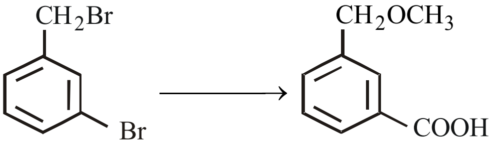
(a)


(b)


(c)


(d)


30. Which of the following combination of reagents can brought transformation ?



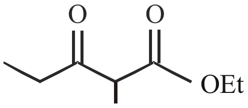
(a) $CH_3O^- \overset{+}{Na}$, Mg/ether, $CO_2, H_2O/H^+$

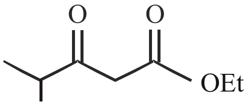
(b) $CH_3O^- \overset{+}{Na}$, KCN/DMSO, H_2O/H_2SO_4 heat

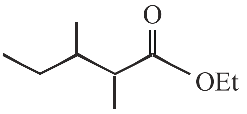
(c) Mg/ether, $CO_2, H_2O/H^+$, $CH_3O^- \overset{+}{Na}$

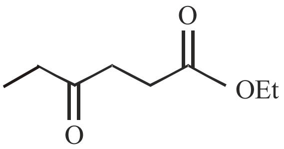
(d) NaOH, Mg/ether, $CO_2, H_2O/H^+, CH_3I$

31. Which of the following is the Claisen condensation product of ethyl propanoate CH_3CH_2COOEt ?

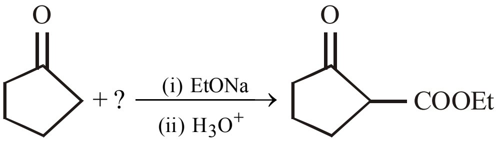
(a)


(b)


(c)


(d)


32. Identify the missing reagent in the reaction given below



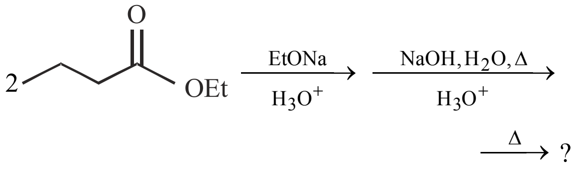
(a) Diethyl carbonate $(EtO)_2C = O$

(b) Ethyl acetate CH_3COOEt

(c) Ethyl formate HCOOEt

(d) Diethyl oxalate Et. OOC. COOEt

33. The correct product of the following sequence of reactions

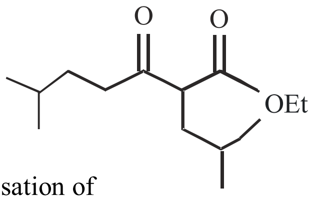


(a) 4 - heptanone

(b) 4 - methyl - 3 - hexanone

(c) 2 - ethyl pentanoic acid

(d) 2 - propyl butanoic acid

34. The compound


is obtained by Claisen condensation of

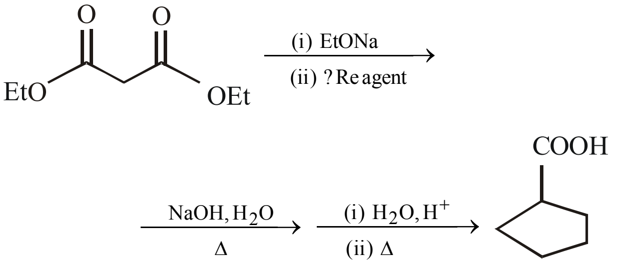
(a) ethyl -2 - methyl pentanoate

(b) ethyl-5-methyl hexanoate

(c) ethyl -4 - methyl pentanoate

(d) ethyl -3, 3 - dimethyl butanoate

35. What is the missing reagent in the synthesis shown below



(a) bromocyclopentane

(b) 1, 5 - dibromo pentane

(c) 1, 4 - dibromo butane

(d) 1, 1 - dibromo cyclo pentane

36. 5 - methyl -2 -hexanone can be synthesised from acetoacetic ester and RX. Which of the following RX is used ?

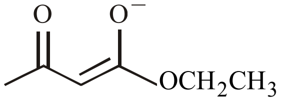
(a) $(CH_3)_2CHBr$

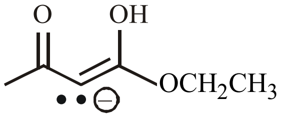
(b) $(CH_3)_2CHCH_2Br$

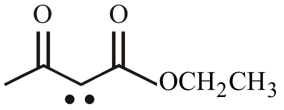
(c) $CH_3CH_2CHBrCH_3$

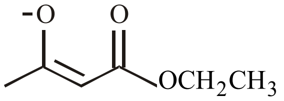
(d) $(CH_3)_2CHCH_2CH_2Br$

37. Which one of the following is not resonance form of the enolate ion formed from aceto acetic ester ?

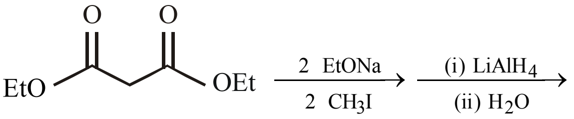
(a)


(b)


(c)


(d)


38. The correct product of the following reactions



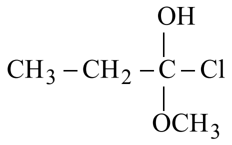
(a) 2, 2-dimethyl propane diol

(b) 2-methyl-1-propanol

(c) 2, 2-dimethyl propanedioic acid

(d) 2-methyl propanoic acid

39. The following tetrahedral intermediate breaks down to



$$CH_3-CH_2-\underset{OCH_3}{\overset{OH}{C}}-Cl$$

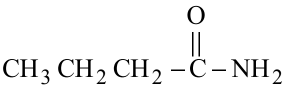
(a) propanal and HCl

(b) methyl propanoate and HCl

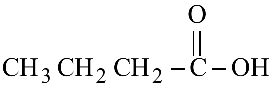
(c) propanoic acid and CH_3Cl

(d) propyl chloride and CH_3OH

40. Which of the following compounds on reaction with aq. NaOH yield $CH_3CH_2CH_2COONa$ at the lowest speed

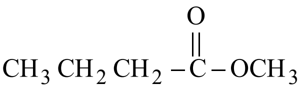
(a) 

$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-NH_2$

(b) 

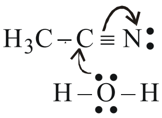
$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH$

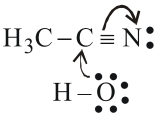
(c) $(CH_3CH_2CH_2CO)_2O$

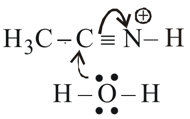
(d) 

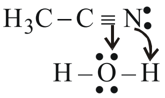
$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_3$

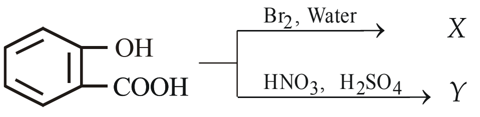
41. Which of the following is the best mechanistic step in the acid catalysed hydrolysis of acetonitrile ?

(a) 

(b) 

(c) 

(d) 

42. 

X and *Y* respectively are

(a) 5 - bromosalicylic acid and 5 - nitrosalicylic acid

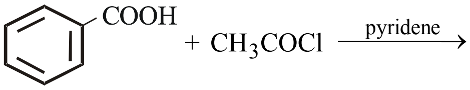
(b) o - bromophenol and o - nitro phenol

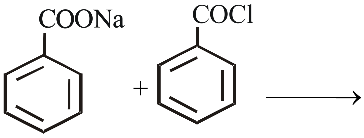
(c) 2, 4, 6 - tribromophenol and picric acid

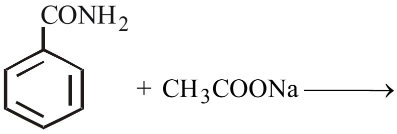
(d) 3, 5- dibromo salicylic acid and 3, 5 - dinitro salicylic acid

43. Which of the following will not yield an acid anhydride?

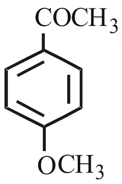
(a) 

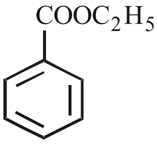
(b) 

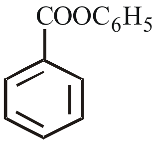
(c) 

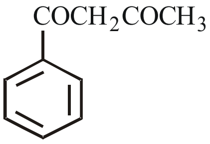
(d) 

44. An ester $A(C_9H_{10}O_2)$ with excess of CH_3MgBr upon hydrolysis and then with conc. H_2SO_4 gives an olefin (B). Ozonolysis of (B) gave a ketone (C_8H_8O) which gave + ve iodoform test. What is A

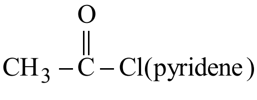
(a) 

(b) 

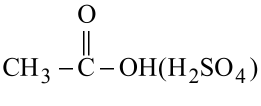
(c) 

(d) 

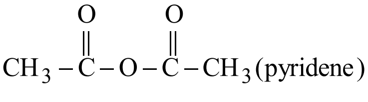
45. Which of the following will not give butyl acetate when treated with 1- butanol

(a) 

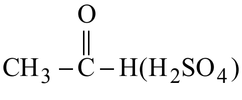
$CH_3-\overset{O}{\overset{\|}{C}}-Cl(\text{pyridene})$

(b) 

$CH_3-\overset{O}{\overset{\|}{C}}-OH(H_2SO_4)$

(c) 

$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3(\text{pyridene})$

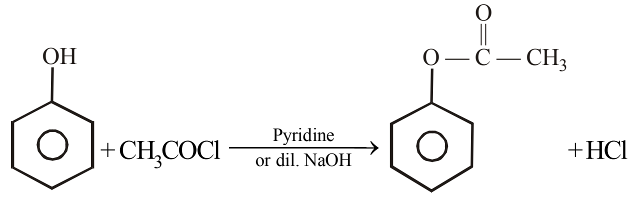
(d) 

$CH_3-\overset{O}{\overset{\|}{C}}-H(H_2SO_4)$

Hints & Solutions

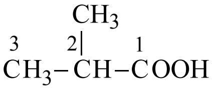
EXERCISE 1

1. $C_2H_5OH < C_6H_5OH < CH_3COOH < HCOOH$.

2. 

4. $CH_3CONH_2 < (CH_3CO)_2O < CH_3COOC_2H_5 < CH_3COCl$.
5. Ethanoate ion is stabilized by resonance but ethoxide ion is not.
6. Due to larger hydrocarbon part in benzoic acid.
7. An 8 – 10% solution of acetic acid in water is called vinegar.
8. CH_3COOH contains α-hydrogens and hence gives HVZ reaction but HCOOH does not contain an α-hydrogen and hence does not give HVZ reaction.
10. X is CH_3CONH_2, Y is $CH_3C\equiv N$ and Z is CH_3COOH.
11. A is $KMnO_4/H^+$, B is $SOCl_2$ and C is CH_3COONa.
16. **(c) 17. (d) 18. (a) 19. (d) 20. (c) 21. (a) 22. (b)**

EXERCISE 2

1. **(c)** 

$$\overset{3}{C}H_3-\overset{2}{C}H(CH_3)-\overset{1}{C}OOH$$

2. **(a)**
3. **(b)** $C_6H_5CN + 2H_2O + HCl \longrightarrow C_6H_5COOH + NH_4Cl$
4. **(a)** $RCH_2CH_2OH \xrightarrow{PBr_3} RCH_2CH_2Br$

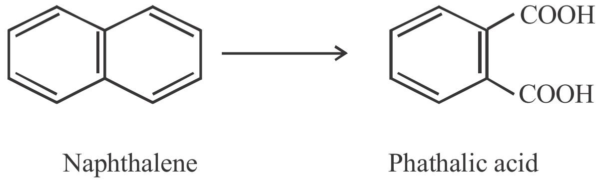
$$\xrightarrow{KCN} RCH_2CH_2CN \xrightarrow{H^+} RCH_2CH_2COOH$$

5. **(b)** 6. **(d)**
7. **(d)** $KMnO_4$ is a strong oxidising agent, so it oxidises carbon-carbon double bond to aldehyde and/or ketone. However, aldehydes are more easily oxidised so these are further oxidised to carboxylic acids, while ketones are difficult to oxidise so these are isolated as such.

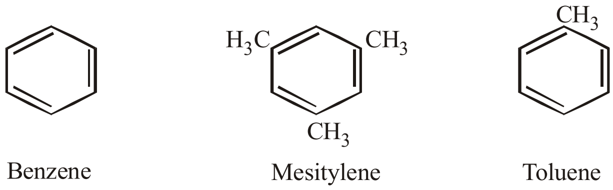
$$(CH_3)_2C = CHCH_2CH_3 \xrightarrow{KMnO_4} \mathbf{(CH_3)_2C = O} + OHCCH_2CH_3$$

$$\longrightarrow \mathbf{HOOCCH_2CH_3}$$

8. **(a)** In naphthalene, the two benzene rings are fused in *o*-positions, so one ring acts as two alkyl substituents present in the *o*-positions on the other ring.

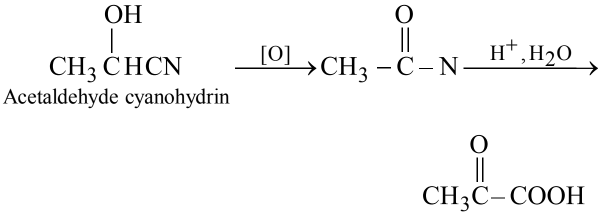


Other compounds do not have alkyl groups on *o*-positions.



9. **(b)** Alkaline potassium permanganate, oxidises secondary alcoholic group to ketone, which is not further oxidised.

$$\underset{\text{Lactic acid}}{CH_3CH\,OH\,COOH} \xrightarrow[KMnO_4]{alk.} \underset{\text{Pyruvic acid}}{CH_3CO\,COOH}$$

10. **(a)** 

$$\underset{\text{Acetaldehyde cyanohydrin}}{CH_3\overset{OH}{\overset{|}{C}}HCN} \xrightarrow{[O]} CH_3-\overset{O}{\overset{||}{C}}-N \xrightarrow{H^+,H_2O} CH_3\overset{O}{\overset{||}{C}}-COOH$$

11. **(b)** 12. **(b)** 13. **(c)** 14. **(b)**
15. **(b)** In benzene, benzoic acid undergoes dimerization and hence the molecular weight of benzoic acid is twice the actual molecular weight.
16. **(d)**
17. **(b)** Due to –I effect of the –COOH group, H-bonds in acids are much stronger than in alcohols; while aldehydes do not exhibit H-bonding.
18. **(d)**
19. **(b)** Since acetic acid freezes at 16.6ºC while water freezes at 0ºC, glacial acetic acid is obtained by crystallising, separating and melting acetic acid.
20. **(c)**
21. **(d)** In carboxylates (conjugate base of carboxylic acids), resonance is more significant because the two resonating structures are similar, while in phenoxide, the resonating structures are not equivalent, alkoxide ions do not show resonance.

22. (a) Only acetic acid is more acidic than carbonic acid (conjugate acid of $NaHCO_3$) hence it dissolves in $NaHCO_3$,

$$\underset{\text{stronger acid}}{CH_3COOH} + NaHCO_3 \longrightarrow$$

$$CH_3COO^-Na^+ + \underset{\text{weaker acid}}{H_2CO_3}\ (H_2O + CO_2)$$

while phenol and *n*-hexanol are less acidic than carbonic acid and hence do not dissolve in $NaHCO_3$.

23. (a) Acidic character of phenol is enhanced by the introduction of $-NO_2$ group. Since in picric acid (2, 4, 6-trinitrophenol) there are three $-NO_2$ groups, acidic character of phenol is enhanced to such an extent that it behaves like carboxylic acids, although it has no $-COOH$ group.

24. (c) A sulphonic acid is stronger acid than a carboxylic acid because the sulphonate ion (conjugate base) of sulphonic acid is more resonance stabilised and hence weaker base than the carboxylate ion.

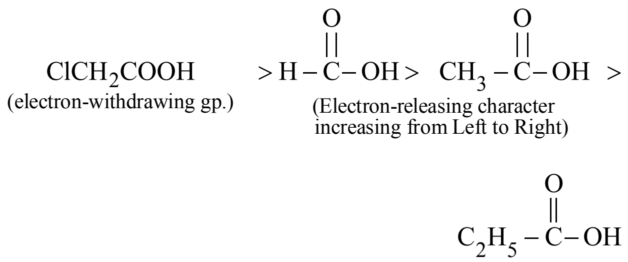
$$-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-O^- \qquad -\overset{O}{\overset{\|}{C}}-O^-$$

(-ve charge delocalised over 3 oxygens) (-ve charge delocalised over two oxygens)

25. (a) **26. (a)**

27. (c) Bromine is less electronegative than F, further in $BrCH_2CH_2COOH$, Br is more away from the $-COOH$ group than in $CH_3CHBrCOOH$.

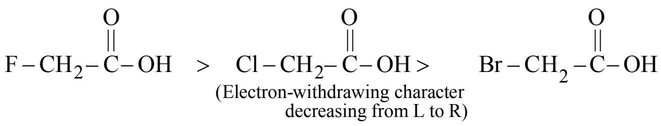
28. (b) Recall that presence of electron-withdrawing group increases, while presence of electron-releasing group decreases the acidity of carboxylic acids.



$$\underset{\text{(electron-withdrawing gp.)}}{ClCH_2COOH} > H-\overset{O}{\overset{\|}{C}}-OH > CH_3-\overset{O}{\overset{\|}{C}}-OH > C_2H_5-\overset{O}{\overset{\|}{C}}-OH$$

(Electron-releasing character increasing from Left to Right)

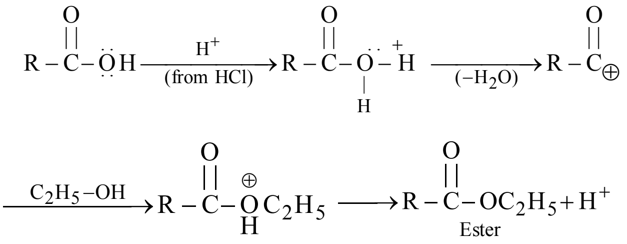
29. (a)



$$F-CH_2-\overset{O}{\overset{\|}{C}}-OH > Cl-CH_2-\overset{O}{\overset{\|}{C}}-OH > Br-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

(Electron-withdrawing character decreasing from L to R)

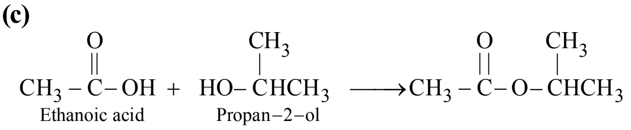
30. (b) $-OH$ is not a good leaving group while H_2O is a good leaving group (recall that weaker a base better is its leaving characteristic). HCl converts OH of ROH to H_2O which is easily lost and hence carbon becomes electron deficient and thus attacked by nucleophile (ROH) very readily.



$$R-\overset{O}{\overset{\|}{C}}-\ddot{O}H \xrightarrow[\text{(from HCl)}]{H^+} R-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{\overset{..}{O}}}\overset{+}{-}H \xrightarrow{(-H_2O)} R-\overset{O}{\overset{\|}{C}}\oplus$$

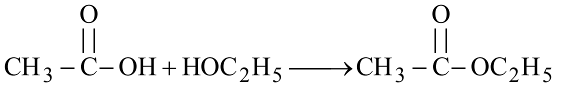
$$\xrightarrow{C_2H_5-OH} R-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{\oplus}{O}}C_2H_5 \longrightarrow \underset{\text{Ester}}{R-\overset{O}{\overset{\|}{C}}-OC_2H_5} + H^+$$

31. (c)



$$\underset{\text{Ethanoic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{Propan-2-ol}}{HO-\overset{CH_3}{\overset{|}{C}}HCH_3} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{CH_3}{\overset{|}{C}}HCH_3$$

32. (c) Fruity smell is due to the formation of ester, ethyl acetate.



$$CH_3-\overset{O}{\overset{\|}{C}}-OH + HOC_2H_5 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

33. (a) P_2O_5 is a dehydrating agent and removes a molecule of water from two molecules of acetic acid

$$CH_3COOH + HOOCCH_3 \xrightarrow{P_2O_5} CH_3COOCOCH_3$$

34. (c) **35. (a)** **36. (d)** **37. (b)**

38. (d)

$$CH_3CH_2COOH \xrightarrow{\text{red P, } Br_2} CH_3CHBrCOOH \xrightarrow{NH_3}$$

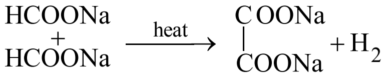
$$\underset{\alpha\text{-Aminopropionic acid (Alanine)}}{CH_3CHNH_2COOH}$$

39. (d) **40. (a)**

41. (b) Acetic acid does not have $-CHO$ grouping, while all others (HCOOH, HCHO and CH_3CHO) have $-CHO$ grouping

42. (d)

43. (b)

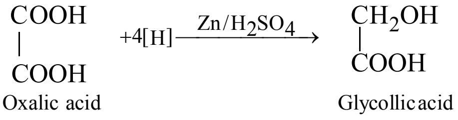


$$\begin{array}{c}HCOONa\\+\\HCOONa\end{array} \xrightarrow{\text{heat}} \begin{array}{c}COONa\\|\\COONa\end{array} + H_2$$

44. (a) Conc. H_2SO_4 acts as dehydrating agent

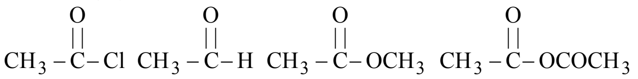
$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O$$

45. (c)



$$\underset{\text{Oxalic acid}}{\begin{array}{c}COOH\\|\\COOH\end{array}} + 4[H] \xrightarrow{Zn/H_2SO_4} \underset{\text{Glycollic acid}}{\begin{array}{c}CH_2OH\\|\\COOH\end{array}}$$

46. (a) More the magnitude of positive charge on the carbonyl carbon, higher will be its reactivity toward nucleophilic attack.



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \quad CH_3-\overset{O}{\overset{\|}{C}}-H \quad CH_3-\overset{O}{\overset{\|}{C}}-OCH_3 \quad CH_3-\overset{O}{\overset{\|}{C}}-OCOCH_3$$

Chlorine being more electron-withdrawing than O develops more positive charge on carbonyl carbon. The order of reactivity of the various carboxyl derivatives toward nucleophile is

$$\underset{\text{Most reactive}}{RCOCl} > (RCO)_2O > RCOOR > \underset{\text{Least reactive}}{RCONH_2}$$

47. **(c)**

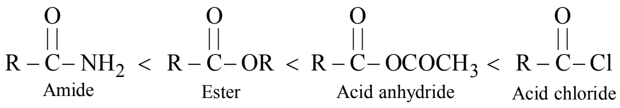
48. **(a)** Weaker the base, better the leaving group and hence more is the reactivity of the compound. The relative basic character of the four groups is

$$NH_2^- > OR^- > OCOCH_3^- > Cl^-$$

Thus the relative leaving ability of the four groups is

$$NH_2^- < OR^- < OCOCH_3^- < Cl^-$$

Hence the relative reactivity of the four acyl derivatives toward nucleophile is



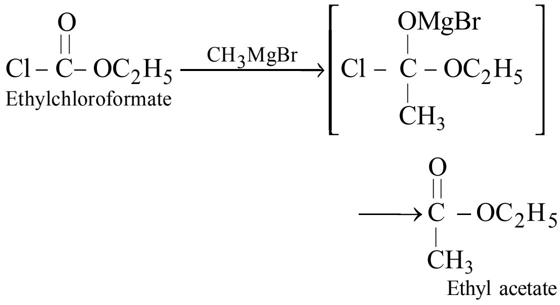
$$\underset{\text{Amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2} < \underset{\text{Ester}}{R-\overset{O}{\overset{\|}{C}}-OR} < \underset{\text{Acid anhydride}}{R-\overset{O}{\overset{\|}{C}}-OCOCH_3} < \underset{\text{Acid chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl}$$

49. **(c)** $C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl$

50. **(d)** NaCl is not a Lewis acid, so it cannot convert RCOOH into its conjugate base, necessary for the further reaction with the nucleophile

51. **(d)**

52. **(b)**



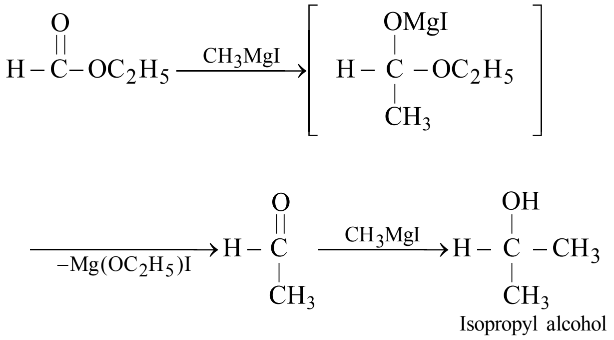
$$\underset{\text{Ethylchloroformate}}{Cl-\overset{O}{\overset{\|}{C}}-OC_2H_5} \xrightarrow{CH_3MgBr} \left[Cl-\underset{\underset{CH_3}{|}}{\overset{\overset{OMgBr}{|}}{C}}-OC_2H_5 \right]$$

$$\longrightarrow \underset{\text{Ethyl acetate}}{\underset{\underset{CH_3}{|}}{\overset{\overset{O}{\|}}{C}}-OC_2H_5}$$

53. **(b)** **54.** **(a)** **55.** **(d)** **56.** **(b)**

57. **(a)** Under moist and warm conditions, glycerides present in butter are hydrolysed to give butanoic acid (along with other volatile acids like caproic and caprylic acids) which produces disagreable smell ; this reaction is called **rancidity**

58. **(d)** Alkyl formate reacts with excess of RMgX to form secondary alkyls having both alkyl group corresponding to the alkyl group of the Grignard reagent



$$H-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{CH_3MgI} \left[H-\underset{\underset{CH_3}{|}}{\overset{\overset{OMgI}{|}}{C}}-OC_2H_5 \right]$$

$$\xrightarrow[-Mg(OC_2H_5)I]{} H-\underset{\underset{CH_3}{|}}{\overset{\overset{O}{\|}}{C}} \xrightarrow{CH_3MgI} \underset{\text{Isopropyl alcohol}}{H-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3}$$

59. **(b)** **60.** **(a)** **61.** **(c)**

62. **(d)** Ethyl benzoate on hydrolysis gives benzoic acid which is a solid, other esters give CH_3COOH and HCOOH, both of which are liquids

63. **(b)** Ethane is obtained by the electrolysis of sodium or potassium salt of ethanoic acid (CH_3COOH), hence the ester must be ethanoate CH_3COOR.

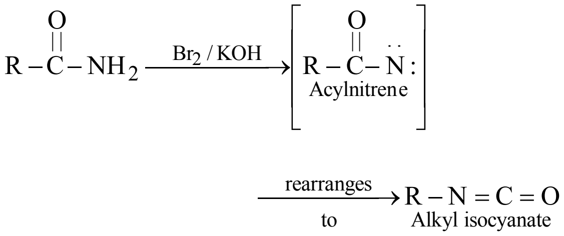
64. **(c)** $(CH_3)_2NCOCH_3$ is dimethylacetamide, hence on refluxing with acid, it undergoes hydrolysis in the following way

$$(CH_3)_2NCOCH_3 \xrightarrow{H^+,\text{reflux}} (CH_3)_2NH + HOOCCH_3$$

65. **(a)** Urea is a salt of weak acid, H_2CO_3, and weak base, NH_3

66. **(a)** **67.** **(c)** **68.** **(b)** **69.** **(c)**

70. **(b)**



$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br_2/KOH} \left[\underset{\text{Acylnitrene}}{R-\overset{O}{\overset{\|}{C}}-\ddot{N}:} \right]$$

$$\xrightarrow[\text{to}]{\text{rearranges}} \underset{\text{Alkyl isocyanate}}{R-N=C=O}$$

71. **(c)**

72. **(b)** Only amides (but not acids and esters) undergo hydrolysis in presence of soda-lime to form sodium salt of a carboxylic acid and ammonia gas. Further, since the given compound is a liquid, it must be formamide, because propanamide is a solid

73. **(b)** $\underset{59\,g\ (1\,mole)}{RCONH_2} + NaOH \rightarrow RCOONa + \underset{17\,g\ (1\,mole)}{NH_3}$

Thus wt. of 1 mole of $RCONH_2 = 59$

In other words, $R + 12 + 16 + 14 + 2 = 59$

$\therefore\ R = 59 - 44 = 15$

Molecular mass of R as 15 corresponds to CH_3 group, hence RCOOH should be CH_3COOH

74. **(d)** Methyl salicylate occurs in essential oils of winter green; other three statements are correct

EXERCISE 3

1. **(c)** Electron withdrawing substituent (like halogen, $—NO_2$, C_6H_5 etc.) would disperse the negative charge and hence stabilise the carboxylate ion and thus increase acidity of the parent acid. On the other hand, electron-releasing substituents would intensify the negative charge, destabilise the carboxylate ion and thus decrease acidity of the parent acid.

Electronegativity decreases in order

$$F > Cl > Br$$

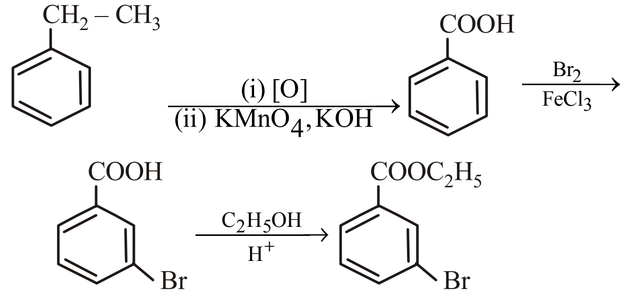
and hence –I effect also decreases in the same order, therefore the correct option is

$$[FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH]$$

2. **(c)** This reaction is an example of Hell - Volhard Zelinsky reaction. In this reaction acids containing α – H on treatment with X_2 /P give di-halo substituted acid.

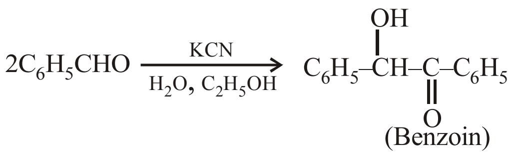
$$CH_3-CH_2COOH \xrightarrow{Br_2/P} CH_3-CBr_2-COOH$$

3. **(d)**



4. **(d)**

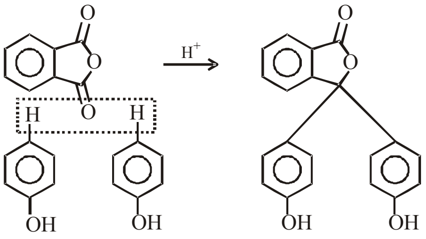
(a)



$$2C_6H_5CHO \xrightarrow[H_2O,\ C_2H_5OH]{KCN} C_6H_5-\overset{OH}{\overset{|}{C}H}-\underset{O}{\underset{||}{C}}-C_6H_5$$

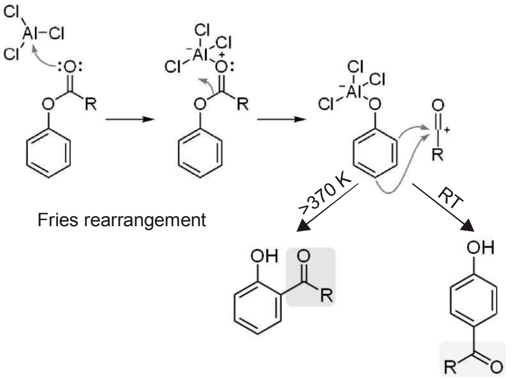
(Benzoin)

(b)

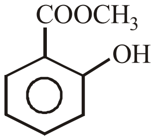


Phenolphthalein

(c)



(d)



(Oil of wintergreen)

5. **(d)** Since, C when heated with Br_2 in presence of KOH produces ethylamine, hence it must be propanamide and hence the organic compound (A) will be propanoic acid. The reactions follows.

$$\underset{(A)}{CH_3-CH_2-COOH} \xrightarrow{NH_3}$$

$$\underset{(B)}{CH_3-CH_2-CO\overset{-}{O}\overset{+}{N}H_4} \xrightarrow{\Delta}$$

$$CH_3-CH_2-CONH_2 \xrightarrow[\substack{\text{Hoffmann}\\ \text{bromamide}\\ \text{reaction}}]{KOH+Br_2} \underset{\text{(Ethylamine)}}{CH_3-CH_2-NH_2}$$

6. **(a)** $CF_3COOH > CCl_3COOH > HCOOH > CH_3COOH$ (K_a order)

The halogenated acids are much stronger acids than the parent acid and more over the acidity among the halogenated acid is increased almost proportionately with the increase in electronegativity of the halogen present. Further formic acid having no alkyl group is more acidic than acetic acid.

7. **(c)** $CH_3CH_2COOH \xrightarrow[\text{red P}]{Cl_2} CH_3CHClCOOH$

$$\xrightarrow[-HCl]{\text{alc.KOH}} \underset{\text{Acrylic acid}}{CH_2=CHCOOH}$$

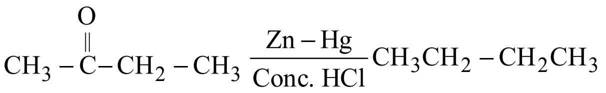
8. **(c)** The given compound is aspirin which is antipyretic and analgesic

9. **(a)** $LiAlH_4$ can reduce COOH group and not the double bond.

$$CH_2=CH-COOH \xrightarrow{LiAlH_4} CH_2=CH-CH_2OH$$

10. **(c)** There is no reaction hence the resultant mixture contains $CH_3COOC_2H_5 + NaCl$.

11. **(d)** It is Clemmensen's reduction



$$CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3 \xrightarrow[\text{Conc. HCl}]{Zn-Hg} CH_3CH_2-CH_2CH_3$$

12. **(c)** $pK_a = -\log K_a$; HCOOH is the strongest acid and hence it has the highest K_a or lowest pK_a value.

13. **(a)** Addition of HCN to carbonyl compounds is nucleophilic addition reaction. The order of reactivity of carbonyl compounds is

Aldehydes (smaller to higher) Ketones (smaller to higher), Then

$HCHO > CH_3COCH_3 > Ph.COCH_3 > PhCOPh$

The lower reactivity of ketones is due to presence of two alkyl group which shows +I effect. The reactivity of ketones decreases as the size of alkyl group increases.

14. **(a)** The correct order of increasing acid strength

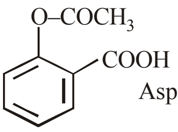
$$CF_3COOH > MeOCH_2COOH > CH_3COOH > (Me)_2CH.COOH$$

Electron withdrawing groups increase the acid strength and electron donating groups decrease the acid strength.

15. **(c)** Fruity smell is due to ester formation which is formed between ethanol and acid.

$$CH_3COOH + C_2H_5OH \xrightarrow{\text{Conc.}H_2SO_4} CH_3COOC_2H_5 + H_2O.$$

16. **(a)**

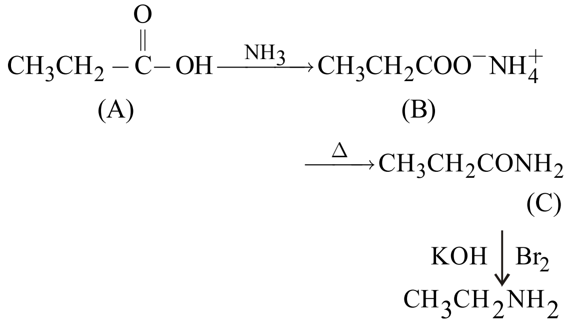


Aspirin (Acetyl salicylic acid)

17. **(d)** $A \xrightarrow[(I)]{NH_3} B \xrightarrow[II]{\Delta} C \xrightarrow[KOH,(III)]{Br_2} CH_3CH_2NH_2$

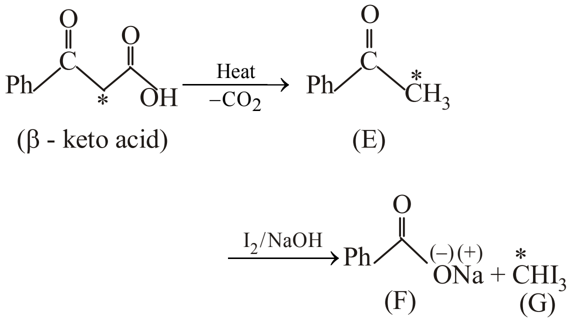
Reaction (III) is a Hofmann bromamide reaction. Now formation of $CH_3CH_2NH_2$ is possible only from a compound $CH_3CH_2CONH_2$(C) which can be obtained from the compound $CH_3CH_2COO^- NH_4^+$ (B).

Thus (A) should be CH_3CH_2COOH

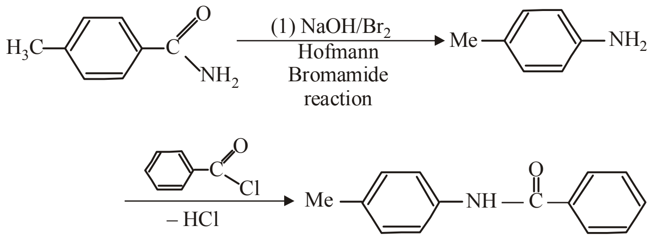


$$\underset{(A)}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow{NH_3} \underset{(B)}{CH_3CH_2COO^-NH_4^+} \xrightarrow{\Delta} \underset{(C)}{CH_3CH_2CONH_2} \xrightarrow[KOH]{Br_2} CH_3CH_2NH_2$$

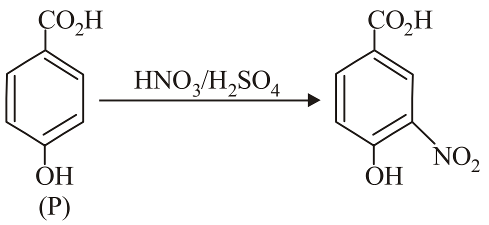
18. **(c)**



19. **(c)**

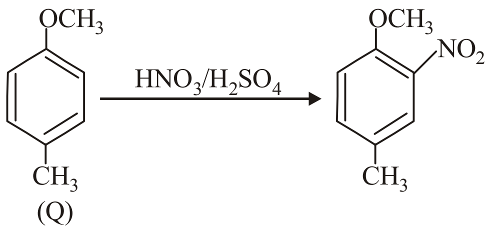


20. **(c)**



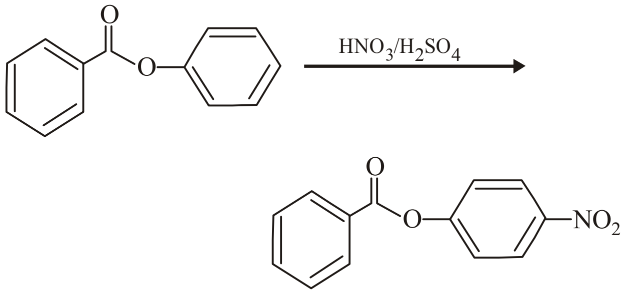
(P)

(OH group is activing)



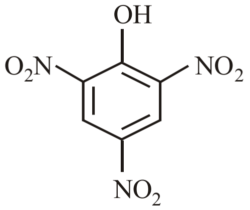
(Q)

(OCH_3 group is more activating)

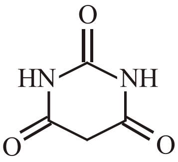


(Benzene ring having –O– is activated)

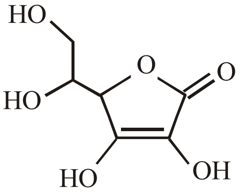
21. **(d)**



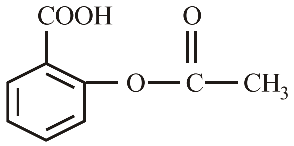
(Picric acid)



(Barbituric acid)

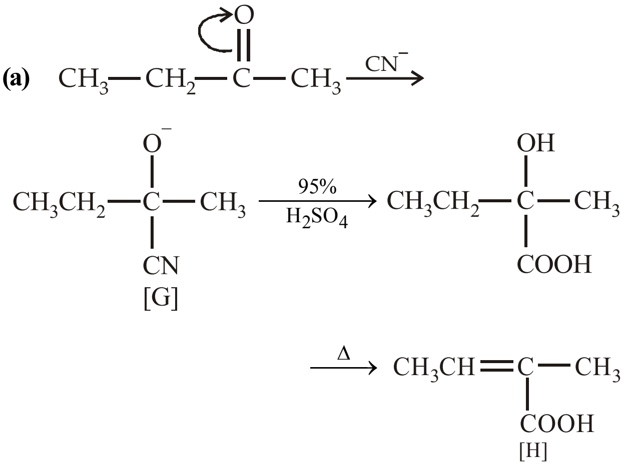


(Ascorbic acid)



(Aspirin)

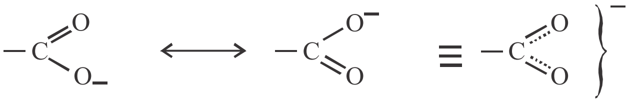
22. **(a)**



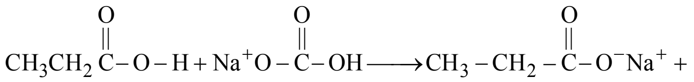
23. **(b)** β-Ketoacids undergo decarboxylation easily.

EXERCISE 4

1. **(b)**
2. **(c)** Remember that alkyl group present on benzene ring when oxidised by strong oxidising agent is always oxidised to –COOH group, ignoring its length.
3. **(c)** Due to resonance in carboxylate ion, the double bond character of C = O bond in carboxylic acids is greatly reduced as compared to that in aldehydes and ketones.

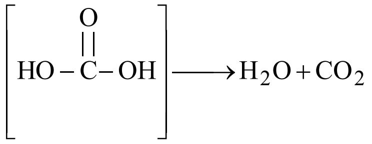


4. (d)



$$CH_3CH_2\overset{O}{\overset{||}{C}}-O-H+Na^+O-\overset{O}{\overset{||}{C}}-OH\longrightarrow CH_3-CH_2-\overset{O}{\overset{||}{C}}-O^-Na^+ +$$

Sod. bicarbonate



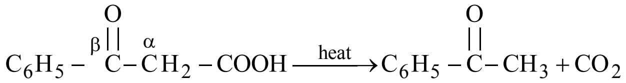
$$\left[HO-\overset{O}{\overset{||}{C}}-OH\right]\longrightarrow H_2O+CO_2$$

Carbonic acid

So remember that in such reaction, C of CO_2 always comes from bicarbonate.

5. (a) $RCOOH > ROH > HC\equiv CH$. Water is more acidic then alcohol.

6. (a) β-Keto carboxylic acids, on heating, undergo decarboxylation easily to form ketone as the product.



$$C_6H_5-\overset{O}{\overset{\beta||}{C}}\overset{\alpha}{-}CH_2-COOH\xrightarrow{heat}C_6H_5-\overset{O}{\overset{||}{C}}-CH_3+CO_2$$

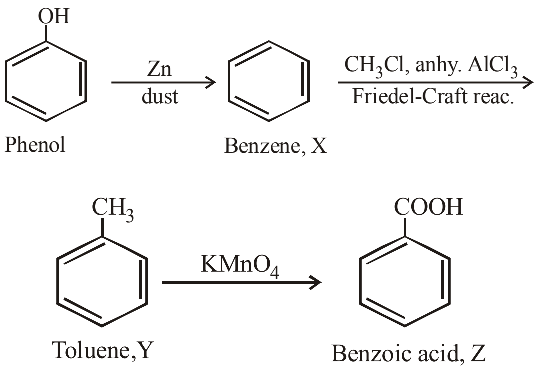
7. (a)

$$\underset{\text{Propionic acid}}{CH_3CH_2COOH}+Br_2\xrightarrow[\text{HVZ reaction}]{\text{red P}}\underset{\text{2–Bromopropionic acid}}{CH_3CHBrCOOH}$$

Since a chiral carbon is introduced, the product will be a mixture of enantiomers.

8. (c)

9. (c)



10. (a)

11. (b) $CH_3CHO\xrightarrow{MnO_4^-/H^+}\underset{X}{CH_3COOH}\xrightarrow{SOCl_2}$

$$\underset{Y}{CH_3COCl}\xrightarrow[\text{heat}]{CH_3COONa}\underset{Z}{CH_3COOCOCH_3}$$

12. (b) Claisen condensation is given by esters having two α-hydrogen atoms

13. (c) $CH_3COONH_4\xrightarrow[(-H_2O)]{\text{heat}}\underset{X}{CH_3CONH_2}$

$$\xrightarrow[(-H_2O)]{P_2O_5}\underset{Y}{CH_3CN}\xrightarrow[(-NH_3)]{H_3O^+}\underset{Z}{CH_3COOH}$$

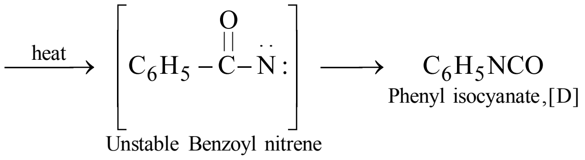
14. (c) Proceed backward, since the product is a primary amine and formed by Br_2/KOH ; so the reaction involved must be Hofmann's bromamide reaction. Hence C_4H_9ON should be $CH_3CH_2CH_2CONH_2$ and thus X (C_4H_7OCl) should be $CH_3CH_2CH_2COCl$

15. (d) $CH_3Cl\xrightarrow{KCN}\underset{[A]}{CH_3CN}\xrightarrow{H_3O^+}\underset{[B]}{CH_3COOH}$

$$\xrightarrow{NH_3}\underset{[C]}{CH_3COONH_4}\xrightarrow{heat}\underset{[D]}{CH_3CONH_2}$$

16. (c) $C_6H_5CH_3\xrightarrow{[O]}\underset{[A]}{C_6H_5COOH}\xrightarrow{SOCl_2}$

$$\underset{[B]}{C_6H_5COCl}\xrightarrow{NaN_3}\underset{[C]}{C_6H_5CON_3}$$



$$\xrightarrow{heat}\left[C_6H_5-\overset{O}{\overset{||}{C}}-\ddot{N}:\right]\longrightarrow C_6H_5NCO$$

Phenyl isocyanate,[D]

Unstable Benzoyl nitrene

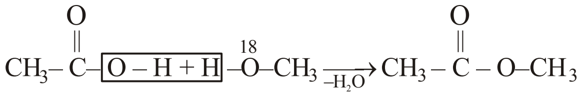
17. (c)

18. (b) $RCOOH+NaHCO_3\longrightarrow RCOONa+CO_2+H_2O$
Salts are soluble in aqueous solution

19. (b) $-COOH\xrightarrow[H_2O]{LiAlH_4}-CH_2OH\xrightarrow{PBr_3}-CH_2Br$

$$\xrightarrow[DMSO]{KCN}-CH_2CN\xrightarrow[H_2O]{H^+}-CH_2COOH$$

20. (a)



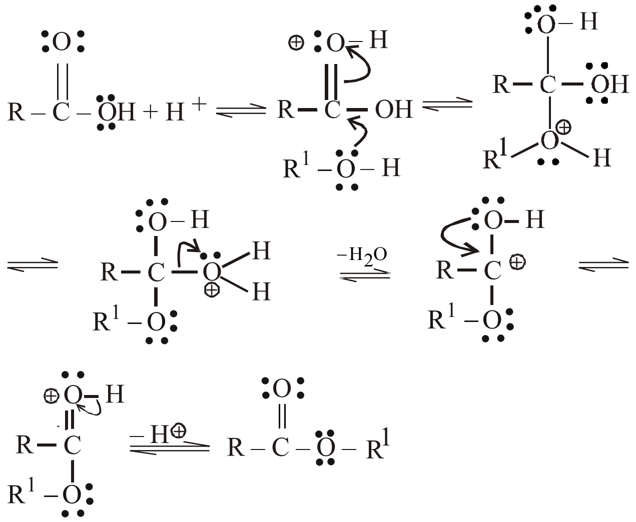
$$CH_3-\overset{O}{\overset{||}{C}}-\boxed{O-H+H}-\overset{18}{O}-CH_3\xrightarrow[-H_2O]{}CH_3-\overset{O}{\overset{||}{C}}-O-CH_3$$

21. (c) $-CH_2Br\xrightarrow[DMSO]{NaCN}-CH_2CN\xrightarrow[H_2O]{H^+}$

$$-CH_2COOH$$

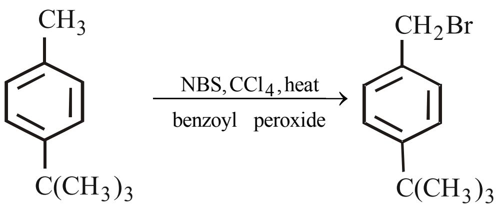
The neuclear Br is not replaced by CN under ordinary conditions

22. (b) Mechanism of esterification

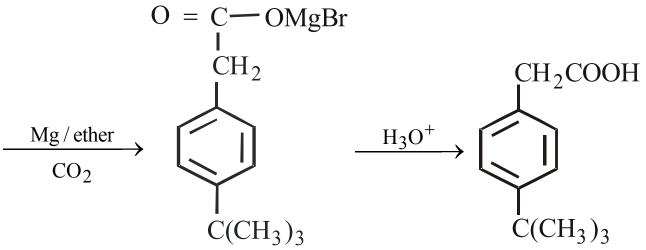


23. (b) $RX + CN^- \rightarrow RCN + X^-$. The reaction fails with R_3CX which gives elimination reaction.

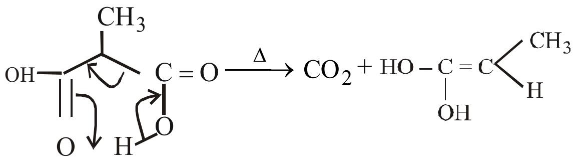
24. (b)



Allylic subsitution

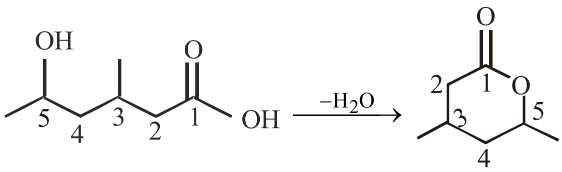


25. (d)



26. (d) β - Keto acids are decarboxylated by above mechanism

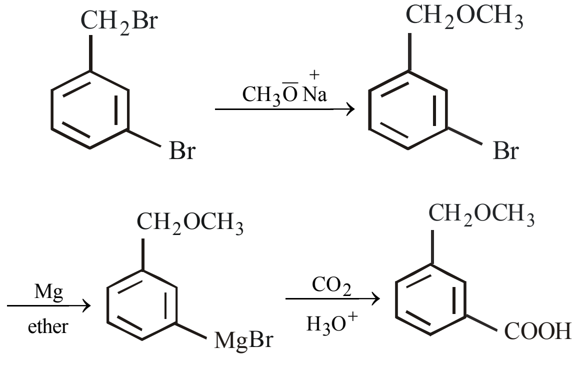
27. (c)



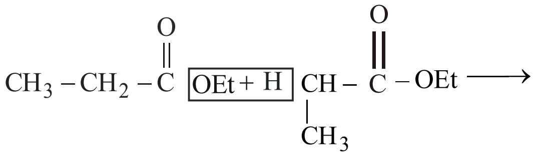
28. (b)

29. (c) Only acids form sodium salt with NaOH and not alcohols nuclear Cl is not replaced by OH under ordinary condctions

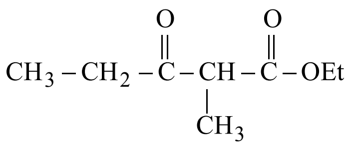
30. (a)



31. (a)

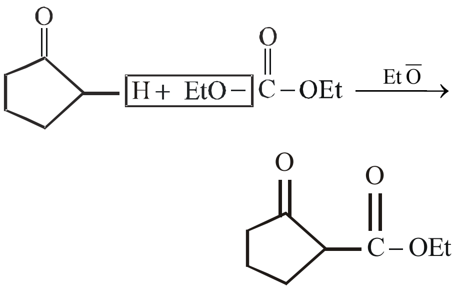


$CH_3-CH_2-\overset{O}{\overset{\|}{C}}\boxed{OEt+H}\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OEt \longrightarrow$

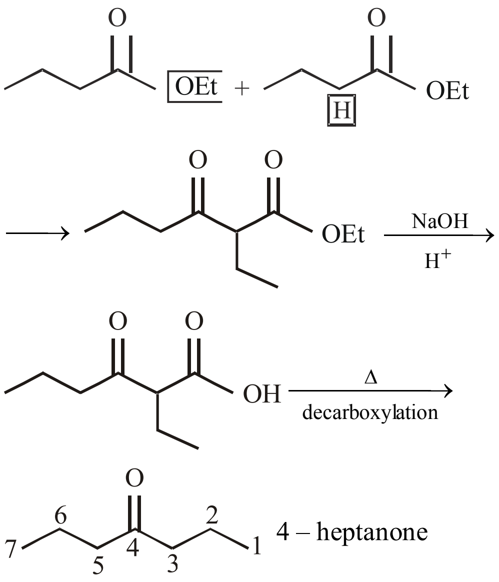


$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OEt$

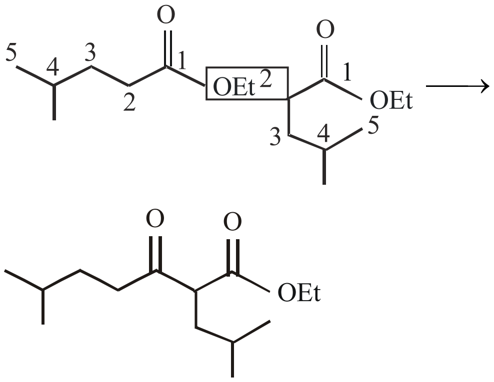
32. (a)



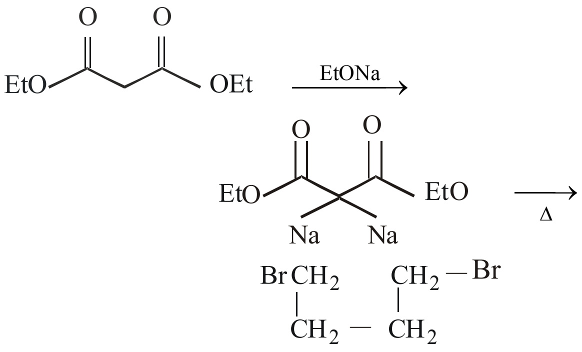
33. (a)

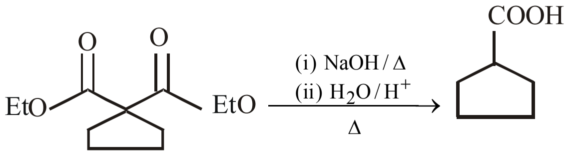


34. (c)

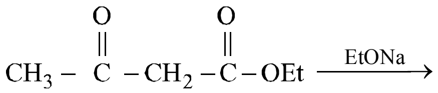


35. (c)

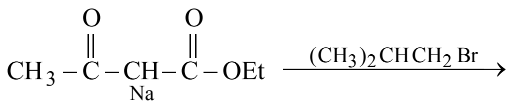




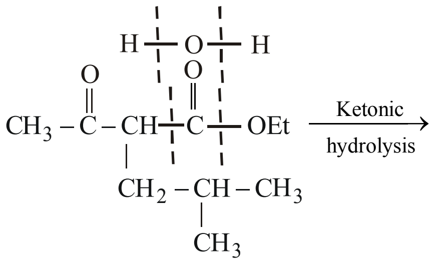
36. (b)

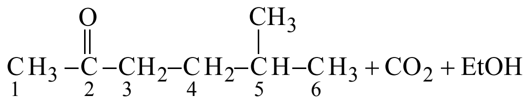


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow{EtONa}$$



$$CH_3-\overset{O}{\overset{\|}{C}}-\underset{Na}{CH}-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow{(CH_3)_2CHCH_2Br}$$

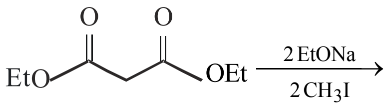


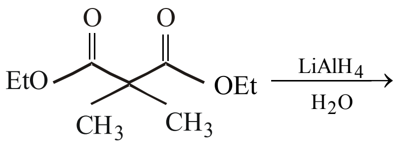


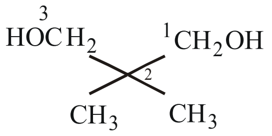
$$\underset{1}{CH_3}-\underset{2}{\overset{O}{\overset{\|}{C}}}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{\overset{CH_3}{\overset{|}{C}}H}-\underset{6}{CH_3}+CO_2+EtOH$$

37. (b) The structure (b) differs in the position of H hence not resonating structure.

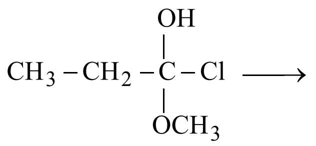
38. (a)



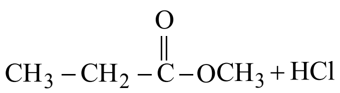




39. (b)



$$CH_3-CH_2-\overset{OH}{\overset{|}{\underset{OCH_3}{\underset{|}{C}}}}-Cl \longrightarrow$$

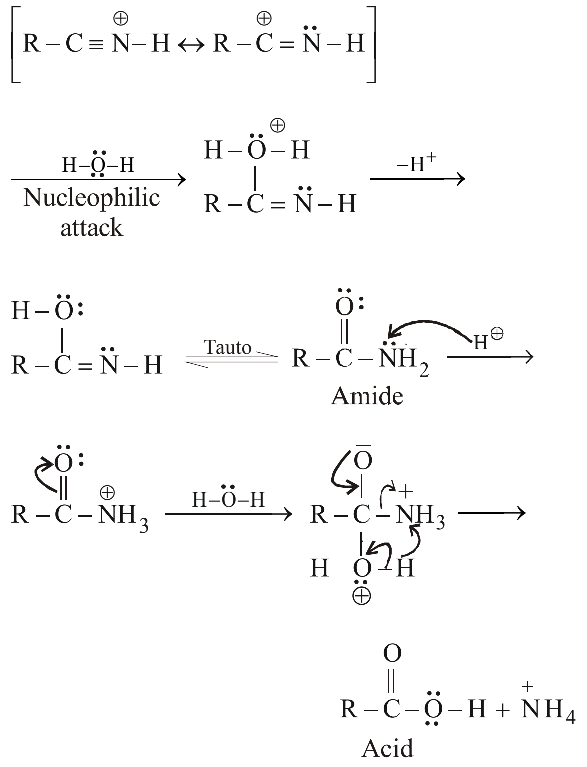


$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OCH_3+HCl$$

40. (a) Amides are hydrolysed with the lowest speed

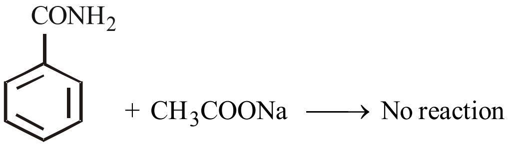
41 (c) Mechanism of acid hydrolysis of nitrites

$R-C\equiv N:+H^+\longrightarrow$

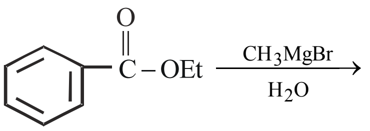


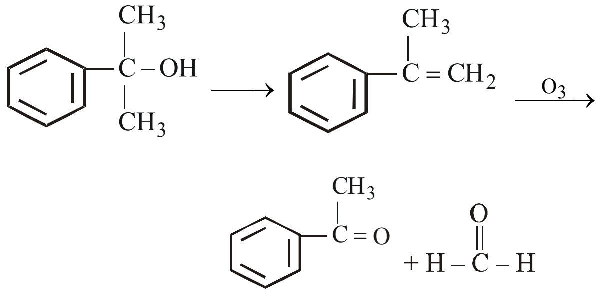
42. (c) During nitration and bromination of Salicylic acid – COOH group is eliminated.

43. (d)



44. (b)





All methyl ketones give iodoform test.

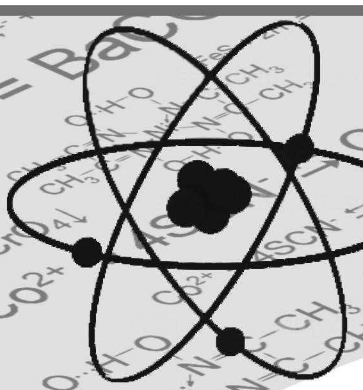
45. (d) Acid chlorides, anhydrides, acids give ester with alcohol

ROH + R'COCl ⟶ ROCOR' + HCl

ROH + (R'CO)$_2$O ⟶ ROCOR' + RCOOH

ROH + R'COOH ⟶ ROCOR' + H_2O

27



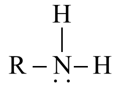
Amines

AMINES :

Amines are derivatives of ammonia (NH_3) in which one or more hydrogen atoms have been replaced by alkyl groups.

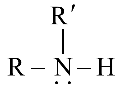
CLASSIFICATION :

Amines are classified as primary (1º), secondary (2º) or tertiary (3º) according to the number of alkyl groups attached to the nitrogen atom



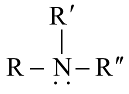
$R-\underset{\cdot\cdot}{\overset{H}{\overset{|}{N}}}-H$

Primary (1º)



$R-\underset{\cdot\cdot}{\overset{R'}{\overset{|}{N}}}-H$

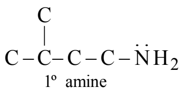
Secondary (2º)



$R-\underset{\cdot\cdot}{\overset{R'}{\overset{|}{N}}}-R''$

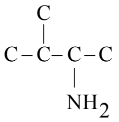
Tertiary (3º)

The carbon atom of alkyl groups to which nitrogen is attached may be 1º, 2º or 3º but amine is always 1º, 2º or 3º if it has the grouping $-\ddot{N}H_2, \dot{N}H$ or $\ddot{N}$ eg.



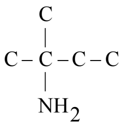
$C-\overset{C}{\overset{|}{C}}-C-C-\ddot{N}H_2$

1º amine



$C-\overset{C}{\overset{|}{C}}-C-C$ with NH_2 below the third carbon

1º amine

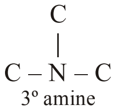


$C-\underset{NH_2}{\underset{|}{\overset{C}{\overset{|}{C}}}}-C-C$

1º amine

$\overset{C}{\overset{|}{C}}-NH$

2º amine

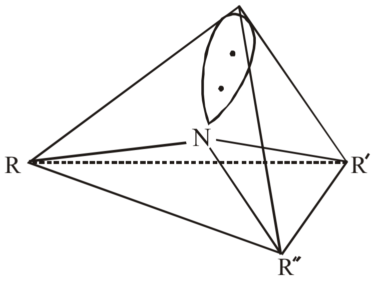


$C-\overset{C}{\overset{|}{N}}-C$

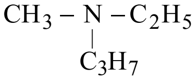
3º amine

STRUCTURE :

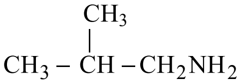
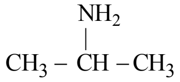
The nitrogen atom in amine is sp^3 hybridised. The three hybrid atomic orbitals are involved in bond formation and one hybrid atomic orbital contains the unshared pair of electrons, giving the **pyramidal** structure to amine.



The bond angles are approximately tetrahedral

NOMENELATURE :	Common System Alkylamine	IUPAC System Aminoalkane or Alkanamine
CH_3NH_2	Methylamine	1-Aminomethane or Methanamine
$CH_3CH_2CH_2NH_2$	n-Propylamine	1 - Aminopropane or 1 - Propanamine
$CH_3-NH-C_2H_5$	Ethylmethylamine	N-Methylaminoethane or N–methylethanamine
 $CH_3-\underset{C_3H_7}{\underset{|}{N}}-C_2H_5$	Ethylmethylpropylamine	N - Ethyl - N - methyl amino propane or N - Ethyl - N - methyl propanamine
$H_2N.CH_2CH_2.NH_2$	–	1, 2-diamino ethane or 1, 2-ethane-diamine

ISOMERISM : Amines exhibit following types of Isomerism

(I) Chain Isomerism :	$CH_3.CH_2.CH_2CH_2NH_2$ n-Butylamine	 $CH_3-\underset{}{\overset{CH_3}{\overset{\vert}{C}H}}-CH_2NH_2$ iso butylamine	
(II) Functional isomerism	$CH_3CH_2.CH_2.NH_2$ n-Propylamine (Primary)	$CH_3CH_2NH-CH_3$ Ethylmethylamine (Secondary)	$(CH_3)_3N$ Trimethylamine (Tertiary)
(III) Position Isomerism	$CH_3CH_2CH_2NH_2$ 1-Aminopropane	 $CH_3-\overset{NH_2}{\overset{\vert}{C}H}-CH_3$ 2-Aminopropane	
(IV) Metamerism	$C_2H_5-NH.C_2H_5$ Diethylamine	$CH_3-NH.C_3H_7$ methylpropylamine	

METHODS OF PREPARATION :

These methods yielding mixture of amines

(I) ***Hofmann's method*** (ammonolysis of an alkyl halide). Using aqueous or alcoholic NH_3

$$R\text{–}X + NH_3 \xrightarrow[100°C]{\text{Sealed tube}} R\overset{+}{N}H_3\overset{-}{X} + NH_3 \xrightleftharpoons[1°\text{amine}]{} RNH_2 + NH_4X$$

$$R-NH_2 + R-X \longrightarrow R_2\overset{+}{N}H_2\overset{-}{X} \xrightleftharpoons[2°\text{amine}]{NH_3} R_2NH + NH_4X$$

$$R_2-NH + RX \longrightarrow R_3\overset{+}{N}H\overset{-}{X} \xrightleftharpoons[3°\text{amine}]{NH_3} R_3N + NH_4X$$

$$R_3N + RX \longrightarrow \underset{\text{Quaternary ammonium compound.}}{R_4\overset{+}{N}\overset{-}{X}}$$

When NH_3 is in excess, 1° amine is the main product
When RX is in excess, 3° amine is the main product

(II) ***Sabatier method (Ammonolysis of alcohals)***

$$ROH + NH_3 \xrightarrow[\text{or alumina, or thiourea, 350°C}]{\text{Copper Chromite}} RNH_2 + H_2O$$

$$RNH_2 + ROH \xrightarrow{\text{alumina}} R_2NH + H_2O$$

$$R_2NH + ROH \longrightarrow R_3N + H_2O$$

When NH_3 is in excess, 1° amine is main product.

SEPARATION OF AMINE MIXTURE :

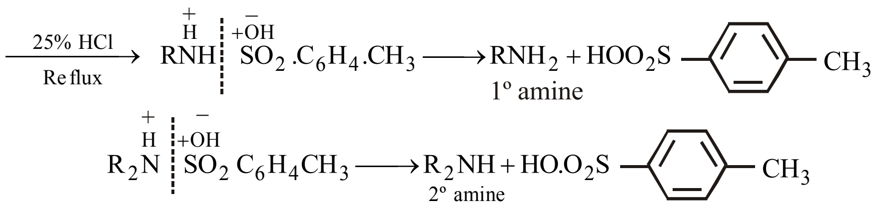
(I) ***Hinsberg's method :*** Reagent used is Benzenesulphonyl chloride ($C_6H_5SO_2$ Cl) which has been replaced by p-toluenesulphonyl chloride, $CH_3C_6H_4.SO_2Cl$

$$RNH_2 + ClSO_2C_6H_4CH_3 \longrightarrow \underset{\text{N-alkyl p-toluenesulphonamide}}{R.NH.SO_2C_6H_4CH_3} \xrightarrow{\text{aqs KOH}} \underset{\text{K-Salt (soluble)}}{RNK.SO_2C_6H_4CH_3}$$

$$R_2NH + ClSO_2.C_6H_4CH_3 \longrightarrow \underset{\text{N, N-dialkyl p-toluene Sulphonamide}}{R_2NSO_2C_6H_4.CH_3} \xrightarrow{\text{aqs KOH}} \text{No K-Salt (Insoluble)}$$

$$R_3N + ClSO_2.C_6H_4CH_3 \longrightarrow. R_3N \xrightarrow{\text{aqs KOH}} R_3N$$

$\xrightarrow{\text{distillation}}$ R_3N distills off(3°amine) Residual liquid filtered
- Filtrate, $RNKSO_2C_6H_4CH_3$
- Solid $R_2NSO_2.C_6H_4CH_3$



$$\xrightarrow[\text{Re flux}]{25\%\ \text{HCl}} RN\overset{+}{H} \overset{+\overset{-}{O}H}{\vdots} SO_2.C_6H_4.CH_3 \longrightarrow \underset{1°\text{ amine}}{RNH_2} + HOO_2S-C_6H_4-CH_3$$

$$R_2N \overset{\overset{+}{H}\ +\overset{-}{O}H}{\vdots} SO_2\,C_6H_4CH_3 \longrightarrow \underset{2°\text{ amine}}{R_2NH} + HO.O_2S-C_6H_4-CH_3$$

(II) ***Hofmann's method:*** Reagent used is Diethyl oxalate

$$\begin{array}{l} COOC_2H_5 + H.NHR \\ | \\ COOC_2H_5 + HNHR \end{array} \xrightarrow{-2C_2H_5OH} \begin{array}{l} CO.NHR \\ | \\ CONHR \end{array} \text{ Dialkyloxamide (Solid)}$$

$$\begin{array}{l} COOC_2H_5 + HNR_2 \\ | \\ COOC_2H_5 \end{array} \xrightarrow{-C_2H_5OH} \begin{array}{l} CO.NR_2 \\ | \\ COOC_2 \end{array}$$

Dialkyloxamicester (Liquid)

$$\begin{array}{l} COOC_2H_5 + R_3N \\ | \\ COOC_2H_5 \end{array} \longrightarrow \text{No reaction}$$

$$\begin{array}{l} CO\boxed{NHR.H}OK \\ | \\ CO\boxed{NHR.H}OK \end{array} \xrightarrow[KOH]{\Delta} \begin{array}{l} COOK \\ | \\ COOK \end{array} + \underset{1^\circ \text{ amine}}{2RNH_2}$$

$$\begin{array}{l} CO\boxed{NR_2 + H}OK \\ | \\ CO\boxed{OC_2H_5\ H}OK \end{array} \longrightarrow \begin{array}{l} COOK \\ | \\ COOK \end{array} + C_2H_5OH + \underset{2^\circ \text{ amine}}{R_2NH}$$

METHODS GIVING PRIMARY AMINES ONLY :

(i) **Reduction of nitro compounds** by Sn/HCl, H_2/Ni, Zn/HCl or $LiAlH_4$

$$RNO_2 + 6H \xrightarrow{Sn/HCl} RNH_2 + 2H_2O$$

(ii) **Reduction of cyanides (Mendius reaction)**

$$R-C \equiv N + 4H \xrightarrow[\text{or } H_2/pt \text{ or } LiAlH_4]{C_2H_5OH+Na} RCH_2NH_2$$

(iii) **Reduction of oximes :** H_2 / Ni, C_2H_5OH / Na or $LiAlH_4$ are reducing agents

$$RCH = NOH + 4H \xrightarrow{LiAlH_4} RCH_2NH_2 + H_2O$$

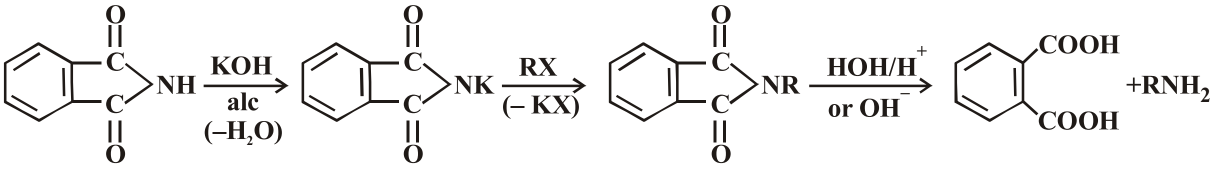
(iv) **Reduction of amide**

$$RCONH_2 + 4H \xrightarrow{LiAlH_4} RCH_2NH_2 + H_2O$$

(v) **Hofmann's bromamide Reaction:** R can be alkyl or aryl (Conversion of an amide to 1° amine)

$$RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$$

(vi) **Gabriel's phthalimide reaction**



Phthalimide **Pot. phthalimide** **N-alkyl phthalimide** **Phthalic acid** **1° amine**

This method is not suitable for 1°arylamine due to less nucleophilic character.

(vii) **From α-amino acids**

$$H_2N.CH_2.COOH \xrightarrow[\text{distill}]{Ba(OH)_2} CH_3NH_2 + CO_2$$

(viii) **Reductive ammination of aldehydes and Ketones**

$$RCHO + NH_3 + H_2 \xrightarrow[300P]{Ni\ 150°C} RCH_2NH_2 + H_2O$$

$$\begin{matrix}R\\R\end{matrix}\!\!>C=O+NH_3+H_2 \xrightarrow[300P]{Ni\ 150°C} \begin{matrix}R\\R\end{matrix}\!\!>CH-NH_2+H_2O$$

(ix) **From Chloramine and Grignard's Reagent**

$$R\,MgX + ClNH_2 \longrightarrow RNH_2 + Cl\,MgX$$

(x) **Reduction of azide**

$$R-X+NaN_3 \longrightarrow \underset{\text{Alkyl azide}}{RN_3} \xrightarrow[H_2O]{NaBH_4} \underset{1°-\text{amine}}{RNH_2}$$

(xi) **Ritter reaction : for amines containing tertiary alkyl groups**

$$R_3COH \xrightarrow{H+} H_2O + R_3C^+ \xrightarrow{HCN} R_3C\overset{+}{N}\equiv CH \xrightarrow{H_2O} R_3CNH.CHO$$

$$\xrightarrow{OH^-} R_3CNH_2 + HCO_2^-$$

(xii) **By Lossen rearrangement:** From Hydroxamic acid

$$RCONHOH \xrightarrow{HCl} RCONHOH_2^+ \xrightarrow{-H_2O} R-\overset{\overset{O}{||}}{C}-\overset{+}{\ddot{N}}-H \xrightarrow{-H^+} R-N=C=O \xrightarrow{+H_2O} RNH_2 + CO_2$$

(xiii) **Schmidt reaction:**

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Hydrazoic acid}}{HN_3} \xrightarrow{H_2SO_4} RNH_2 + CO_2 + N_2$$

(xiv) **Curtius rearrangement**

$$RCOOH + SOCl_2 \longrightarrow \underset{\text{Acyl chloride}}{RCOCl} \xrightarrow{NaN_3} \underset{\text{Acylazide}}{RCON_3} \xrightarrow{-N_2} \underset{\text{Isocyanate}}{RNCO} \xrightarrow{2NaOH} RNH_2 + Na_2CO_3$$

(xv) **By Leuckart reaction:**

$$\underset{\substack{\text{Aldehyde}\\\text{or}\\\text{Ketone}}}{>C=O} + \underset{\text{Amm. Formate}}{2HCOONH_4} \longrightarrow >CHNH-\overset{\overset{O}{||}}{C}-H + 2H_2O + CO_2 + NH_3 \xrightarrow[H+]{HOH} \underset{1°.\text{amine}}{>CHNH_2} + H_2O + CO_2$$

$$\underset{\substack{\text{Aldehyde}\\\text{or Ketone}}}{>C=O} + \underset{\text{Formamide}}{2HCONH_2} \longrightarrow >CHNH-\overset{\overset{O}{||}}{C}H + CO_2 + NH_3 \xrightarrow{HOH/H^+} \underset{1°-\text{amine}}{>CHNH_2} + H_2O + CO_2$$

PREPARATION OF SECONDARY AMINES :

(i) From p-amines $RNH_2 + RX \longrightarrow R_2NH + HX$

(ii) From calcium cyanamide

$$CaCN_2 \xrightarrow[-Ca(OH)_2]{2NaOH} Na_2CN_2 \xrightarrow[-2NaX]{2RX} R_2CN_2 \xrightarrow[OH^-]{\overset{+}{H}\text{ or}} R_2NH + CO_2 + NH_3$$

(iii) Secondary amine containing phenyl group

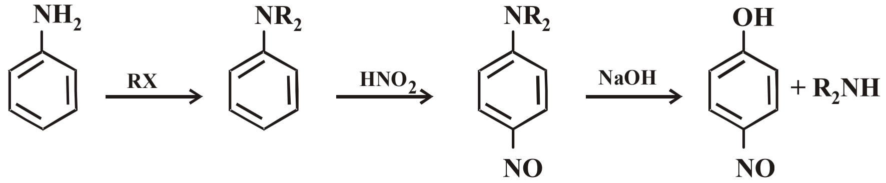
$$C_6H_5CHO + RNH_2 \longrightarrow \underset{\text{Schiff's base (Anils)}}{C_6H_5CH=NR} \xrightarrow{H_2/Ni} C_6H_5CH_2NHR$$

$$C_6H_5CH=NR + RX \longrightarrow (C_6H_5CH=\overset{+}{N}R_2)X^- \xrightarrow{H^+} C_6H_5CHO + R_2NH$$

(iv) From 1°-amine by the action of diazomethane

$$RNH_2 + CH_2N_2 \longrightarrow RNH.CH_3 + N_2$$

(v) From aniline. It is one of the best methods



(vi) Reduction of isocyanides $RNC + 4H \xrightarrow[Na]{C_2H_5OH} RNHCH_3$ (Mendius Reaction)

(vii) Reduction of N-Substituted amides

$$RNHCOCH_3 + 4H \xrightarrow{LiAlH_4} RNH.CH_2CH_3 + H_2O$$

PREPARATION OF TERTIARY AMINES:

(i) By heating ethanolic solution of ammonia with excess of alkyl halide

$$3RX + NH_3 \longrightarrow R_3N + 3HX$$

(ii) Reduction of N, N-disubstituted amide

$$RCON(CH_3)_2 + 4H \xrightarrow{LiAlH_4} RCH_2.N(CH_3)_2 + H_2O$$

(iii) Decomposition of alkyl tetraammonium hydroxides

$$(R_4N)^+OH^- \xrightarrow{\Delta} R_3N + Olefin + H_2O$$

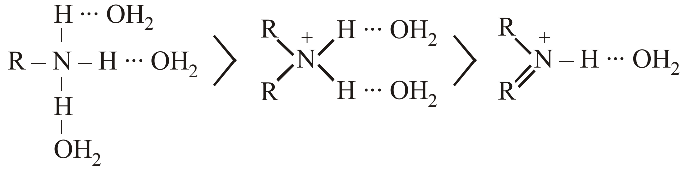
PROPERTIES :

Amines are soluble in water due to H-bonding. Lower members have fishy ammonical odour and are combustible gases. From C_3 to C_{11} volatile liquids and from C_{12} are solids. The b.p. increases with increase in molecular weight.

Basic character: Amines are stronger bases than ammonia

$$RNH_2 + H_2O \rightleftharpoons R\overset{+}{N}H_3 + OH^-$$

The stability of ions by H–bonding in water follows the order



The order of basicity ought to be 1° > 2° > 3° which is practicaly not. In fact it depends upon this factor

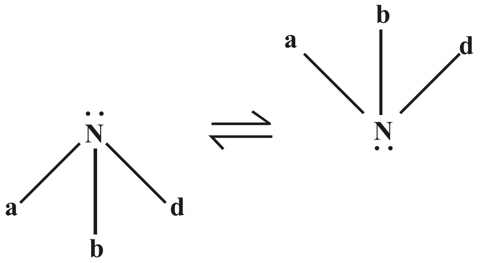
(i) Inductive effect

(ii) Steric hundarence

Basic character follows the order $(CH_3)_2\ddot{N}H > CH_3\ddot{N}H_2 > (CH_3)_3\ddot{N} > \ddot{N}H_3$

K_b. 54×10^{-5} 37×10^{-5} 6.7×10^{-5} 1.8×10^{-5}

Ammonia and amines oscillate between two structures as follows

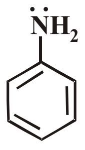


Although the electron density on nitrgen is maximum (due to + I effect of alkyl groups) in case of tertiary amine but approach and bonding by proton is relatively difficult due to steric hindrance. The steric hindrance increases with the bulk of group and basic character decreases

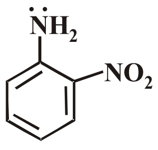
Alkyl group	Relative strength
$-CH_3$	$Me_2NH > MeNH_2 > Me_3N > NH_3$
$-C_2H_5$	$Et_2NH > EtNH_2 > NH_3 > Et_3N$
$-CH(CH_3)_2$	$Iso\,Pr.NH_2 > NH_3 > Iso\,Pr_2\,NH > Iso\,Pr_3\,N$
$-C(CH_3)_3$	$NH_3 > tert.Bu.NH_2 > tert.\ Bu_2NH > tert.\ Bu_3N$

Note : The order of basicity of amines in the gaseous phase is tertiary amine > secondary amine > primary amine > ammonia

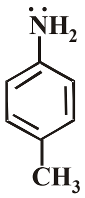
Aromatic amines are less basic than aliphatic amine. The electron withdrawing groups (-NO_2, COOH, –CN, –SO_3H) decrease the basic character and electron donating groups (–CH_3; –OH) increase the basic character of aniline



$K_b = 4.2 \times 10^{-10}$



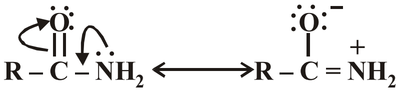
$K_b = 5 \times 10^{-15}$



$K_b = 2 \times 10^{-9}$

Due to Resonance the lone pair of electrons is delocalised within benzene nucleus and not available for protonation and basic character is suppressed.

Amides are much less basic than amines due to Resonance



$$R-\overset{\overset{\ddot{O}}{\parallel}}{C}-\ddot{N}H_2 \longleftrightarrow R-\overset{\overset{:\ddot{O}:^-}{|}}{C}=\overset{+}{N}H_2$$

CHEMICAL PROPERTIES :

$R\ddot{N}H_2$

- $\xrightarrow{HCl} R\overset{+}{N}H_3\overset{-}{Cl}$ (Salt formation)
- $\xrightarrow[\text{Chloroplatinic acid}]{H_2PtCl_6}$ $(R\overset{+}{N}H_3)_2(PtCl)_6^{2-}$ (Chloroplatinate)

  insoluble salt used to determine Eq.wt and molecular weight of amines
- $\xrightarrow{RCOCl\ \text{Acylation}}$ RNH.COR + HCl
- $\xrightarrow[\text{Benzoylation}]{C_6H_5COCl/\,NaOH}$ $RNH.CO.C_6H_5 + NaCl + H_2O$

  This is **Schotten-Baumann reaction**
- $\xrightarrow[-HX]{RX\ \text{Alkylation}}$ $\underset{\text{Sec. amine}}{R_2NH} \xrightarrow[-HX]{RX} \underset{\text{tertiary amine}}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary Compound}}{(R_4\overset{+}{N})\overset{-}{X}}$
- $\xrightarrow{AgCl}$ $[Ag(H_2NR)_2]Cl$

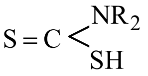
  Soluble Complex
- $\xrightarrow[\text{Carbylamine reaction}]{CHCl_3, 3KOH(alc)\,\Delta}$ $R-N\overset{\rightarrow}{=}C + 3KCl + 3H_2O$

  Carbylamine or Isocyanide compound

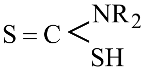
  Bad odour. only 1° amines give this reaction.

  (hence distinction from 2° and 3° amines)
- $\xrightarrow[0-5°C]{HNO_2(NaNO_2+HCl)}$ $\underset{\text{Alcohol}}{ROH} + N_2 + H_2O$ (from 1° amine except CH_3NH_2 which gives CH_3OCH_3 and CH_3ONO)
- $\xrightarrow[0-5°C]{HNO_2(NaNO_2+HCl)}$ $\underset{\text{oily nitrosamine}}{R_2N.NO} + H_2O$ (from 2° amine)
- $\xrightarrow[0-5°C]{HNO_2(NaNO_2+HCl)}$ $R_3N.HNO_2$ Salt from 3° amine which decomposes on heating to $ROH + R_2N.NO$
- $\xrightarrow[0-5°C]{HNO_2\,\text{diazotisation}}$ $C_6H_5\overset{+}{N_2}\overset{-}{Cl}$ benzene diazonium chloride from aniline. At higher temp. it is decomposed to $C_6H_5OH + N_2 + HCl$

$RNH_2 \rightarrow$



$\xrightarrow[\text{Hofmann Mustard oil reation}]{S=C=S} S=C\langle^{NR_2}_{SH} \xrightarrow{HgCl_2} \underset{\text{Alkyl isothiocyanate (mustard oil smell)}}{R-N=C=S+HgS+2HCl}$ (from 1° amine)



$\xrightarrow{S=C=S} S=C\langle^{NR_2}_{SH} \xrightarrow{HgCl_2}$ No reaction (2° amine)

$\xrightarrow{S=C=S}$ No reaction with 3° amine

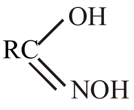
Oxidation of 1° amines with permanganate

$RCH_2NH_2 \xrightarrow{[O]} \underset{\text{Aldimine}}{RCH=NH} \xrightarrow{H+} \underset{\text{Aldehyde}}{RCHO+NH_3}$

$R_2CH.NH_2 \xrightarrow{[O]} \underset{\text{Ketimine}}{R_2C=NH} \xrightarrow{H+} \underset{\text{Ketone}}{R_2CO+NH_3}$

$R_3C.NH_2 \xrightarrow{[O]} R_3C.NO_2$

Oxidation of 1° amines with Caro's Acid (H_2SO_5)



$RCH_2NH_2 \xrightarrow{[O]} \underset{\text{N-alkyl hydroxylamine}}{RCH_2.NHOH} + \underset{\text{Aldoxime}}{RCH=NOH} + \underset{\text{Hydroxamic acid}}{RC\langle^{OH}_{NOH}}$

$R_2CH.NH_2 \xrightarrow{[O]} R_2C=NOH$

$R_3C.NH_2 \xrightarrow{[O]} R_3CNO$

$\xrightarrow[\text{with } KMnO_4]{\text{Oxidation of 2° amine}} \underset{\text{Tetra alkylhydrazine}}{R_2N-NR_2+H_2O}$

$\xrightarrow[\text{with } H_2SO_5 \text{(Caro's Acid)}]{\text{Oxidation of 2° amine}} R_2N\text{-}OH$

dialkyl hydroxylamine

$\xrightarrow[H_2O_2 \text{ or } O_3 \text{ or } H_2SO_5]{\text{Oxi of 3° amine}} R_3N \rightarrow O$

Amine N-oxide

$\xrightarrow{COCl_2 \text{ Phosgene}} RNH-\overset{\overset{O}{||}}{C}-NHR+2HCl$ (from 1° amine)

Sym. disubstituted urea

$\xrightarrow{COCl_2} R_2N-\overset{\overset{O}{||}}{C}-NR_2+2HCl$ (from 2° amine)

Sym. tetrasubstituted urea

$\xrightarrow{COCl_2} C_6H_5.N=C=O$ (from aniline)

Phenyl Isocyanate

$\xrightarrow{Na\text{(Sodium)}} RNH.Na+1/2H_2$ (from 1° amine)

$R_2N.Na+1/2H_2$ (from 2° amine)

$\xrightarrow[X_2+NaOH]{\text{Action of halogens}}$ $RNHX \xrightarrow[NaOH]{X_2} RNX_2$ (from 1° amine)

Dihaloalkylamine

R_2NX (from 2° amine)

Halo dialkylamine

$\xrightarrow{R'MgX(G.R.)}$ $R'H + RNH.MgX$

Hydrocarbon

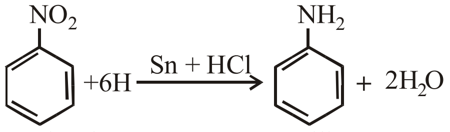
$\xrightarrow{O{=}CHR'\text{ aldehyde}}$ $RN = CHR' + H_2O$

Schiff's base

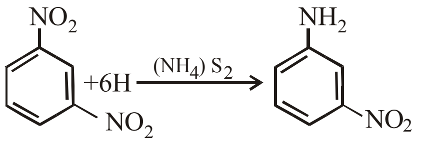
AROMATIC AMINES :

General methods of preparation

(i) Reduction of nitro compounds

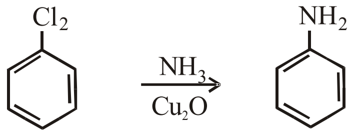


Nitro benzene Aniline



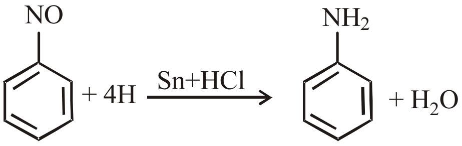
m-dinitro benzene m-nitroaniline

(ii) From aryl halides by action of ammonia

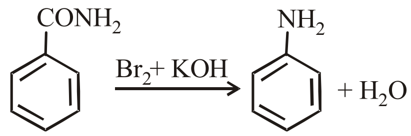


Chloro benzene Aniline

(iii) Reduction of nitroso compounds.

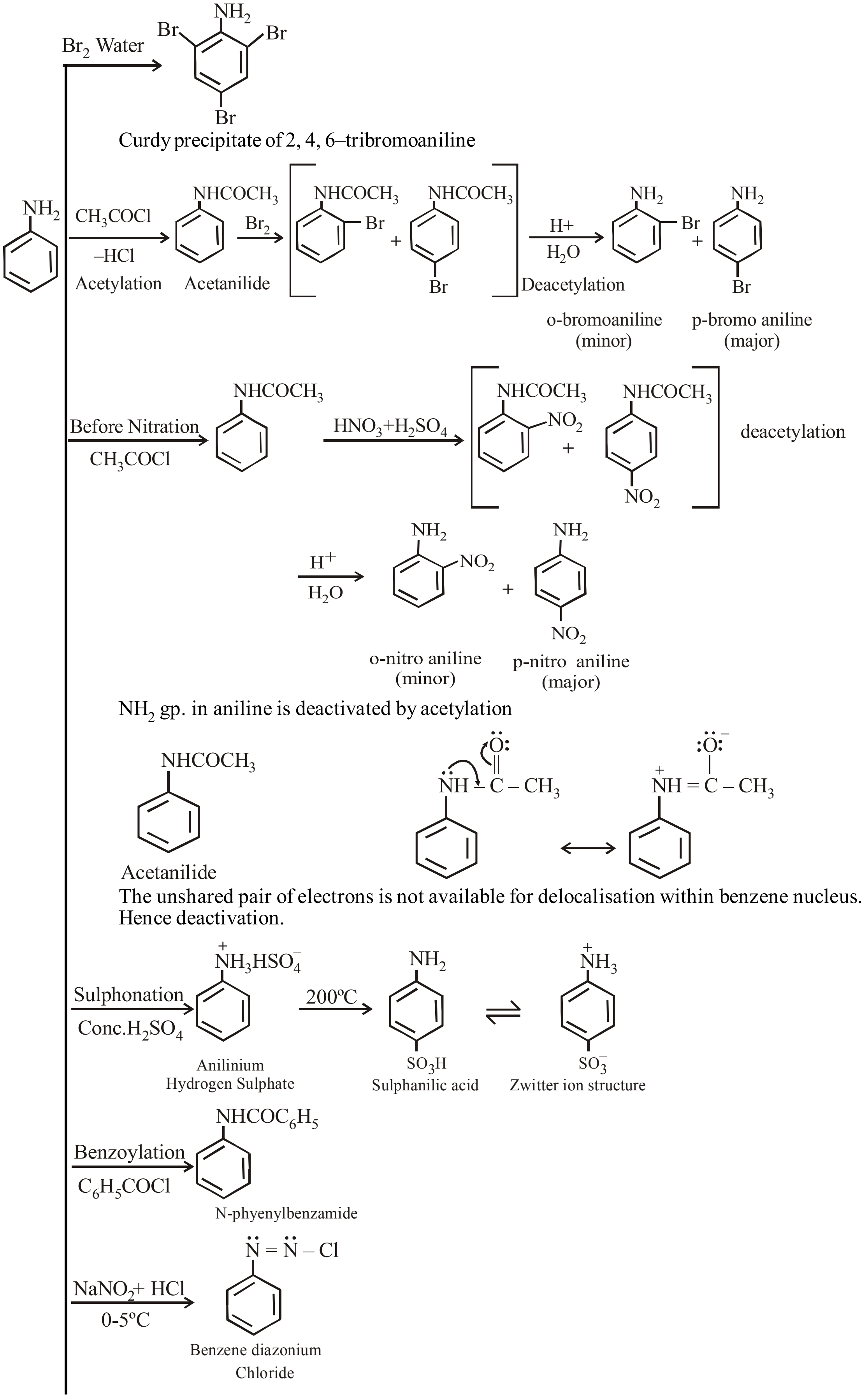


(iv) Hofmann's bromamide reaction



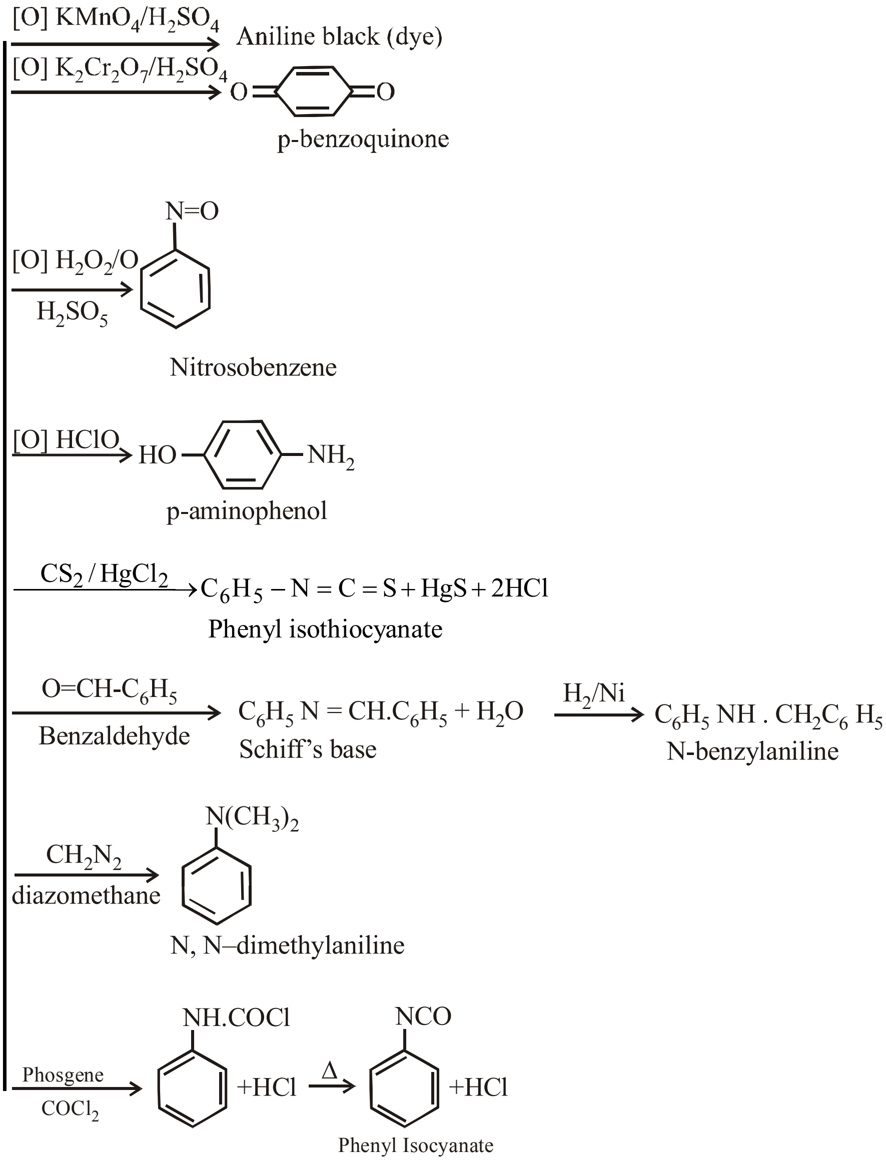
Benzamide Aniline

CHEMICAL REACTIONS :



NH_2 gp. in aniline is deactivated by acetylation

The unshared pair of electrons is not available for delocalisation within benzene nucleus. Hence deactivation.

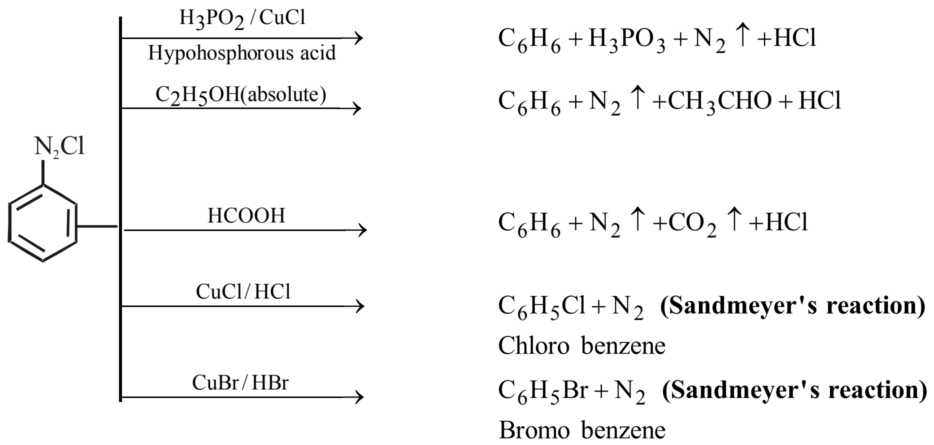


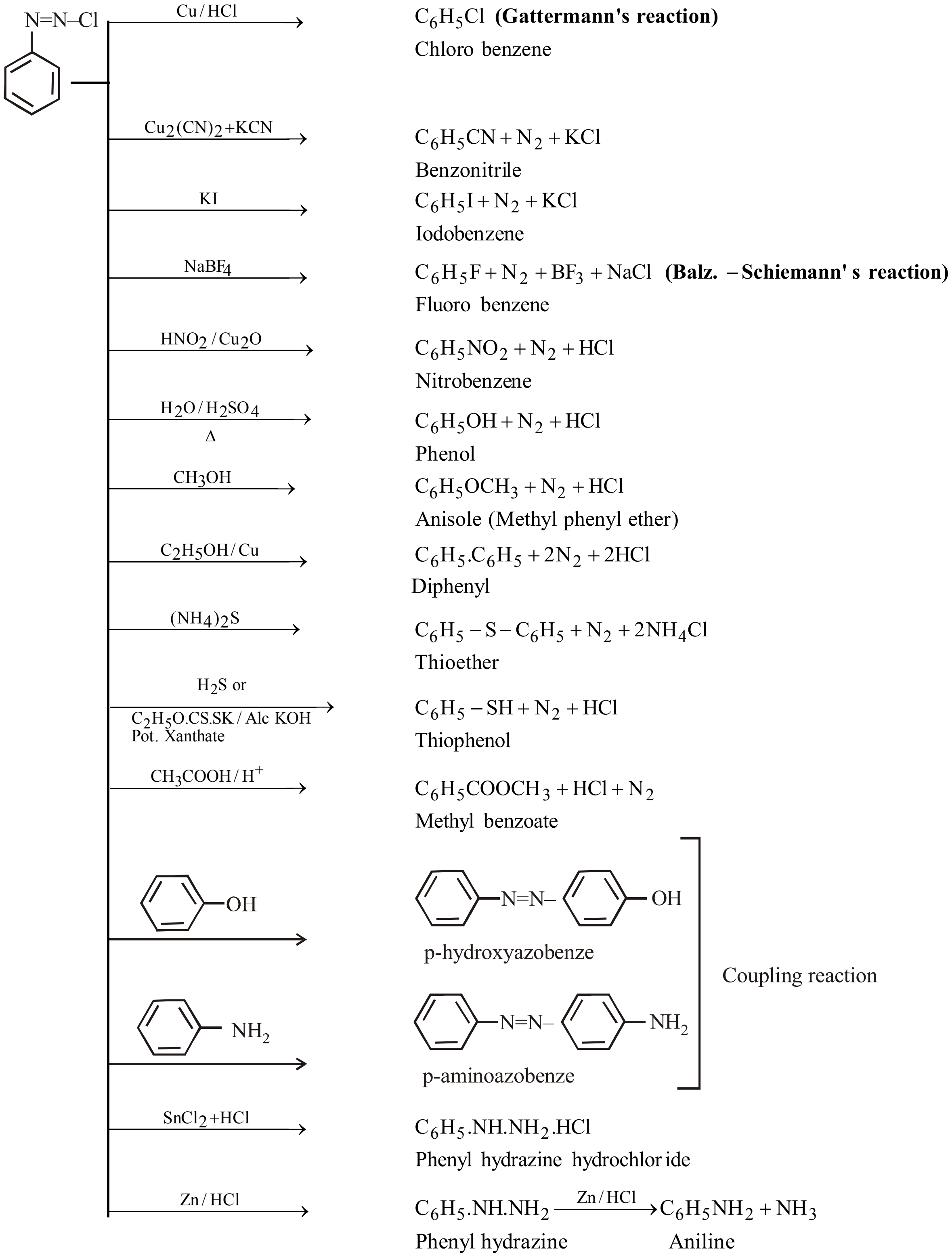
BENZENE DIAZONIUM CHLORIDE : C_6H_5 N= NCl

Preparation: $C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0-5°C} C_6H_5N = N - Cl + NaCl + 2H_2O$

Properties: Colurless crystalline solid soluble in water. It has tendency to explode when dry

Chemical reactions : Replacement of - N_2Cl group is unimolecular nucleophilic in nature

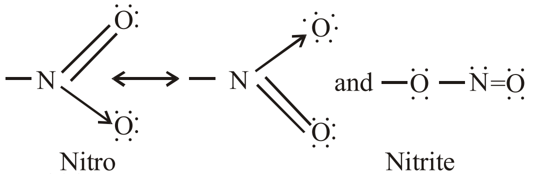




NITRO COMPOUNDS :

Nitro compounds are characterised by the presence of nitro group (–NO_2).

(i) Structure of NO_2 group :



Hence – NO_2 group is ambident group.

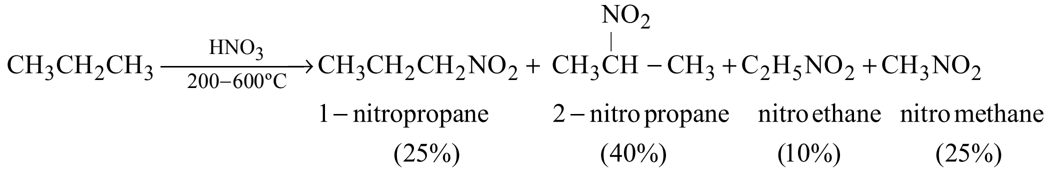
(ii) Classification : They may be primary, secondary and tertiray

$R.CH_2NO_2(1^\circ)$; $R_2CH.NO_2(2^\circ)$ and $R_3C.NO_2(3^\circ)$

(iii) Nomenclature: They are named as **nitroalkanes** (aliphatic) and **nitroarenes** (aromatic)

(iv) Preparation:

(1) Direct nitration of paraffins



$$\underset{}{CH_3CH_2CH_3} \xrightarrow[200-600^\circ C]{HNO_3} \underset{\substack{1-\text{nitropropane}\\(25\%)}}{CH_3CH_2CH_2NO_2} + \underset{\substack{2-\text{nitro propane}\\(40\%)}}{CH_3\overset{\overset{NO_2}{|}}{C}H - CH_3} + \underset{\substack{\text{nitro ethane}\\(10\%)}}{C_2H_5NO_2} + \underset{\substack{\text{nitro methane}\\(25\%)}}{CH_3NO_2}$$

Ease of replacement of hydrogen atom 3° > 2° > 1°

(2) From alkyl halides with $AgNO_2$ or KNO_2

$$RI + AgNO_2 \longrightarrow \underset{\text{Major (80\%)}}{RNO_2} + \underset{\text{Minor (20\%)}}{RO-N=O} + AgI$$

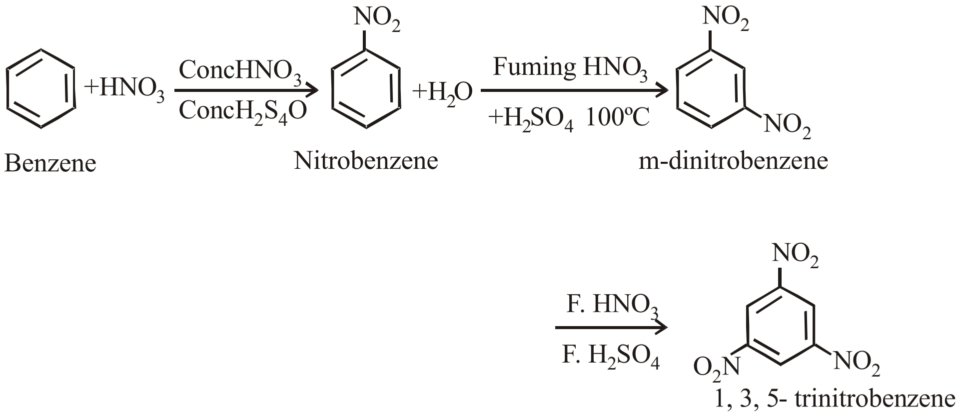
$$RI + KNO_2 \longrightarrow \underset{\text{Major}}{R-O-N=O} + \underset{\text{Minor}}{RNO_2} + KI$$

(3) Hydrolysis of α-nitro alkenes

$$(CH_3)_2C = CH.NO_2 \longrightarrow (CH_3)_2CO + CH_3NO_2$$

PREPARATION OF AROMATIC NITRO COMPOUNDS :

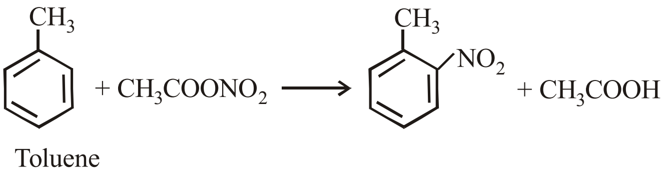
(i)



Nitration is electrophilic substitution reaction. The electrophile is $\overset{+}{NO_2}$ nitronium ion

- Mixture of conc. nitric acid + acetic anhydride gives better yield (**Pictet and Kholinsky's method**)
- $N_2O_4 + AlCl_3$ **(Schaar's Schmidt method)**

(ii)



Nitro benzene has high dipole moment 4.0D, bpt. 209°C, it has odour of bitter almonds and also known as oil of mirbane.

CHEMICAL PROPERTIES OF NITROALKANES :

$$RNO_2 \xrightarrow[2H\,(CH_2O)]{\text{Reduction}} \underset{\text{Nitroso compound}}{RNO} \xrightarrow{2H} \underset{\text{N-alkyl hydroxylamine}}{RNHOH} \xrightarrow[-H_2O]{2H} \underset{\text{primary amine}}{RNH_2}$$

$$RNO_2 \xrightarrow[NaOH]{Cl_2 \text{ or } Br_2} Cl_3CNO_2$$

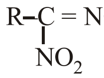
(α-hydrogen are successively replaced by chlorine atoms and chloropricrin is formed)

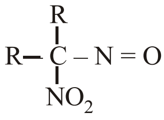
$$RNO_2 \xrightarrow{Zn/NH_4Cl} \underset{\text{Alkyl Hydroxyl amine}}{RNHOH} + H_2O$$

$$RNO_2 \xrightarrow{Fe,\ Sn \text{ or } Zn/HCl \text{ or } LiAlH_4} \underset{\text{primary amine}}{RNH_2}$$

$$RNO_2 \xrightarrow[\text{or } 80\%\ H_2SO_4]{\text{Hydrolysis HCl}} \begin{cases} RCOOH + NH_2OH.HCl \text{ from } 1^\circ \text{ nitro} \\ \begin{matrix} R \\ R \end{matrix} \!>\! C=O + H_2O + N_2O \text{ from } 2^\circ \text{ nitro} \\ 3^\circ \text{Nitro not hydrolysed} \end{cases}$$

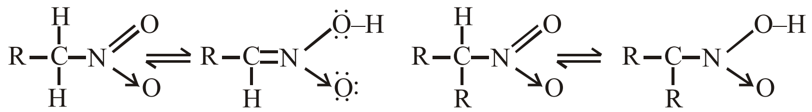
RNO_2 Action of HNO_2 →


$R-\underset{NO_2}{\underset{|}{C}}=NOH$ Nitrolic acid (from 1° nitro)


$R-\overset{R}{\overset{|}{\underset{NO_2}{\underset{|}{C}}}}-N=O$ Pseudo nitrole (from 2° Nitro)

3° Nitro do not react due to absence of H–atom

RNO_2 Tautomerisation by 1° and 2° Nitro alkanes →



Nitro Compound or pseudo acid form

Nitrolic acid or acid form

CHEMICAL PROPERTIES OF ALKYL NITRITES :

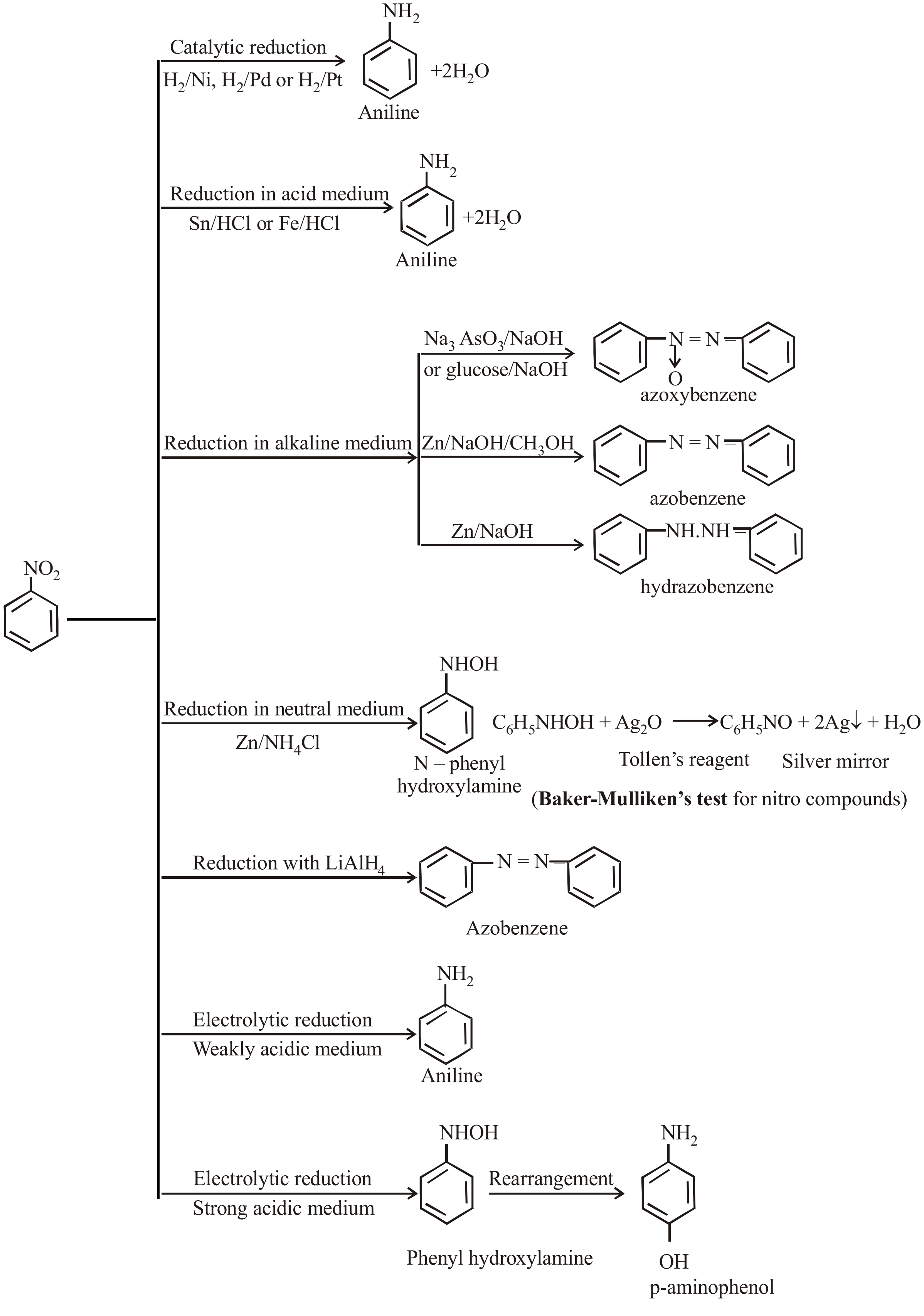
$$R\text{–}O\text{–}N{=}O \xrightarrow[6H]{\text{Reduction}} ROH + NH_3 + H_2O$$

$$R\text{–}O\text{–}N{=}O \xrightarrow[NaOH]{\text{Alk. Hydrolysis}} ROH + NaNO_2$$

$$R\text{–}O\text{–}N{=}O \xrightarrow{\text{acid Hydrolysis}} ROH + HNO_2 \,(HNO_2 \text{ decomposes to } HNO_3 \text{ and } NO)$$

CHEMICAL PROPERTIES OF NITRO BENZENE :

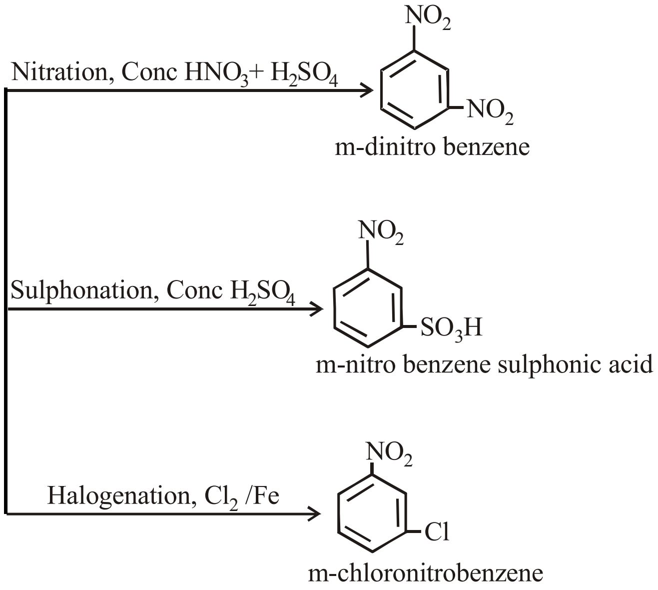
(A) Reduction of nitrobenzene under different conditons :



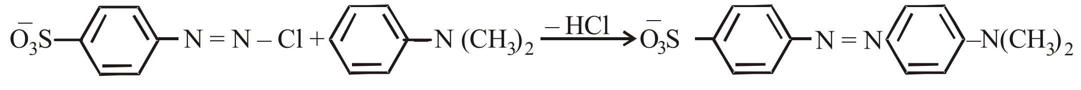
$$\underset{\text{Tollen's reagent}}{C_6H_5NHOH + Ag_2O} \longrightarrow C_6H_5NO + \underset{\text{Silver mirror}}{2Ag\downarrow} + H_2O$$

(**Baker-Mulliken's test** for nitro compounds)

(B) **Electrophilic substitution reactions :**



METHYL ORANGE:



Diazotised sulphanilic acid N, N-dimethyl aniline Methyl Orange

It is used as an internal indicator. It gives yellow colour in alkaline medium and red colour in acid medium. Its pH range is 3.2 – 4.5.

ALKYL CYANIDES, NITRILES $RC \equiv N$:

Preparation :

(i) $RI + KCN \xrightarrow[100^\circ]{Alc} RCN + KI$ (RNC Present small amount)

$RI + AgCN \longrightarrow RNC + AgI$ (RCN present small amount)

(ii) $\underset{\text{Amm. Salt of fatty acid}}{RCOONH_4} \xrightarrow[-H_2O]{P_2O_5} \underset{\text{Amide}}{RCONH_2} \xrightarrow[-H_2O]{P_2O_5} \underset{\text{Alkyl cyanide}}{RCN}$

(iii) $\underset{\text{Aldoxime}}{RCH = NOH} \xrightarrow{(CH_3CO)_2O} \underset{\text{Alkyl Cyanide}}{R - CN} + H_2O$

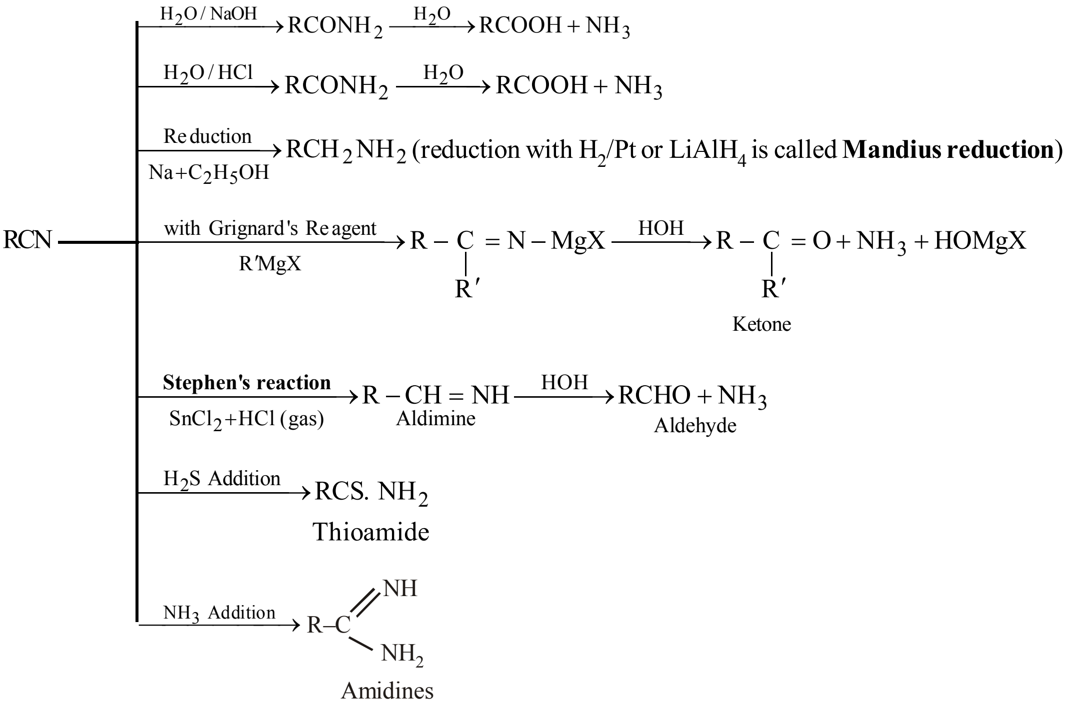
(iv) $RMgX + CN.Cl \xrightarrow{\text{dry ether}} RCN + ClMgX$

(v) $\underset{\text{Alkyl potassium sulphate}}{RKSO_4} + KCN \longrightarrow RCN + K_2SO_4$

(vi) $\underset{\text{Arene diazonium Chloride}}{Ar\ N_2Cl} + KCN \xrightarrow[\text{Cu powder}]{CuCN} \underset{\text{Aryl Cyanide}}{Ar\ C \equiv N + KCl}$

Properties : Alkylcyanides are neutral with pleasant smell, moderately soluble in water

Chemical reactions:-

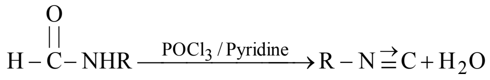


ALKYLISOCYANIDES: ISONITRILES OR CARBYLAMINE $R-N\overset{\rightarrow}{=}C$:

Preparation :

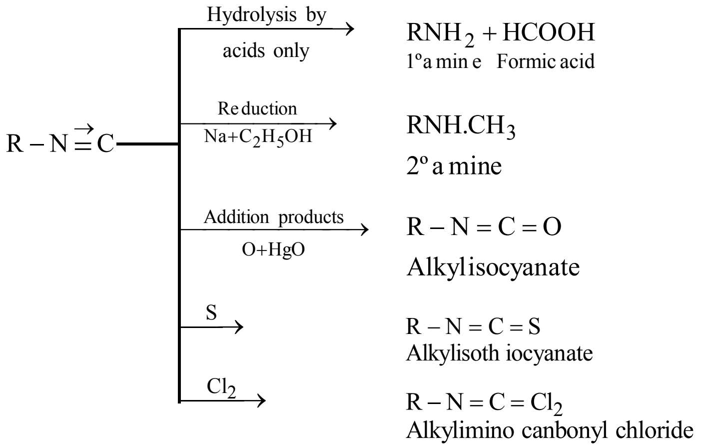
(i) **Carbylamine reaction :** $RNH_2 + CHCl_3 + 3KOH \longrightarrow R-NC + 3KCl + 3H_2O$

(ii) $RI + AgCN \longrightarrow R-NC + AgI$ (Small amount RCN)

(iii) 
$H-\overset{\overset{O}{||}}{C}-NHR \xrightarrow{POCl_3/Pyridine} R-N\overset{\rightarrow}{=}C + H_2O$

N – Alkyl formamide

Properties: They are colourless, extremely poisonous, unpleasant liquids. Insoluble in water. They have low bpt. than cyanides



Uses:

(i) For synthesis of 1° amines and acids

(ii) Acrylonitriles ($CH_2 = CHCN$) for manufacturing of polymers like orlon, acrilan fibres and rubbers etc.

Exercise-1 | NCERT BASED QUESTIONS

Very Short/Short Answer Questions

1. Arrange the following amines in increasing order of their basic character.
Ethylamine, Aniline, Dimethylamine, Methylamine.

2. Account for the fact that before nitration aniline is converted to acetanilide.

3. Why do quaternary ammonium salts having four different groups attached to nitrogen show optical activity?

4. How will you convert benzonitrile to acetophenone ($C_6H_5COCH_3$)?

5. Like ammonia, amines are good nucleophiles. Explain.

6. Why is carbon nitrogen bond length in aromatic amines shorter than in aliphatic amines?

7. What happens when
(*a*) methyl amine is heated with chloroform in the presence of an alkali.
(*b*) the mixture of alcohol and ammonia in vapour state is passed over heated aluminium oxide as catalyst?

8. An organic compound A has molecular formula $C_8H_{11}N$ and is optically active. The compound A dissolves in dil. HCl and gives effervescence of nitrogen gas with HNO_2. Suggest a structural formula of compound A.

9. An organic compound A (C_3H_5N) on boiling with alkali gives NH_3 and sodium salt of an acid B ($C_3H_6O_2$). The compound A on reduction gives C (C_3H_9N) which on treatment with nitrons acid gives an alcohol D (C_3H_8O). Identify A, B, C and D.

10. Aniline is primary amine but it cannot be prepared by Gabriel synthesis. Why?

11. Illustrate the following with an example of reaction in each case:
(i) Sandmeyer's reaction
(ii) Coupling reaction

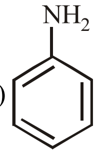
12. Write chemical equations for the following conversion:
(i) Nitrobenzene to benzoic acid.
(ii) Benzyl chloride to 2-phenylethanamine.
(iii) Aniline to benzyl alcohol.

13. How are the following conversions carried out:
(a) Aniline to p-hydroxyazobenzene.
(ii) Ethanoyl chloride to Ethanenitrile.

14. Give the structures of A, B and C in the following reactions–

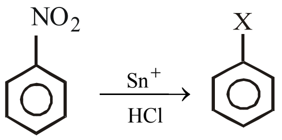
(i) $$C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$$

(ii) $$C_6H_5NO_2 \xrightarrow{Sn+HCl} A \xrightarrow[273\,K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$$

15. Complete the following reactions:
(i) $CH_3CH_2NH_2 + CHCl_3 + \text{alc. } KOH \rightarrow$
(ii) $C_6H_5N_2^+Cl^- \xrightarrow[\text{(Room temp.)}]{H_2O}$
(iii)  + HCl (aq.) ⟶

Multiple Choice Questions

16. In the given reaction,



X- stands for
(a) $-NH_2$ (b) $SnCl_2$
(c) $-Cl$ (d) $-NH_3^+Cl^-$

17. Gabriel's phthalimide synthesis is used for the preparation of
(a) primary aromatic amines
(b) secondary amines
(c) primary aliphatic amines
(d) tertiary amines

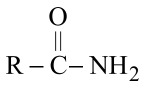
18. Which of the following reaction takes place when a mixture of conc. HNO_3 and H_2SO_4 reacts with benzene at 300 K ?
(a) Sulphonation (b) Nitration
(c) Hydrogenation (d) Dehydration

19. Indicate which nitrogen compound amongst the following would undergo Hofmann reaction (i.e.., reaction with Br_2 and strong KOH) to furnish the primary amine ($R-NH_2$)
(a) $RCONHCH_3$
(b) $RCOONH_4$
(c) $RCONH_2$
(d) $R-CO-NHOH$.

20. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4 in the mixture, nitric acid acts as a/an:
(a) acid (b) base
(c) catalyst (d) reducing agent

21. Amides may be converted into amines by reaction named after :
(a) Perkin (b) Claisen
(c) Hofmann (d) Kekule

22. Methyl cyanide can be converted into acetic acid by one of the following reaction :
(a) reduction (b) hydrolysis
(c) electrolysis (d) decarboxylation



$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$

23. on reduction with Lithium aluminimum hydride gives :
(a) 4° ammonium salt (b) 1° amine
(c) 2° amine (d) 3° amine

24. Which one of the following methods is neither meant for the synthesis nor for separation of amines?
(a) Curtius reaction
(b) Wurtz reaction
(c) Hofmann method
(d) Hinsberg method

25. The consituent of the powerful explosive RDX is formed during the nitration of
(a) toluene (b) phenol
(c) glycerol (d) urotropine

Exercise-2 | CONCEPTUAL MCQs

1. $C_6H_5C\equiv N$ and $C_6H_5N\overset{\rightarrow}{=}C$ exhibit which type of isomerism?
(a) Position (b) Functional
(c) Dextroisomerism (d) Position isomerism

2. Identify 'Z' in the following series

$$C_2H_5I\xrightarrow[KOH]{\text{Alcoholic}}X\xrightarrow{Br_2}Y\xrightarrow{KCN}Z$$

(a) CH_3CH_2CN (b) $CN-CH_2CH_2-CN$
(c) $Br-CH_2-CH_2CN$ (d) $Br-CH=CHCN$

3. Acetaldoxime reacts with P_2O_5 to give
(a) Methyl cyanide (b) Methyl cyanate
(c) Ethyl cyanide (d) None of these

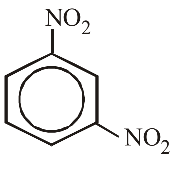
4. Tautomerism will be exhibited by
(a) $(CH_3)_3CNO$ (b) $(CH_3)_2NH$
(c) R_3CNO_2 (d) RCH_2NO_2

5. Tertiary nitro compounds do not tautomerise because
(a) there is no double bond
(b) there is no α-hydrogen
(c) oxygen is more electronegative than hydrogen
(d) All of the above

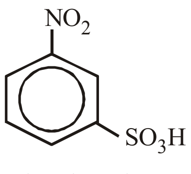
6. Attacking species in nitration of benzene in presence of fuming HNO_3 is
(a) SO_3 (b) SO_3^+
(c) NO_3^- (d) NO_2^+

7. Which one of the following products will be formed when benzene reacts with a mixture of conc. HNO_3 and conc. H_2SO_4 at 60ºC?
(a) $C_6H_5NO_2$ (b) $C_6H_5SO_3H$

(c)

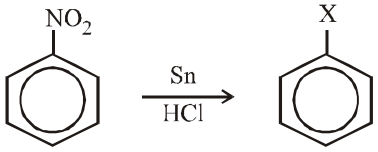


(d)



8. Nitrobenzene on further excessive nitration gives
(a) *sym*-Trinitrobenzene (b) *m*-Dinitrobenzene
(c) *p*-Dinitrobenzene (d) All of these

9.



In the above reaction, X stands for
(a) $SnCl_2$ (b) $NH_3^+Cl^-$ $NH_3^+Cl^-$
(c) NH_2 (d) Cl

10. The reduction of nitrobenzene with zinc and alkali results in the formation of
(a) aniline (b) hydrazobenzene
(c) nitrosobenzene (d) phenylhydroxylamine

11. Reduction of nitrobenzene in the presence of Zn/NH_4Cl gives
(a) azobenzene (b) aniline
(c) N-phenylhydroxylamine (d) hydrazobenzene

12. The reagent that reacts with nitromethane to form methylhydroxylamine is
(a) Zn/HCl (b) Zn/NH_4Cl
(c) Zn/NaOH (d) Sn/HCl

13. Nitrobenzene on electrolytic reduction in strongly acidic medium gives
(a) aniline (b) p-aminophenol
(c) m-nitroaniline (d) nitrosobenzene

14. Which of the following compounds does not react with $NaNO_2$ and HCl?
(a) C_6H_5OH (b) $C_6H_5NH_2$
(c) $(CH_3)_3CNO_2$ (d) $(CH_3)_2CHNO_2$

15. Hydrolysis of $CH_3CH_2NO_2$ with 85% H_2SO_4 gives
(a) CH_3CH_2OH (b) C_2H_6
(c) $CH_3CH=NOH$ (d) CH_3COOH

16. Which of the following is not an explosive?
(a) Nitroglycerine (b) o-Aminotoluene
(c) Dynamite (d) Trinitrotoluene

17. C_7H_9N has how many isomeric forms that contain a benzene ring?
(a) 4 (b) 5
(c) 6 (d) 7

18. Treatment of ammonia with excess of ethyl iodide will yield
(a) diethylamine
(b) ethylamine
(c) triethylamine
(d) tetraethylammonium iodide

19. Butanenitrile may be prepared by heating
(a) propyl alcohol with KCN
(b) butyl alcohol with KCN
(c) butyl chloride with KCN
(d) propyl chloride with KCN

20. Which of the following gives primary amine on reduction?
(a) $CH_3CH_2NO_2$ (b) $CH_3CH_2-O-N=O$
(c) $C_6H_5N=NC_6H_5$ (d) CH_3CH_2NC

21. Intermediates formed during reaction of $RCONH_2$ with Br_2 and KOH are
(a) RCONHBr and RNCO (b) RNHCOBr and RNCO
(c) RNHBr and RCONHBr (d) $RCONBr_2$

22. Gabriel phthalimide reaction is used for preparing
(a) primary aromatic amines (b) secondary amines
(c) primary aliphatic amines (d) tertiary amines

23. Which of the following reactions will not give a primary amine?
(a) $CH_3CONH_2 \xrightarrow{Br_2/KOH}$
(b) $CH_3CN \xrightarrow{LiAlH_4}$
(c) $CH_3NC \xrightarrow{LiAlH_4}$
(d) $CH_3CONH_2 \xrightarrow{LiAlH_4}$

24. On reduction, secondary amine is given by
(a) nitrobenzene (b) methylcyanide
(c) nitroethane (d) methyl isocyanide

25. Which is formed when $(CH_3)_4$ NOH is heated?
(a) CH_3NH_2 (b) $C_2H_5NH_2$
(c) $(CH_3)_3N$ (d) $(CH_2)_3N$

26. The one which is least basic is
(a) NH_3 (b) $C_6H_5NH_2$
(c) $(C_6H_5)_3N$ (d) $(C_6H_5)_2NH$

27. Which one of the following will be most basic?
(a) Aniline (b) p-Methoxyaniline
(c) p-Nitroaniline (d) Benzylamine

28. Which of the following statement is not correct?
(a) Methylamine is more basic than NH_3
(b) Amines form hydrogen bonds
(c) Ethylamine has higher boiling point than propane
(d) Dimethylamine is less basic than methylamine

29. The correct order of increasing basicity in aqueous solution is
(a) $NH_3 < C_6H_5NH_2 < (C_2H_5)_2NH$
$< C_2H_5NH_2 < (C_2H_5)_3N$
(b) $C_6H_5NH_2 < NH_3 < (C_2H_5)_3N$
$< C_2H_5NH_2 < (C_2H_5)_2NH$
(c) $C_6H_5NH_2 < NH_3 < C_2H_5NH_2$
$(C_2H_5)_3N < (C_2H_5)_2NH$
(d) None of the above

30. The amine that does not react with acetyl chloride is
(a) CH_3NH_2 (b) $(CH_3)_2NH$
(c) $(CH_3)_3N$ (d) None of these

31. Aniline on reaction with acetyl chloride gives
(a) phenol (b) acetamide
(c) acetanilide (d) benzene

32. $CH_3CH_2Cl \xrightarrow{NaCN} X \xrightarrow{Ni/H_2} Y$
$\xrightarrow{\text{acetic anhydride}} Z$

Z in the above reacting sequence is
(a) $CH_3CH_2CH_2NHCOCH_3$
(b) $CH_3CH_2CH_2NH_2$
(c) $CH_3CH_2CH_2CONHCH_3$
(d) $CH_3CH_2CH_2CONHCOCH_3$

33. Consider the following reaction

$C_6H_5NO_2 \xrightarrow{Sn/HCl} X \xrightarrow{C_6H_5COCl} Y + HCl$

What is Y?
(a) Acetanilide (b) Benzanilide
(c) Azobenzene (d) Hydrazobenzene

34. Hinsberg reagent is
(a) $C_6H_5SO_3H$ (b) C_6H_5NO
(c) $C_6H_5SO_2Cl$ (d) $C_6H_5N_2Cl$

35. Reaction of nitrous acid with aliphatic primary amine in the cold gives
(a) a diazonium salt (b) an alcohol
(c) a nitrite (d) a dye

36. Diazonium salts are reaction products between nitrous acid and
(a) primary aliphatic amine
(b) N-alkyl substituted aromatic amines
(c) primary aromatic amines
(d) secondary amines

37. Aniline reacts with $NaNO_2$ and HCl at room temperature to give
(a) nitroaniline (b) phenol
(c) chloroaniline (d) diazonium chloride

38. Which of the following reacts with $NaNO_2 + HCl$ at 273-278 K to give alcohol/phenol?
(a) $C_6H_5CH_2NHCH_3$ (b) $(CH_3)_2NH$
(c) CH_3NH_2 (d) $C_6H_5NH_2$

39. In the diazotisation of arylamines with sodium nitrite and hydrochloric acid, an excess of hydrochloric acid is used primarily to
(a) supress the concentration of free aniline available for coupling
(b) supress hydrolysis of phenol
(c) ensure a stoichiometric amount of nitrous acid
(d) neutralise the base liberated

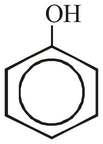
40. Nitrosoamines ($R_2N-N=O$) are insoluble in water. On heating with conc. H_2SO_4, they give secondary amines. The reaction is called
(a) Liebermann nitroso reaction
(b) Etard reaction
(c) Fries reaction
(d) Perkin reaction

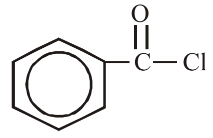
41. Phenyl isocyanide is prepared by which of the following reaction?
(a) Rosenmund's reduction (b) Carbylamine reaction
(c) Reimer-Tiemann reaction (d) Wurtz reaction

42. Unpleasant smelling carbylamines are formed by heating alkali and chloroform with
(a) any aliphatic amine (b) any aromatic amine
(c) any amine (d) any primary amine

43. Which of the following compounds cannot be identified by carbylamine test?
(a) $CH_3CH_2NH_2$ (b) $CHCl_3$
(c) $C_6H_5NH_2$ (d) $C_6H_5–NH–C_6H_5$

44. Aniline reacts with phosgene and KOH to form

(a)


(b)


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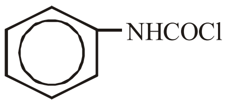

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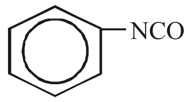


45. Primary amines on heating with CS_2 followed by excess of mercuric chloride yields isothiocyanates. The reaction is called
(a) Hofmann mustard oil reaction
(b) Perkin reaction
(c) Fries reaction
(d) Diels-Alder reaction

46. Reaction of aniline with benzaldehyde is
(a) substitution (b) addition
(c) condensation (d) polymerization

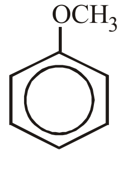
47. Which of the following statements is not correct regarding aniline?
(a) It is less basic than ethylamine
(b) It can be steam-distilled
(c) It reacts with sodium to give hydrogen
(d) It is soluble in water

48. Aniline when treated with conc. HNO_3 gives
(a) p-Phenylenediamine (b) m-Nitroaniline
(c) p-Benzoquinone (d) Nitrobenzene

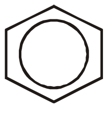
49. Aniline on heating with conc. HNO_3 + conc. H_2SO_4 mixture yields
(a) o– and p–Nitroanilines (b) m-Nitroaniline
(c) a black tarry matter (d) No reaction

50. Towards electrophilic substitution, the most reactive will be
(a) Nitrobenzene (b) Aniline
(c) Aniline hydrochloride (d) N-Acetylaniline

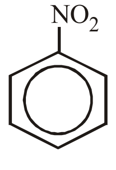
51. Among the following compounds (I-III), the correct order of reactivity towards electrophilic substitution reaction is



I



II



III

(a) II > III > I (b) III < I < II
(c) I > II > III (d) I = II > III

52. Which of the following reagent can be used to convert benzenediazonium chloride into benzene?
(a) CH_3OH (b) H_3PO_2
(c) $Br_2–H_2O$ (d) $LiAlH_4$

53. When benzenediazonium chloride in hydrochloric acid reacts with cuprous chloride, then chlorobenzene is formed. The reaction is called
(a) Gattermann reaction (b) Perkin reaction
(c) Etard reaction (d) Sandmeyer reaction

54. The reaction $C_6H_5N_2{}^+Cl^-$ with CuCl gives
(a) C_6H_5Cl (b) C_6H_6
(c) $C_6H_5-C_6H_5$ (d) $C_6H_4Cl_2$

55. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives
(a) Diphenyl ether (b) *p*-Hydroxyazobenzene
(c) Chlorobenzene (d) Benzene

56. The indicator that is obtained by coupling the diazonium salt of sulphanilic acid with N, N-dimethylaniline is
(a) phenanthroline (b) methyl orange
(c) methyl red (d) phenolphthalein

57. Primary nitro compounds react with nitrous acid to form nitrolic acids which dissolve in NaOH giving
(a) yellow solution (b) blue solution
(c) colourless solution (d) red solution

58. The compound that will react most readily with NaOH to form methanol is
(a) $(CH_3)_4N^+I^-$ (b) CH_3OCH_3
(c) $(CH_3)_3S^+I^-$ (d) $(CH_3)_3CCl$

59. Which of the following compounds gives dye test?
(a) Aniline (b) Methylamine
(c) Diphenylamine (d) Ethylamine

60. Primary and secondary amines can be distinguished by
(a) Schiff's reagent
(b) Carbylamine reaction
(c) Hofmann's bromamide reaction
(d) Biuret reaction

61. Acetamide and ethylamine can be distinguished by reacting with
(a) aqueous HCl and heat (b) aqueous NaOH and heat
(c) acidified $KMnO_4$ (d) bromine water

62. The reaction of benzyl chloride with sodium cyanide followed by reduction with hydrogen in the presence of nickel gives
(a) β-Phenylethylamine (b) N-Isobutylaniline
(c) Benzylamine (d) Aniline.

63. Identify the prdouct C in the series

$$CH_3CN \xrightarrow{Na/C_2H_5OH} A \xrightarrow{HNO_2} B \xrightarrow{Cu/573K} C$$

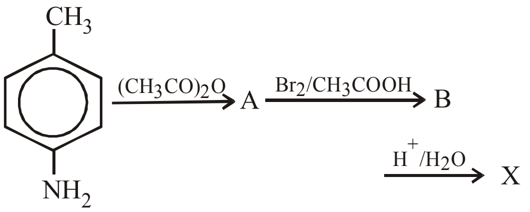
(a) CH_3COOH (b) CH_3CH_2NHOH
(c) CH_3CONH_2 (d) CH_3CHO

64. $C_6H_6 \xrightarrow[H_2SO_4]{HNO_3} X \xrightarrow[FeCl_3]{Cl_2} Y$

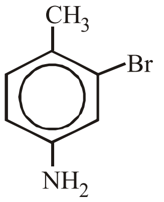
In the above sequence, Y can be
(a) 4-Nitrochlorobenzene (b) 1-Nitrochlorobenzene
(c) 3-Nitrochlorobenzene (d) None of these

65. Acetanilide on nitration followed by alkaline hydrolysis mainly gives
(a) o-Nitroacetanilide (b) p-Nitroaniline
(c) m-Nitroaniline (d) 2, 4, 6-Trinitroaniline

66.



What is X?

(a)


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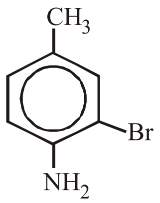

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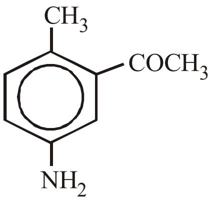

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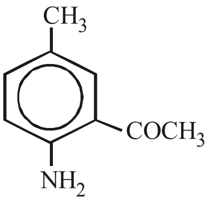


67. Which reaction sequence would be best to prepare 3-chloroanilne from benzene ?
(a) Chlorination, nitration, reduction
(b) Nitration, chlorination, reduction
(c) Nitration, reduction, chlorination
(d) Nitration, reduction, acetylation, chlorination, hydrolysis

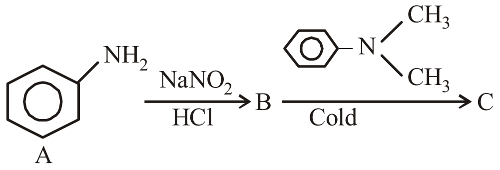
68. A compound 'A' when treated with HNO_3 (in presence of H_2SO_4) gives compound 'B', which is then reduced with Sn and HCl to aniline? The compound 'A' is
(a) toluene (b) benzene
(c) ethane (d) acetamide

69. An organic compound 'A' having molecular formula C_2H_3N on reduction gave another compound 'B'. Upon treatment with nitrous acid, 'B' gave ethyl alcohol. On warming with chloroform and alcoholic KOH, B formed an offensive smelling compound 'C'. The compound 'C' is
(a) $CH_3CH_2NH_2$
(b) $CH_3CH_2N \overset{\rightarrow}{=} C$
(c) $CH_3C \equiv N$
(d) CH_2CH_2OH

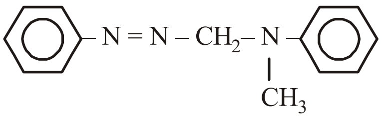
Exercise-3 | PAST COMPETITION MCQs

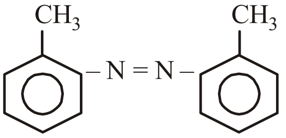
1. Which one of the following on reduction with lithium aluminium hydride yields a secondary amine? **[CBSE-PMT 2007]**
(a) Methyl isocyanide (b) Acetamide
(c) Methyl cyanide (d) Nitroethane

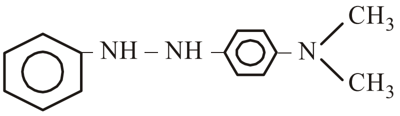
2. In a reaction of aniline a coloured product C was obtained.



The structure of C would be : **[CBSE-PMT 2008]**

(a)


(b)


(c)


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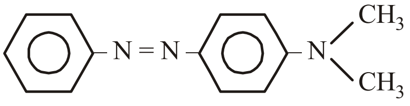
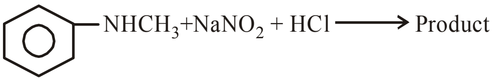
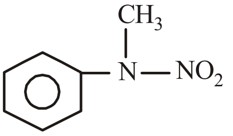


3. Predict the product: **[CBSE-PMT 2009]**



(a)


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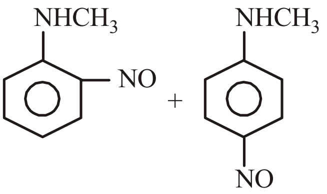

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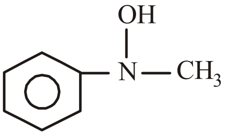

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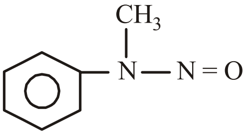


4. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4 in the mixture, nitric acid acts as a/an : **[CBSE-PMT 2009]**

(a) acid (b) base
(c) catalyst (d) reducing agent

5. Acetamide is treated with the following reagents separately. Which one of these would yield methylamine? **[CBSE-PMT 2010]**

(a) $NaOH - Br_2$ (b) Sodalime
(c) Hot conc. H_2SO_4 (d) PCl_5

6. Which of the following statements about primary amines is **'False'** ? **[CBSE-PMT 2010]**

(a) Alkyl amines are stronger bases than aryl amines
(b) Alkyl amines react with nitrous acid to produce alcohols
(c) Aryl amines react with nitrous acid to produce phenols
(d) Alkyl amines are stronger bases than ammonia

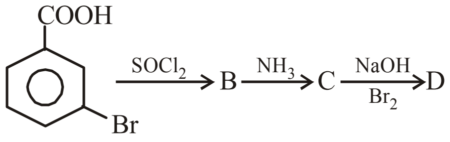
7. Match the compounds given in List - I with their characteristic reactions given in List - II. Select the correct option. **[CBSE-PMT 2010]**

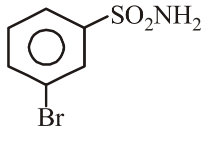
	List - I **Compounds**		**List - II** **Reactions**
(1)	$CH_3CH_2CH_2CH_2NH_2$	(i)	alkaline hydrolysis
(2)	$CH_3C \equiv CH$	(ii)	with KOH (alcohol) and $CHCl_3$ produces bad smell
(3)	$CH_3CH_2COOCH_3$	(iii)	gives white ppt. with ammonical $AgNO_3$
(4)	$CH_3CH(OH)CH_3$	(iv)	with Lucas reagent cloudiness appears after 5 minutes

Options :

	(1)	(2)	(3)	(4)
(a)	(iv)	(ii)	(iii)	(i)
(b)	(ii)	(i)	(iv)	(iii)
(c)	(iii)	(ii)	(i)	(iv)
(d)	(ii)	(iii)	(i)	(iv)

8. In a set of reactions *m*-bromobenzoic acid gave a product D. Identify the product D. **[CBSE-PMT 2011]**



(a)


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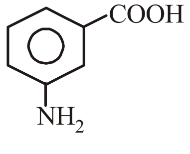

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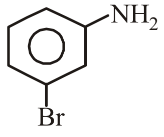

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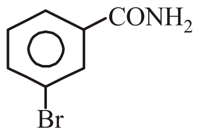
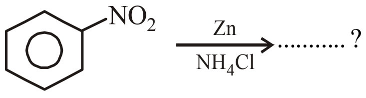
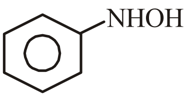


9. What is the product obtained in the following reaction :



[CBSE-PMT 2011]

(a)


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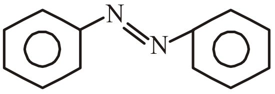

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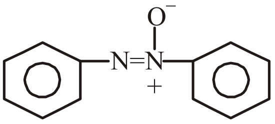

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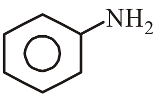
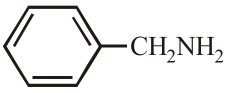


10. Which of the following compounds is most basic? **[CBSE-PMT 2011 M]**

(a)


(b)


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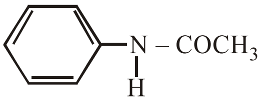

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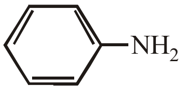
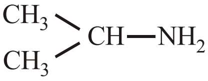
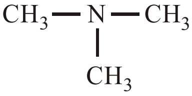


11. An organic compound (C_3H_9N) (A), when treated with nitrous acid, gave an alcohol and N_2 gas was evolved. (A) on warming with $CHCl_3$ and caustic potash gave (C) which on reduction gave isopropylmethylamine. Predict the structure of (A). **[CBSE-PMT 2012 M]**

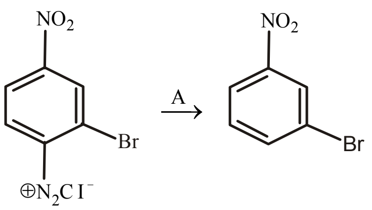
(a)

$(CH_3)_2CH—NH_2$

(b) $CH_3CH_2—NH—CH_3$

(c)

$CH_3—N(CH_3)—CH_3$

(d) $CH_3CH_2CH_2—NH_2$

12. In the reaction **[NEET 2013]**



A is :

(a) Cu_2Cl_2 (b) H_3PO_2 and H_2O
(c) H^+/H_2O (d) $HgSO_4/H_2SO_4$

13. The functional group, which is found in amino acid is **[AIEEE 2002]**

(a) –COOH group (b) $-NH_2$ group
(c) $-CH_3$ group (d) Both (a) and (b).

14. When primary amine reacts with chloroform in ethanoic KOH then the product is **[AIEEE 2002]**
(a) an isocyanide (b) an aldehyde
(c) a cyanide (d) an alcohol.

15. The reaction of chloroform with alcoholic KOH and p-toluidine forms **[AIEEE 2003]**

(a) 

(b) 

(c) 

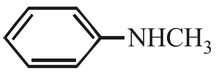
(d) 

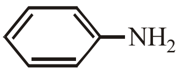
16. The correct order of increasing basic nature for the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is **[AIEEE 2003]**
(a) $(CH_3)_2NH < NH_3 < CH_3NH_2$
(b) $NH_3 < CH_3NH_2 < (CH_3)_2NH$
(c) $CH_3NH_2 < (CH_3)_2NH < NH_3$
(d) $CH_3NH_2 < NH_3 < (CH_3)_2NH$

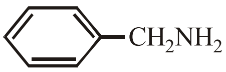
17. Ethyl isocyanide on hydrolysis in acidic medium generates
(a) propanoic acid and ammonium salt **[AIEEE 2003]**
(b) ethanoic acid and ammonium salt
(c) methylamine salt and ethanoic acid
(d) ethylamine salt and methanoic acid

18. Which of the following is the strongest base ? **[AIEEE 2004]**

(a) 

(b) 

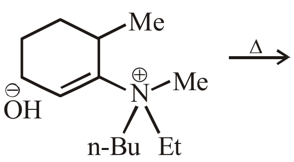
(c) 

(d) 

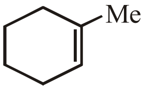
19. Which one of the following methods is neither meant for the synthesis nor for separation of amines? **[AIEEE 2005]**
(a) Curtius reaction (b) Wurtz reaction
(c) Hofmann method (d) Hinsberg method

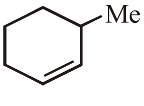
20. Amongst the following the most basic compound is **[AIEEE 2005]**
(a) p -nitroaniline (b) acetanilide
(c) aniline (d) benzylamine

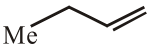
21. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as **[AIEEE 2005]**
(a) an amine (b) an imine
(c) an anemine (d) a Schiff's base

22. 

The alkene formed as a major product in the above elimination reaction is **[AIEEE 2006]**

(a) 

(b) 

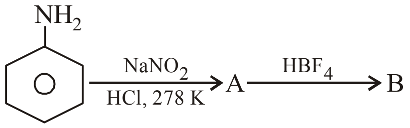
(c) 

(d) $CH_2=CH_2$

23. Which one of the following is the strongest base in aqueous solution ? **[AIEEE 2007]**
(a) Methylamine
(b) Trimethylamine
(c) Aniline
(d) Dimethylamine

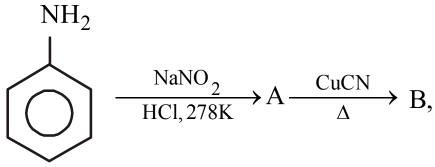
24. In the chemical reaction, **[AIEEE 2007]**
$CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow$
(A) + (B) + $3H_2O$, the compounds (A) and (B) are respectively
(a) C_2H_5NC and 3KCl
(b) C_2H_5CN and 3KCl
(c) $CH_3CH_2CONH_2$ and 3KCl
(d) C_2H_5NC and K_2CO_3

25. In the chemical reactions, **[AIEEE 2010]**



the compounds 'A' and 'B' respectively are
(a) nitrobenzene and fluorobenzene
(b) phenol and benzene
(c) benzene diazonium chloride and fluorobenzene
(d) nitrobenzene and chlorobenzene

26. In the chemical reactions : **[AIEEE 2011 RS]**

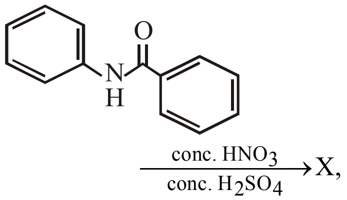


the compounds A and B respectively are :
(a) benzene diazonium chloride and benzonitrile
(b) nitrobenzene and chlorobenzene
(c) phenol and bromobenzene
(d) fluorobenzene and phenol

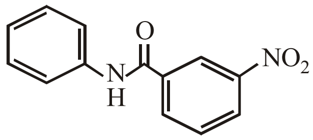
27. Ortho-Nitrophenol is less soluble in water than *p*- and *m*-Nitrophenols because : **[AIEEE 2012]**
(a) *o*-Nitrophenol is more volatile than those of *m*- and *p*-isomers.
(b) *o*-Nitrophenol shows intramolecular H-bonding
(c) *o*-Nitrophenol shows intermolecular H-bonding
(d) Melting point of *o*-Nitrophenol is lower than those of *m*- and *p*-isomers.

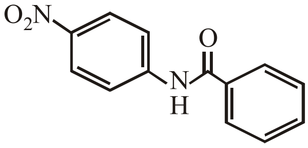
28. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is : **[JEE M 2013]**
(a) 2 (b) 5
(c) 4 (d) 6

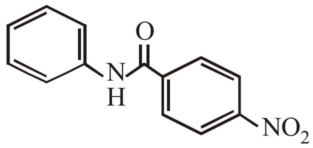
29. In the following reaction **[IIT-JEE 2007]**

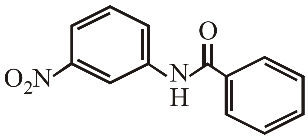


the structure of the major product 'X' is

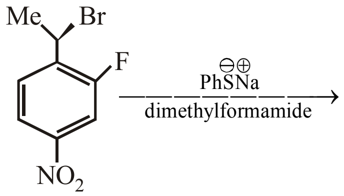
(a)


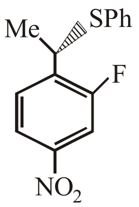
(b)


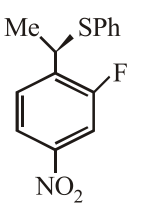
(c)


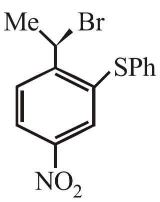
(d)


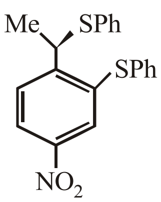
30. The major product of the following reaction is **[IIT-JEE 2008]**



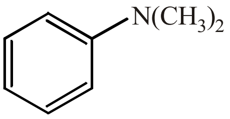
(a)


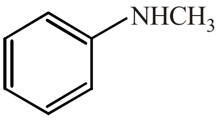
(b)


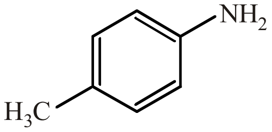
(c)


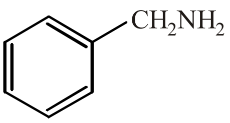
(d)


31. Amongst the compounds given, the one that would form a brilliant colored dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β-naphthol is **[IIT-JEE 2011]**

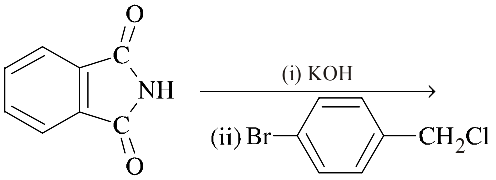
(a)


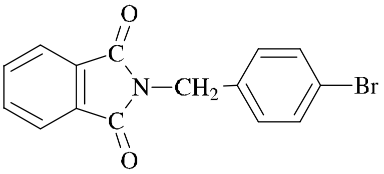
(b)


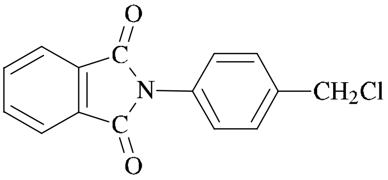
(c)


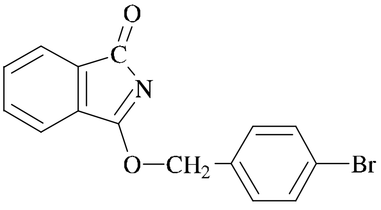
(d)


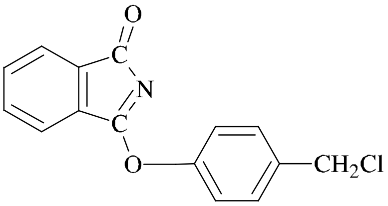
32. The major product of the following reaction is **[IIT-JEE 2011]**



(a)


(b)


(c)


(d)


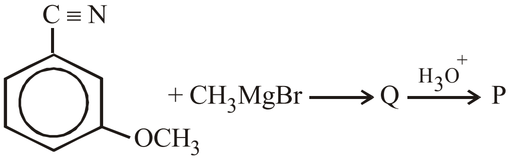
Exercise-4 | Applied MCQs

1. In the reaction,

$CH_3CN + 2H \longrightarrow X \xrightarrow{\text{Boiling } H_2O} Y$, the term Y is

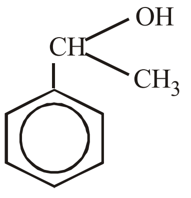
(a) acetone (b) ethanamine
(c) acetaldehyde (d) dimethylamine

2.

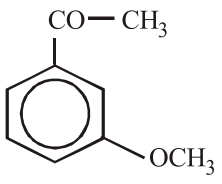


The product 'P' in the above reaction is

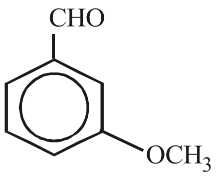
(a)



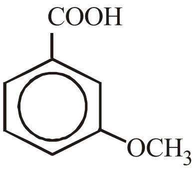
(b)



(c)



(d)

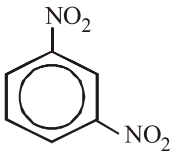


3. In the acidic reduction of nitrobenzene, which of the following is the intermediate?

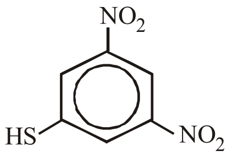
(a) $C_6H_5-N=O$
(b) $C_6H_5NH-NHC_6H_5$
(c) $C_6H_5-N=N-C_6H_5$
(d) $C_6H_5-N=\overset{\overset{O}{\uparrow}}{N}-C_6H_5$

4. The major product (70% to 80%) of the reaction between m-dinitrobenzene with NH_4HS is

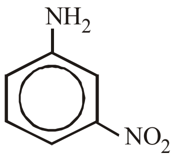
(a)



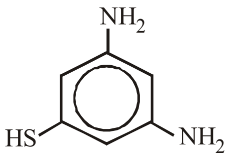
(b)



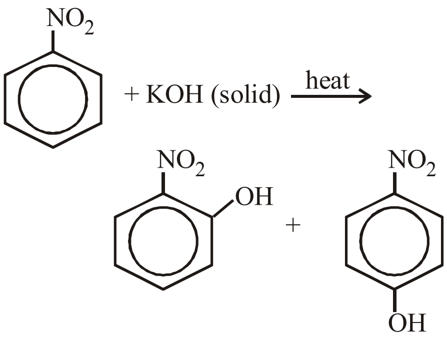
(c)



(d)



5. The following reaction is



(a) nucleophilic substituton (b) electrophilic substitution
(c) free radical substitution (d) electrophilic addition

6. The product 'D' of the reaction,

$CH_3Cl \xrightarrow{KCN} A \xrightarrow{H^+/H_2O} B \xrightarrow{NH_3} C \xrightarrow{\Delta} D$ is

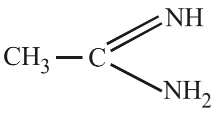
(a) $CH_3CH_2NH_2$ (b) CH_3CN
(c) $HCONH_2$ (d) CH_3CONH_2

7. Match the compounds in List I with their nature from List II, as seen in aqueous medium

List I	**List II**
I. Acetamide	A. Acidic
II. Benzonitrile	B. Basic
III. Triethylamine	C. Neutral
IV. Phenol	

(a) I–C; II–C; III–B; IV–A (b) I–B; II–C; III–C; IV–A
(c) I–C; II–B; III–B; IV–C (d) I–A; II–A; III–C; IV–B

8. The correct order of basicities of the following compounds is



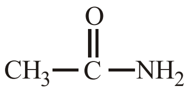
1

$CH_3-CH_2-NH_2$

2

$(CH_3)_2NH$

3



$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$

4

(a) $2>1>3>4$ (b) $1>3>2>4$
(c) $3>1>2>4$ (d) $1>2>3>4$

9. A compound 'Z' reacts with three moles of CH_3I and gives a product which on hydrolysis gives $[(CH_3)_4N]^+OH^-$. Compound 'Z' is

(a) CH_3NH_2 (b) $(CH_3)_2NH$
(c) $(CH_3)_3N$ (d) $(CH_3)_4\overset{+}{N}Cl^-$

10. Match the compounds in List I with the appropriate test that will be answered by each one of them in List II

List I	**List II**
I. Propyne	A. Reduces Fehling's solution
II. Ethyl benzoate	B. Forms a precipitate with $AgNO_3$ in ethanol
III. Acetaldehyde	C. Insoluble in water but dissolves in aqueous NaOH solution upon heating.
IV. Aniline	D. Dissolves in dilute HCl in the cold and is reprecipitated by the addition of alkali

(a) I–A; II–D; III–B; IV–A (b) I–A; II–D; III–C; IV–B
(c) I–D; II–B; III–C; IV–A (d) I–B; II–C; III–A; IV–D

11. What is the end product in the following sequence of operations?

$$C_2H_5NH_2 \xrightarrow{HNO_2} A \xrightarrow{PCl_5} B \xrightarrow{NH_3} C$$

(a) Ethyl cyanide (b) Methylamine
(c) Ethylamine (d) Acetamide

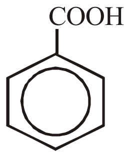
12. In the following reaction, X is

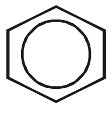
$$X \xrightarrow{\text{Bromination}} Y \xrightarrow{NaNO_2/HCl} Z \xrightarrow[C_2H_5OH]{\text{Boiling}} \text{Tribromobenzene}$$

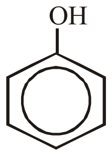
(a) benzoic acid (b) salicylic acid
(c) phenol (d) aniline

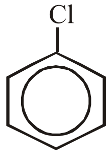
13. 'Z' in the following sequence of reactions is

$$C_6H_6 \xrightarrow[\Delta]{HNO_3/H_2SO_4} W \xrightarrow{Zn/HCl} X \xrightarrow[HCl]{NaNO_2} Y \xrightarrow{H_2O/H_3PO_2} Z$$

(a) 

(b) 

(c) 

(d) 

14. An organic compound (A) on reduction gives compound (B). (B) on treatment with $CHCl_3$ and alcoholic KOH gives (C). (C) on catalytic reduction gives N-methylaniline. The compound A is

(a) Methylamine (b) Nitromethane
(c) Aniline (d) Nitrobenzene

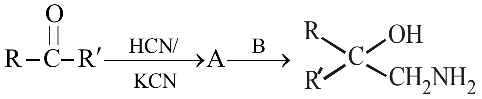
15. A compound A has a molecular formula C_7H_7NO. On treatment with Br_2 and KOH, A gives an amine B which gives carbylamine test. B upon diazotisation and coupling with phenol gives an azo dye. A can be

(a) $C_6H_5CONHCOCH_3$
(b) $C_6H_5CONH_2$
(c) $C_6H_5NO_2$
(d) o–, m– or p– $C_6H_4(NH_2)CHO$

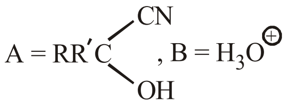
16. Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute HCl. The compound so formed is converted into tetrafluoroborate which is subsequently heated dry. The final product is

(a) *p*-Bromofluorobenzene
(b) *p*-Bromoaniline
(c) 2, 4, 6-Tribromofluorobenzene
(d) 1, 3, 5-Tribromobenzene

17. A and B in the following reactions are

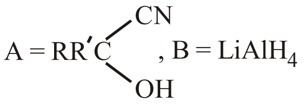


$$R-\overset{O}{\overset{||}{C}}-R' \xrightarrow[KCN]{HCN/} A \xrightarrow{B} \begin{matrix} R \\ R' \end{matrix} C \begin{matrix} OH \\ CH_2NH_2 \end{matrix}$$

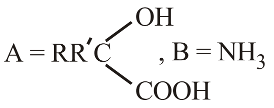
(a) 

$A = RR'C(CN)(OH)$, $B = H_3O^{\oplus}$

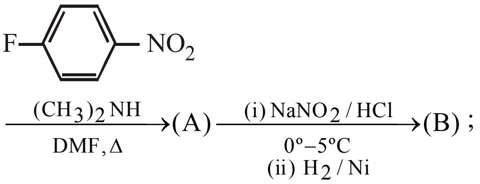
(b) $A = RR'CH_2CN$, $B = NaOH$

(c) 

$A = RR'C(CN)(OH)$, $B = LiAlH_4$

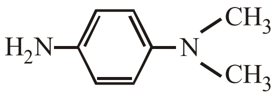
(d) 

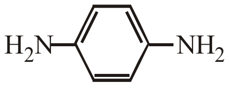
$A = RR'C(OH)(COOH)$, $B = NH_3$

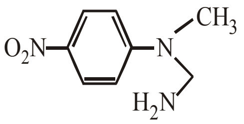
18. 

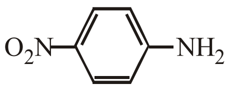
$$F-C_6H_4-NO_2 \xrightarrow[DMF,\Delta]{(CH_3)_2NH} (A) \xrightarrow[\substack{0°–5°C \\ (ii)\ H_2/Ni}]{(i)\ NaNO_2/HCl} (B);$$

B is

(a) 

(b) 

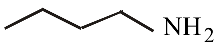
(c) 

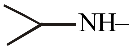
(d) 

19. When acetamide is treated with NaOBr, the product formed is

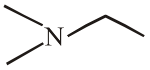
(a) CH_3CN (b) CH_3COBr
(c) CH_3NH_2 (d) CH_3OH

20. Among the following isomeric $C_4H_{11}N$ amines, one having the lowest boiling point

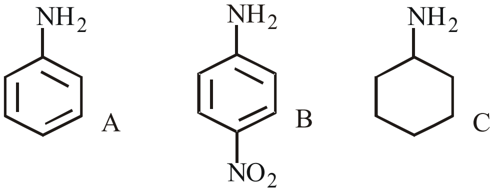
(a) 

(b) 

(c) 

(d) 

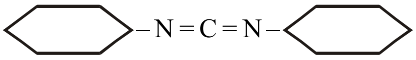
21. The correct order of basicity of the following compounds

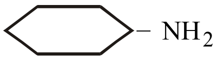


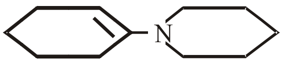
(a) B>A>C (b) A>B>C

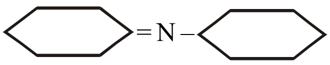
(c) C>A>B (d) C>B>A

22. Which of the following compounds is an enamine ?

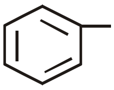
(a)


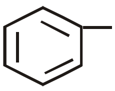
(b)


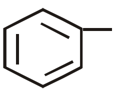
(c)


(d)


23. Which of the following reactions will not give N, N- dimethyl benzamide ?

(a)

$CO.O.C_2H_5 + (CH_3)_2NH \longrightarrow$

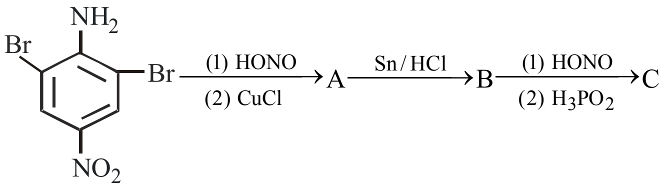
(b)

$CONH_2 + CH_3MgI \longrightarrow$

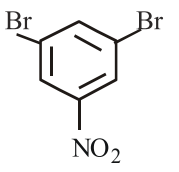
(c)

$COCl + (CH_3)_2NH \longrightarrow$

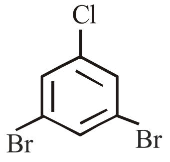
(d)

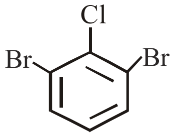

$+ (CH_3)_2NH \longrightarrow$

24. The product – (C) obtained in the following sequence of reactions is



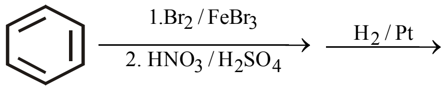
(a)


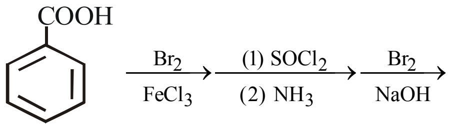
(b)


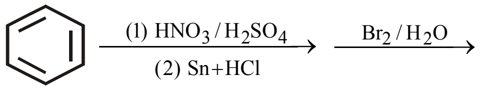
(c)


(d) None of these

25. Which of the following sequence of reactions will give m-bromo aniline ?

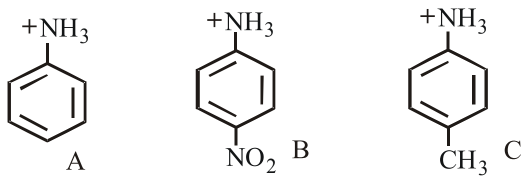
(a)


(b)


(c)


(d) None of these

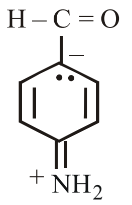
26. Rank the following three compounds in order of decreasing activity

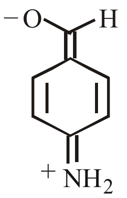


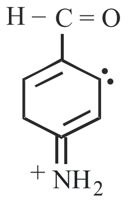
(a) B>A> C (b) B>C>A

(c) C>B> A (d) C>A>B

27. Which of the following is not a resonance form of para amino benzaldehyde ?

(a)


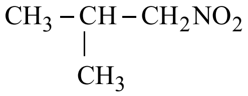
(b)


(c)


(d) None of these

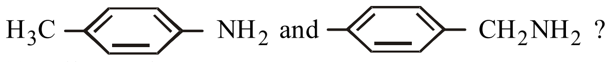
28. A nitro alkane reacts with HONO to give insoluble product in alkali which turns blue on treatment with an alkali. The nitro alkane is

(a) $CH_3CH_2NO_2$

(b)

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2NO_2$

(c) $(CH_3)_2CHNO_2$ (d) $(CH_3)_3CNO_2$

29. Which of the following reagents will be useful to distinguish between



(a) Dilute HCl

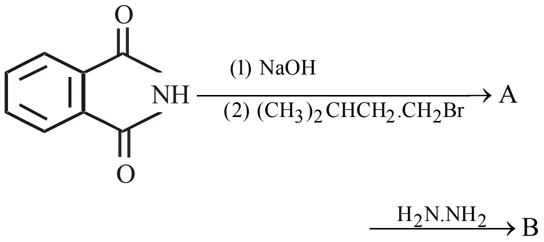
(b) $C_6H_5SO_2Cl$ and OH^- / H_2O

(c) HONO then β -naphthol

(d) $AgNO_3$ in H_2O

30. To convert a nitrile to a primary amine we must
(a) oxidise it with chromatic acid
(b) hydrolyse it with water
(c) reduce it with $LiAlH_4$
(d) substitute it with an alkyl halide

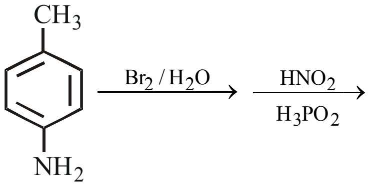
31. What is the final product (B) of the following reaction ?

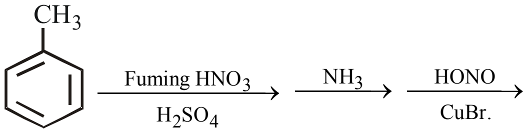


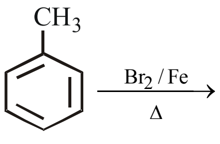
(a) $(CH_3)_2CH.CH_2CH_2NH_2$
(b) $(CH_3)_2CH.CH_2.CH_2NH.NH_2$
(c) $[(CH_3)_2CH.CH_2CH_2]NH$
(d) $(CH_3)_2CH.CH_2CH_2CONH_2$

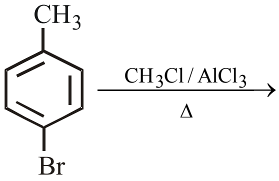
32. Which nitro alkane will give ketone when boiled with HCl?
(a) $(CH_3)_2CHNO_2$
(b) $CH_3CH_2NO_2$
(c) $(CH_3)_3CCH_2NO_2$
(d) $(CH_3)_3CNO_2$

33. 3, 5-dibromotoluene can be best synthesised by

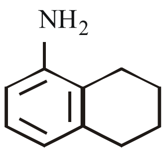
(a)


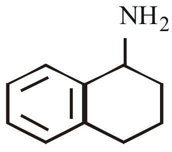
(b)


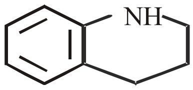
(c)


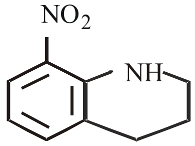
(d)


34. Which of the following is the strongest base ?

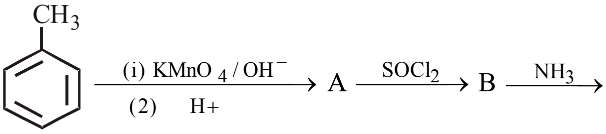
(a)


(b)


(c)


(c)


35. The final product obtained in the following sequence of reactions

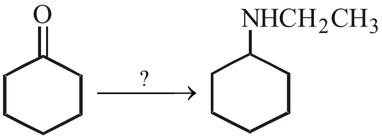


$C \xrightarrow{OBr^-} D$

(a) p-$CH_3C_6H_4NO_2$
(b) $C_6H_5CONH_2$
(c) $C_6H_5NO_2$
(d) $C_6H_5NH_2$

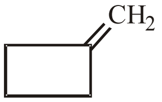
36. In the reaction $C_6H_5NH_2 + CS_2 \xrightarrow[\Delta]{HgCl_2}$ the product obtained is
(a) phenyl isocyanide
(b) phenyl cyanide
(c) p-amino benzene sulphonic acid
(d) phenyl isothiocyanate

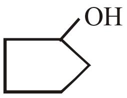
37. Reagents capable of converting cyclohexanone to N-ethyl cyclohexylamine is

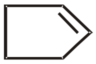


(a) CH_3CH_2Br and NH_3
(b) $CH_3CH_2NH_2$ and H_2/Pt
(c) $CH_3CH=O$ and NH_3
(d) $LiAlH_4$ followed by H_2O and then CH_3CH_2Br

38. The cyclobutyl methylamine with nitrous acid gives

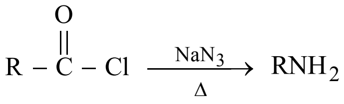
(a)


(b)


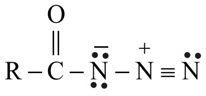
(c)


(d) All of these

39. The intermediate obtained in the following reaction



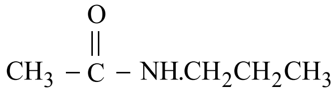
$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow[\Delta]{NaN_3} RNH_2$

(a)


$R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{-}{\ddot{\underset{\cdot\cdot}{N}}}-\overset{+}{N}\equiv\ddot{N}$

(b) $R-N=C=O$
(c) Both (a) and (b)
(d) None of these

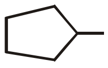
40. Which of the following gives propylamine upon hydrolysis?
(a) $CH_3CH_2C\equiv N$
(b) $(CH_3CH_2CH_2)_2NH$

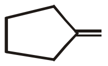
(c)


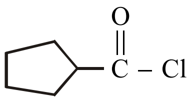
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH.CH_2CH_2CH_3$

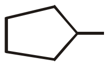
(d) $CH_3CH_2-CH=NH$

41. Which of the following does not give N–ethyl cyclopentylamine as major product ?

(a)  $NH_2 + CH_3CHO \xrightarrow{H_2/Pt}$

(b)  $O + CH_3CH_2NH_2 \xrightarrow{H_2/Pt}$

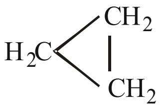
(c)  $\xrightarrow[\text{Pyridine}]{CH_3CH_2NH_2} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4,\ Et_2O}$

(d)  $NH_2 \xrightarrow[\text{Pyridine}]{CH_3COCl} \xrightarrow[\text{(2) } H_2O]{\text{(1) } LiAlH_4}$

42. In the reaction $CH_3CH_2CH_2NH_2 \xrightarrow[0-5°C]{NaNO_2 + \text{dil. } HCl}$

the products formed are

(a) $CH_3CH = CH_2$

(b) 

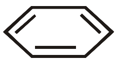
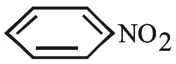
(c) Both a and b

(d) None of these

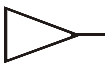
43. Which of the following reactions is not feasible ?

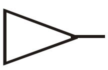
(a) $ICH_2COOC_2H_5 + AgNO_2 \xrightarrow[\text{ether}]{0°C} O_2NCH_2COOC_2H_5 + AgI$

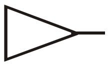
(b) $(CH_3)_3CNH_2 \xrightarrow[\text{acetone + water}]{KMnO_4} (CH_3)_3C - NO_2$

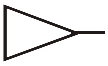
(c)  $\xrightarrow{HONO}$ 

(d) All are feasible

44. In the reaction  $CH_2CN \xrightarrow[NaNH_2,\ NH_3\ -\ 80°C]{CH_3Br}$ the products obtained are

(a)  $\overset{\overset{CH_3}{|}}{CH} - C \equiv N$

(b)  $CH_2.NH_2$

(c)  $CH_2.OH$

(d) None of these

45. Which of the following forms a diazonium ion when treated with $NaNO_2$ in aqueous HCl ?

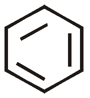
(a) p – nitrotoluene

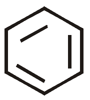
(b) ethylamine

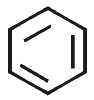
(c) N, N – dimethyl aniline

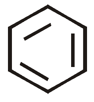
(d) None of these

46. Which of the following gives the best yield of m-bromo aniline ?

(a)  $\xrightarrow[H_2SO_4]{HNO_3} \xrightarrow[\text{(2) NaOH}]{\text{(1) Sn, HCl}} \xrightarrow{Br_2/FeCl_3}$

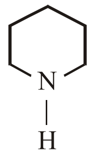
(b)  $\xrightarrow[H_2SO_4]{HNO_3} \xrightarrow[FeBr_3]{Br_2} \xrightarrow[\text{(2) NaOH}]{\text{(1) Sn, HCl}}$

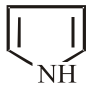
(c)  $\xrightarrow[FeBr_3]{Br_2} \xrightarrow[H_2SO_4]{HNO_3} \xrightarrow[\text{(2) NaOH}]{\text{(1) Sn, HCl}}$

(d)  $\xrightarrow[\text{(2) NaOH}]{\text{(1) Sn, HCl}} \xrightarrow[H_2SO_4]{HNO_3} \xrightarrow[FeBr_3]{Br_2}$

47. Which of the following amines will react with Cyclohexanone to give enamine ?

(a) $(CH_3)_2NH$

(b) 

(c) 

(d) All of these

48. Which of the following statement is correct ?

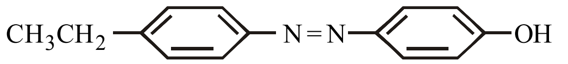
(a) Ammonia is more basic than methylamine.

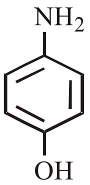
(b) Methylamine is more basic than ammonia.

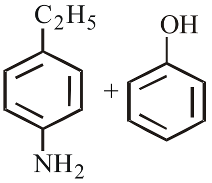
(c) Dimethylamine is less basic than methylamine.

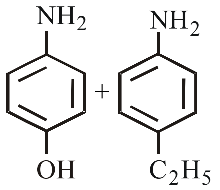
(d) Dimethylamine is less basic than trimethylamine.

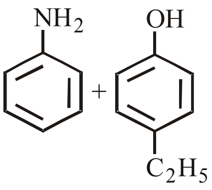
49. The starting reagents needed to make the azo compound shown below



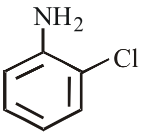
(a)  + ethylamine

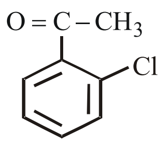
(b) 

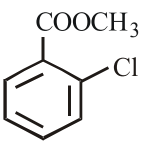
(c) 

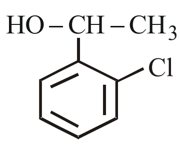
(d) 

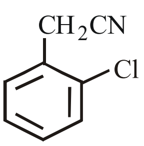
50. What is the product of the following series of reactions?

 $\xrightarrow[H_2O,\ 0°C]{NaNO_2,\ HCl} \xrightarrow{CuCN} \xrightarrow[\text{(2) } H_2O,\ H^+]{\text{(1) } CH_3MgBr}$

(a) 

(b) 

(c) 

(d) 

Hints & Solutions

EXERCISE 1

1. Aniline < Methylamine < Ethylamine < Dimethylamine.
2. Because aniline gets easily oxidised.
5. Amines have lone pair of electrons like $\ddot{N}H_3$
7. (*a*) Methyl isocyanides is formed.
   (*b*) The primary amine is formed.

16. (a) **17. (c)** **18. (b)** **19. (c)** **20. (b)** **21. (c)**
22. (b) **23. (b)** **24. (b)** **25. (d)**

EXERCISE 2

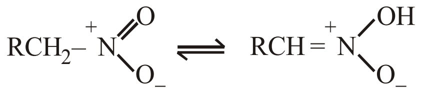
1. (b)

2. (b) $C_2H_5I \xrightarrow{\text{alc.KOH}} \underset{X}{H_2C = CH_2} \xrightarrow{Br_2}$

$$\underset{Y}{BrCH_2\,CH_2Br} \xrightarrow{KCN} \underset{Z}{CNCH_2\,CH_2CN}$$

3. (a) $CH_3CH = NOH \xrightarrow{P_2O_5} CH_3CN + H_2O$

4. (d) Nitro compounds having α-hydrogen show tautomerism



5. (b) **6. (d)** **7. (a)** **8. (b)** **9. (c)** **10. (b)**
11. (c) **12. (b)** **13. (b)**

14. (c) With nitrous acid: (i) phenol gives *p*- nitrosophenol, (ii) aniline gives diazonium salt, and (iii) 2° nitro compounds give pseudonitrole, while 3° nitro compounds do not react because they have no α-hydrogen atom .

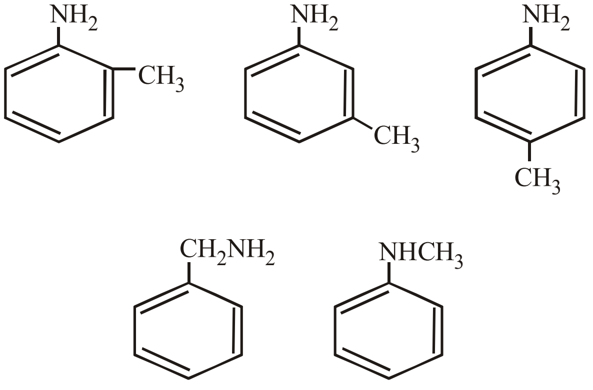
15. (d) 1° Nitroalkanes on hydrolysis with boiling 85% H_2SO_4 give acids.

$$CH_3CH_2NO_2 + H_2O + H_2SO_4 \xrightarrow{\text{heat}}$$

$$CH_3COOH + [NH_3OH]^+ HSO_4^-$$

16. (b) Explosives invariably contain two or more $-NO_2$ groups, hence *o* - aminotoluene (not having any $-NO_2$ group) is not an explosive. All other three compounds have three $-NO_2$ groups per molecule.

17. (b) C_7H_9N having one benzene ring may be represented as $C_6H_5CH_4N$, may be in the form of 1° and 2° amines in the following five isomeric forms.



18. (d) **19. (d)** **20. (a)** **21. (a)** **22. (c)**

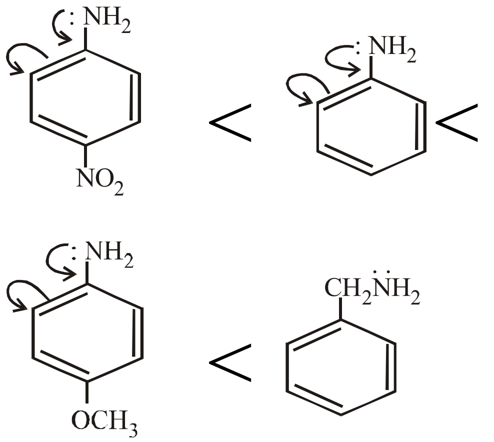
23. (c) CH_3NC (methyl isocyanide) on reduction with $LiAlH_4$ gives secondary amine

24. (d)

25. (c) $(CH_3)_4N^+OH^- \xrightarrow{\text{heat}} (CH_3)_3N + CH_3OH$

26. (c) More the electron density on N, higher will be the basicity. Density on N is influenced by the (i) nature of the group (+I or –I) present in alkyl group or benzene nucleus and (ii) resonance (delocalisation of the electron present on N). In $(C_6H_5)_3N$: electron pair is delocalised to the maximum extent due to three benzene rings and hence least available for protonation, thus it will be least basic.

27. (d) In aniline, *p* - methoxyaniline and *p*- nitroaniline, the lone pair of electrons on the N- atom are delocalized into the benzene ring while in benzylamine they are not, so benzylamine is most basic
Order of basic strength:



increasing basic character →

28. **(d)** Dimethylamine (2°) is more basic than methylamine (1°) therefore statement *d* is incorrect.

29. **(b)**

30. **(c)** The compounds containing active H-atoms (H atoms attached to N, O or S) react with CH_3COCl to form acetyl derivatives.

31. **(c)**

32. **(a)** $\underset{}{CH_3CH_2Cl} \xrightarrow{NaCN} \underset{X}{CH_3CH_2CN} \xrightarrow{Ni/H_2}$

$\underset{Y}{CH_3CH_2CH_2NH_2} \xrightarrow{(CH_3CO)_2O} \underset{Z}{CH_3CH_2CH_2NHCOCH_3}$

33. **(b)** **34.** **(c)** **35.** **(b)** **36.** **(c)**

37. **(b)** Initially formed diazonium chloride decomposes to give phenol.

$$C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} \underset{\text{unstable above } 10° C}{[C_6H_5N^+ \equiv NCl^-]}$$

$$\xrightarrow{\text{room temp.}} C_6H_5OH + HCl + N_2$$

38. **(c)** $RNH_2 \xrightarrow[273\text{-}278K]{NaNO_2/HCl} ROH + N_2 + H_2O$

39. **(a)** Excess of HCl is used to convert free aniline to aniline hydrochloride otherwise free aniline would undergo coupling reaction with benzenediazonium chloride.

40. **(a)** $R_2NNO + H_2O \rightarrow R_2NH + HNO_2$

41. **(b)** **42.** **(d)** **43.** **(d)**

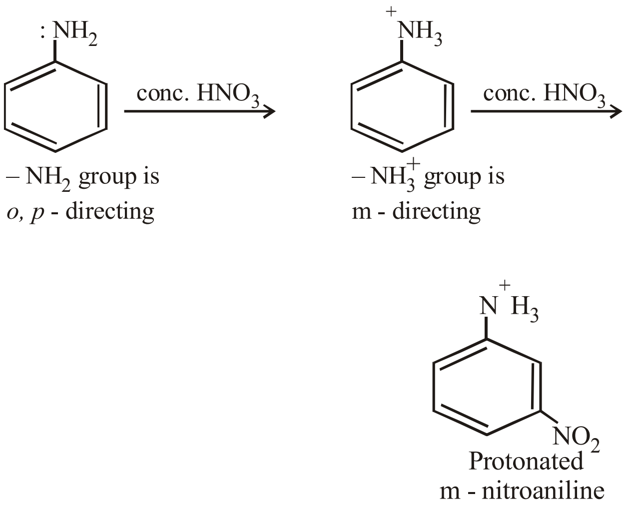
44. **(d)** $C_6H_5NH_2 + COCl_2 + KOH \rightarrow C_6H_5NH.COCl + HCl$

$$\xrightarrow{\Delta} C_6H_5NCO + HCl$$

45. **(a)** **46.** **(c)**

47. **(d)** Aniline is insoluble in water, because its $-NH_2$ group can't form H- bond with water due to bulky phenyl group.

48. **(b)** Although $-NH_2$ group is *o,p* - directing but in presence of conc. HNO_3 it undergoes protonation to form $-\overset{+}{N}H_3$ which, being electron - deficient, becomes *m*- directing.



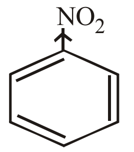
$-NH_2$ group is *o, p* - directing

$-\overset{+}{N}H_3$ group is m - directing

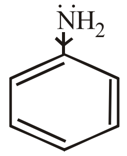
Protonated m - nitroaniline

49. **(c)**

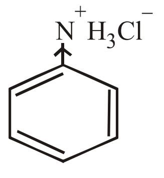
50. **(b)**



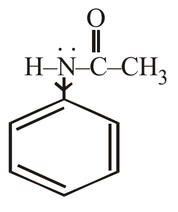
nitrobenzene



Aniline



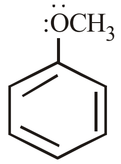
Aniline hydrochloride



N- Acetylaniline

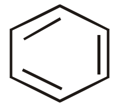
Nitrobenzene and aniline hydrochloride have electron-withdrawing ($-NO_2$ and $-\overset{+}{N}H_3$) groups, hence these will undergo electrophilic substitution with difficulty. Aniline and N– acetylaniline (acetanilide) have electron– releasing groups, however $-NHCOCH_3$ is less electron- releasing than $-NH_2$ due to delocalisation of lone pair of electron on N toward carbonyl group. Hence aniline (having $-NH_2$) will undergo electrophilic substitution most easily.

51. **(c)**



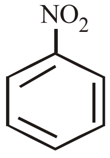
Electron-releasing, $-OCH_3$ group hence activating

>



No group

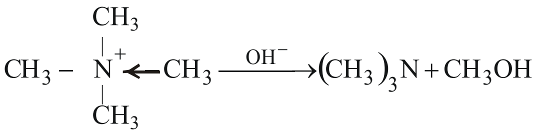
>



Electron-withdrawing, NO_2 group hence deactivating

52. **(b)** **53.** **(d)** **54.** **(a)** **55.** **(b)** **56.** **(b)** **57.** **(d)**

58. **(a)** Due to greater electronegativity of N than S, methyl group in $(CH_3)_4N^+ I^-$ becomes more electron-deficient than the methyl group in $(CH_3)_3S^+I^-$, hence $(CH_3)_4N^+I^-$ is more liable to be attacked by nucleophile OH^- :



$$CH_3 - \underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{N^+}}}} \leftarrow CH_3 \xrightarrow{OH^-} (CH_3)_3N + CH_3OH$$

59. **(a)** Only 1° aromatic amines undergo coupling reactions to form a dye

60. **(b)**

61. **(b)** Amides (acetamide), but not amines, react with NaOH to give NH_3

62. (a) $\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow{NaCN} C_6H_5CH_2CN \xrightarrow{H_2/Ni}$

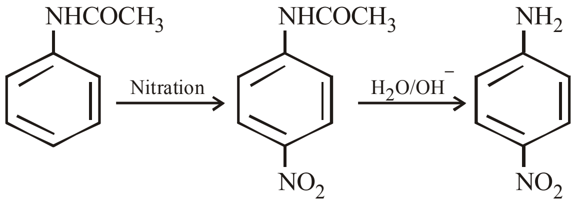
$$\underset{\beta-\text{Phenylethylamine}}{C_6H_5CH_2CH_2NH_2}$$

63. (d) $CH_3CN \xrightarrow{Na/C_2H_5OH} \underset{(A)}{CH_3CH_2NH_2}$

$$\xrightarrow{HNO_2} \underset{(B)}{CH_3CH_2OH} \xrightarrow[573\ K]{Cu} \underset{(C)}{CH_3CHO}$$

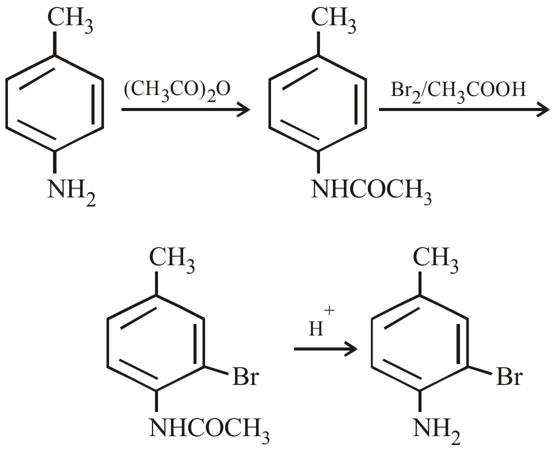
64. (c)

65. (b)



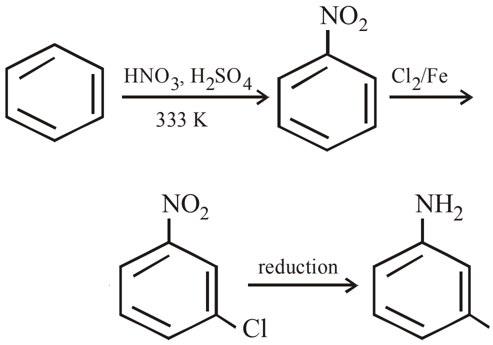
p-Nitroaniline

66. (b)



(–NHCOCH$_3$ is more electron-releasing than –CH$_3$ group)

67. (b)



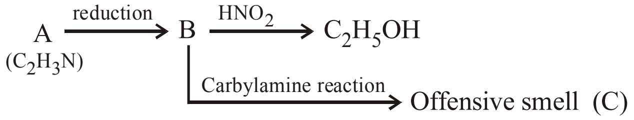
(a) When chlorination is done earlier than nitration, chlorobenzene formed at first step would introduce –NO$_2$ group in ortho-position, not in m-position

(b) Again if –NO$_2$ group is reduced earlier than the chlorination step, –NH$_2$ group formed on reduction will again introduce –Cl in o-position

68. (b) $A \xrightarrow{HNO_3/H_2SO_4} B \xrightarrow{Sn/HCl} C_6H_5NH_2$

This indicates that B is $C_6H_5NO_2$ and hence A is C_6H_6

69. (b)



Given reactions indicate that B has 1° NH$_2$ group, and thus A, C$_2$H$_3$N, should be $CH_3C \equiv N$. Hence C should be CH$_3$CH$_2$NC

$$\underset{A}{CH_3C \equiv N} \xrightarrow{\text{reduction}} \underset{B}{CH_3CH_2NH_2} \xrightarrow[KOH]{CHCl_3} \underset{C}{CH_3CH_2N \overrightarrow{=} C}$$

EXERCISE 3

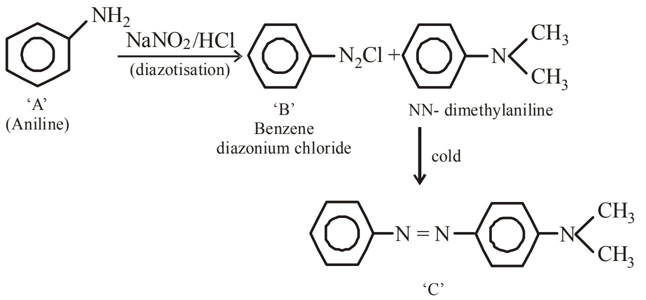
1. (a) Reduction of alkyl isocyanides in presence of LiAlH$_4$ yields secondary amines containing methyl as one of the alkyl group.

$$R - N \equiv C + 4[H] \xrightarrow{LiAlH_4} \underset{2°\text{amine}}{R - NH - CH_3}$$

e.g., $CH_3 - N \equiv C + 4[H] \xrightarrow{LiAlH_4} \underset{\text{dimethyl amine}}{CH_3 - NH - CH_3}$

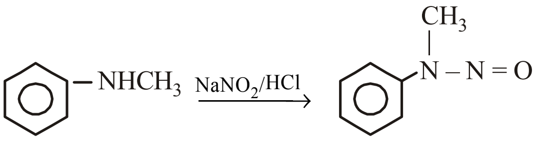
whereas, alkyl cyanides give 1° amine on reduction.

2. (d) The reaction can be completed as follows:



p-dimethylaminazobenzene

3. (d) Secondary amine with (NaNO$_2$ + HCl) gives a nitroso product



N– Nitroso – N– methylaniline

4. (b) $HONO_2 + H_2SO_4 \longrightarrow NO_2^+ + H_2O + HSO_4^-$

Nitric acid acts as a base by accepting a proton.

5. (a) $CH_3CONH_2 \xrightarrow[Br_2]{NaOH} CH_3NH_2$

(Hofmann bromamide reaction)

6. (c) Aryl amines do not produce phenol on treatment with nitrous acid

7. **(d)** (1) $CH_3CH_2-CH_2-CH_2-NH_2$

(ii) with KOH (alcohol) and $CHCl_3$ produces bad smell

(2) $CH_3C\equiv CH$

(ii) gives white ppt with ammonical $AgNO_3$

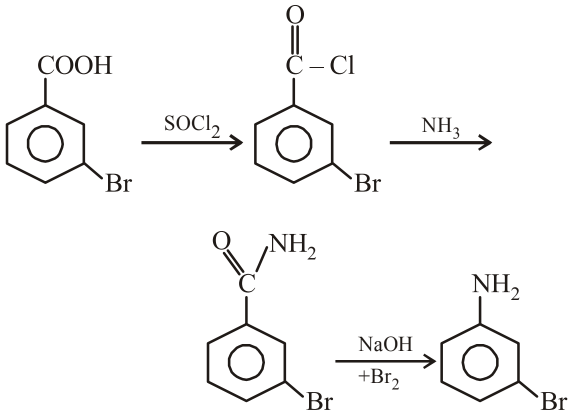
(3) $CH_3CH_2COOCH_3$

(i) alkaline hydrolysis

(4) $CH_3CHOH-CH_3$

(iv) with Lucas reagent cloudiness appears after 5 minutes

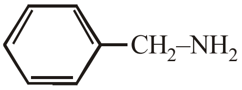
8. **(c)**



9. **(a)** When nitro compound is reduced with a neutral reducing agent (Zn dust + NH_4Cl) the corresponding hydroxyl amine is formed

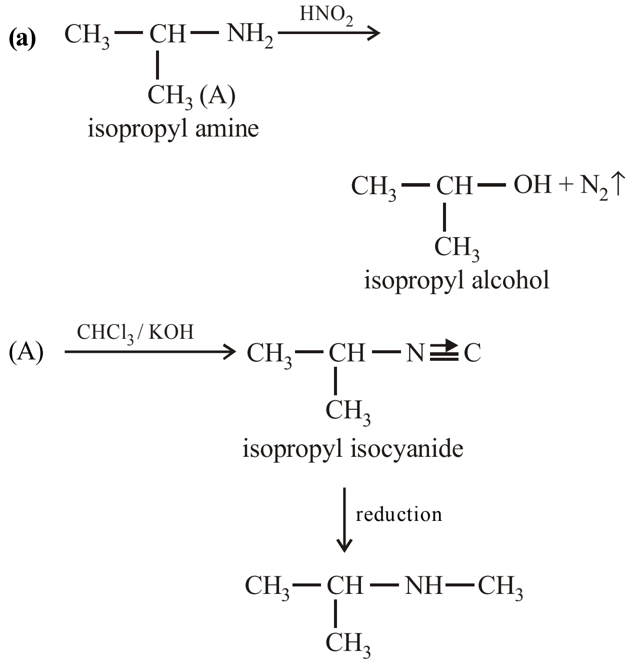
$$C_6H_5NO_2+4[H]\xrightarrow{\text{Zn dust}+NH_4Cl}\underset{\text{Phenyl hydroxyl amine}}{C_6H_5NHOH}$$

10. **(b)**



CH_2–NH_2 compound is most basic due to localized lone pair of electron on nitrogen atom while other compounds have delocalized lone pair of electron.

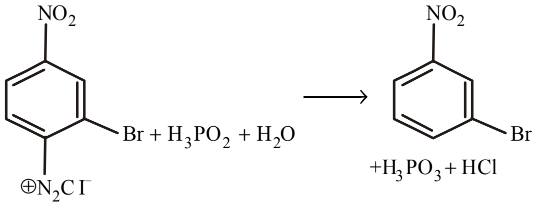
11. **(a)**



$$\underset{\substack{\text{isopropyl amine}}}{CH_3-\underset{\substack{|\\CH_3\ (A)}}{CH}-NH_2}\xrightarrow{HNO_2}\underset{\text{isopropyl alcohol}}{CH_3-\underset{\substack{|\\CH_3}}{CH}-OH}+N_2\uparrow$$

$$(A)\xrightarrow{CHCl_3/KOH}\underset{\text{isopropyl isocyanide}}{CH_3-\underset{\substack{|\\CH_3}}{CH}-N\rightleftarrows C}\xrightarrow{\text{reduction}}\underset{\text{Isopropyl methyl amine}}{CH_3-\underset{\substack{|\\CH_3}}{CH}-NH-CH_3}$$

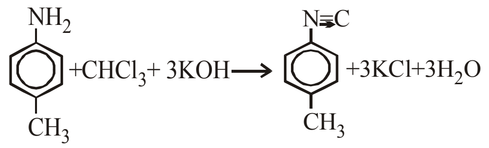
12. **(b)**



13. **(d)** Amino acids contain – NH_2 and – COOH groups

14. **(a)** $C_2H_5NH_2+CHCl_3+3KOH\to C_2H_5N\equiv C+3KCl+3HCl$
Ethyl isocyanide

15. **(c)**



16. **(b)** More is the no. of + I groups attached to N atom greater is the basic character.

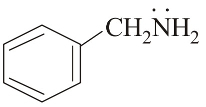
17. **(d)** $CH_3CH_2N\leftrightarrows C+H_2O\xrightarrow{H^+}CH_3CH_2NH_2+HCOOH$

18. **(d)** Lone pair of electrons present on the nitrogen of benzyl amine is not involved in resonance.

19. **(b)** Wurtz reaction is for the preparation of hydrocarbons from alkyl halide

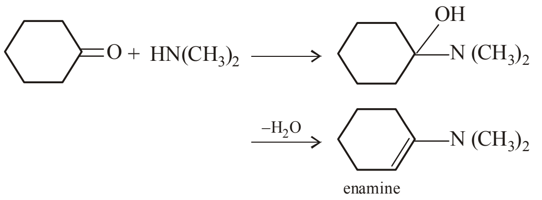
$$RX+2Na+XR\longrightarrow R-R+2NaX$$

20. **(d)** Benzylamine

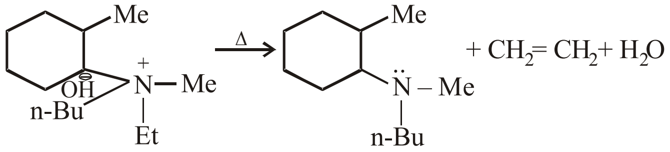


is most basic. In others the basic character is suppressed due to resonance

21. **(c)**



22. **(d)** **Hofmann's rule :** When theoretically more than one type of alkenes are possible, the alkene containing least alkylated double bond is formed. Hence



23. (d) Aromatic amines are less basic than aliphatic amines. Among aliphatic amines the order of basicity is 2° > 1° > 3°. The electron density is decreased in 3° amine due to crowding of alkyl group over N atom which makes the approach and bonding by a proton relatively difficult. Therefore the basicity decreases. Further Phenyl group show – I effect, thus decreases the electron density on nitrogen atom and hence the basicity.

∴ dimethylamine (2° aliphatic amine) is strongest base among given choices.

∴ The correct order of basic strength is Dimethylamine > Methyl amine > Trimethyl amine > Aniline.

24. (a) This is carbylamine reaction.

$$CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5NC + 3KCl + 3H_2O$$

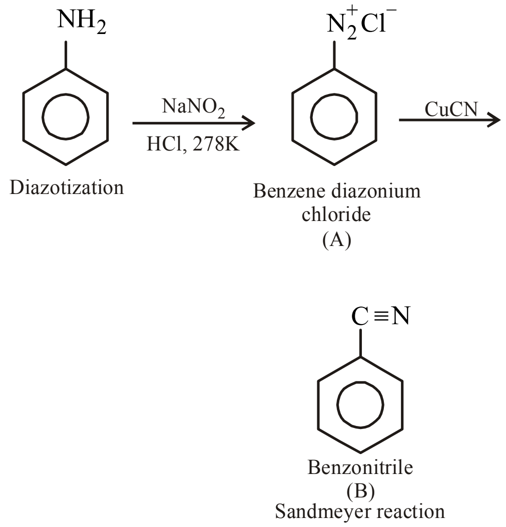
25. (c) Primary aromatic amines react with nitrous acid to yield arene diazonium salts.

$$\underset{1^\circ \text{ Aromatic amine}}{ArNH_2} + NaNO_2 + 2HX \xrightarrow{\text{cold}} \underset{\text{Arene diazonium salt}}{Ar{-}N{=}N^+X^-} + NaX + 2H_2O$$

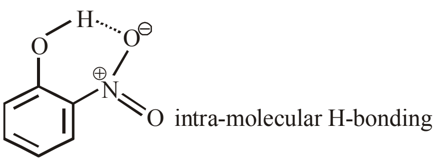
The diazonium group can be replaced by fluorine by treating the diazonium salt with fluoroboric acid (HBF_4). The precipitated diazonium fluoroborate is isolated, dried and heated until decomposition occurs to yield the aryl fluoride. This reaction is known as **Balz-Schiemann reaction.**

$$Ar{-}N_2^+X^- \xrightarrow{HBF_4} Ar{-}N_2^+BF_4^-\downarrow \xrightarrow{\text{heat}} Ar{-}F + BF_3 + N_2$$

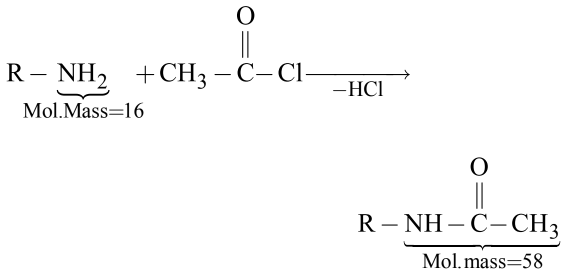
26. (a)



27. (b) *o*-nitrophenol shows intramolecular H-bonding and forms chelate. Compounds involved in chelation become non-polar. Consequently such compounds are soluble in non-polar solvents like ether, benzene etc. and are only sparingly soluble in water whereas meta and para isomers are more soluble in water & less soluble in non-polar solvents.



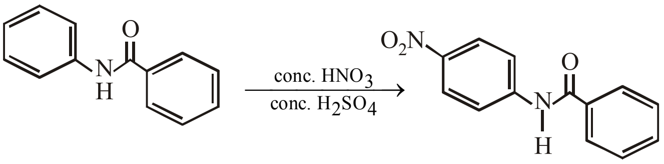
28. (b)



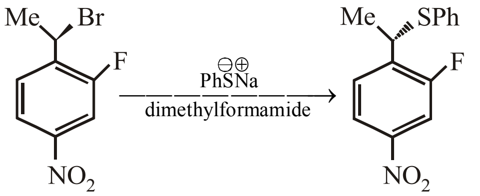
$$\underbrace{R-NH_2}_{\text{Mol.Mass}=16} + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow[-HCl]{} \underbrace{R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}_{\text{Mol.mass}=58}$$

Now since the molecular mass increases by 42 unit as a result of the reaction of one mole of CH_3COCl with one-NH_2 group and the given increase in mass is 210. Hence the number of $-NH_2$ groups is = 210/42 = 5.

29. (b) The benzene ring which is directly attached with nitrogen atom of acidamide group is more activated than the other, so nitration will take place at para position of this activated ring.



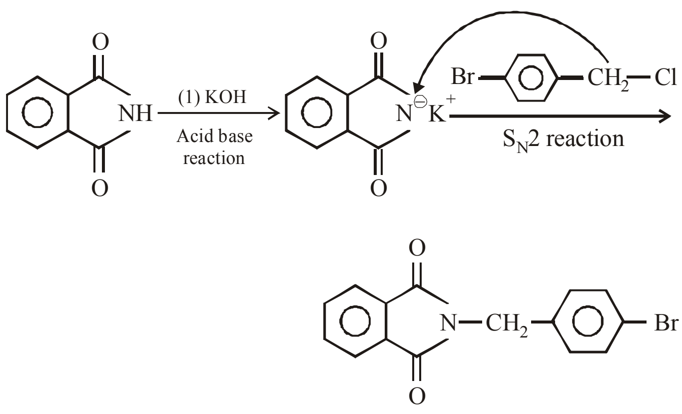
30. (a)



S_N2 Mechanism ∴ Inversion takes place

31. (c) Only primary aromatic amines undergo diazotisation followed by coupling.

32. (a)



Due to resonance C – Br bond shows partial double bond character. Therefore nucleophile does not replace Br in above reaction.

EXERCISE 4

1. **(c)** $$\underset{X}{CH_3CN + 2H \rightarrow CH_3CH = NH} \xrightarrow{H_2O,\ boil} \underset{Y}{CH_3CHO}$$

Note that cyanides are reduced only by 2H atoms, so reduction stops at aldimine stage which on hydrolysis with water gives aldehyde; it is an example of Stephen's reaction

2. **(b)**

3. **(a)** Nitrobenzene is reduced in the following manner through various intermediates to form aniline as the final product.

$$\underset{\text{nitrobenzene}}{C_6H_5NO_2} \xrightarrow{2[H]} \underset{\text{nitrosobenzene}}{C_6H_5NO} \xrightarrow{2[H]}$$

$$\underset{\text{phenylhydroxylamine}}{C_6H_5NHOH} \xrightarrow{2[H]} \underset{\text{aniline}}{C_6H_5NH_2}$$

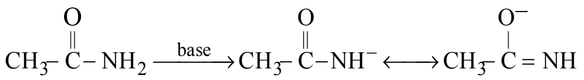
4. **(c)**

5. **(a)** Although benzene does not undergo nucleophilic substitution, nitrobenzene undergoes such reaction due to the presence of electron withdrawing – NO_2 group which makes *o* - and *p* - carbon electron deficient and hence liable to be attacked by OH^- (a nucleophile)

6. **(d)** $$CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow[H_2O]{H^+} CH_3COOH \xrightarrow{NH_3}$$

$$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O$$

7. **(a)** Acetamide is basic due to the presence of lone pair of electrons of N; it is also acidic because its conjugate base shows resonance.

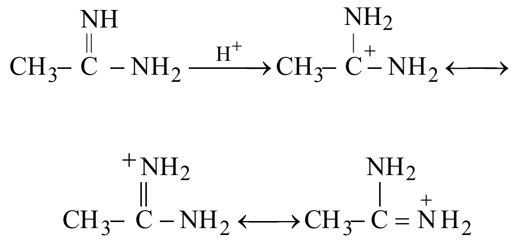


$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{base} CH_3-\overset{O}{\overset{\|}{C}}-NH^- \longleftrightarrow CH_3-\overset{O^-}{\overset{|}{C}}=NH$$

(more stable due to –ve charge on O)

Benzonitrile ($C_6H_5C{\equiv}N$) acts as an electrophile (Lewis acid) due to electron deficiency of C of CN as well as nucleophile (Lewis base) in nature due to presence of lone pair electrons on N; hence it is neutral Triethylamine and phenol are basic and acidic in nature respectively.

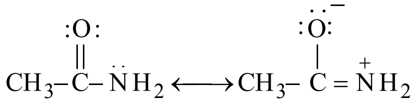
8. **(b)** Guanidine is most basic because its conjugate acid is stabilized by two equivalent resonance structures,.



$$CH_3-\overset{NH}{\overset{\|}{C}}-NH_2 \xrightarrow{H^+} CH_3-\overset{NH_2}{\overset{|}{C^+}}-NH_2 \longleftrightarrow$$

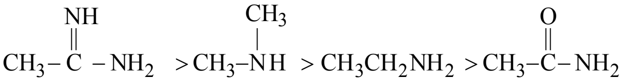
$$CH_3-\overset{^+NH_2}{\overset{\|}{C}}-NH_2 \longleftrightarrow CH_3-\overset{NH_2}{\overset{|}{C}}=\overset{+}{N}H_2$$

Further 2° amines are more basic than 1°, while amides are least basic due to delocalisation of the lone pair of electrons on N



$$CH_3-\overset{:O:}{\overset{\|}{C}}-\ddot{N}H_2 \longleftrightarrow CH_3-\overset{:\ddot{O}:^-}{\overset{|}{C}}=\overset{+}{N}H_2$$

Thus the correct order of basicities is



$$CH_3-\overset{NH}{\overset{\|}{C}}-NH_2 > CH_3-\overset{CH_3}{\overset{|}{N}}H > CH_3CH_2NH_2 > CH_3-\overset{O}{\overset{\|}{C}}-NH_2$$

9. **(a)**

10. **(d)**

$$CH_3C\equiv CH + AgNO_3 \xrightarrow{C_2H_5OH} CH_3C\equiv CAg\downarrow + HNO_3$$

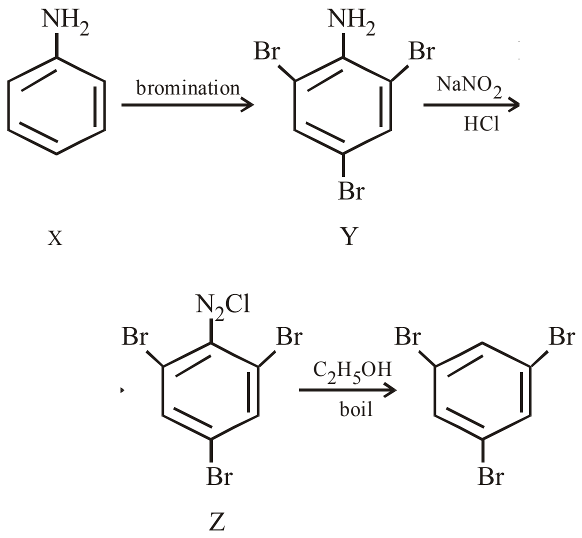
$$CH_3CHO + 2Cu(OH)_2 \rightarrow CH_3COOH + Cu_2O + 2H_2O$$

$$\underset{\text{Insoluble in } H_2O \text{ due to no H–bond}}{C_6H_5COOC_2H_5} + NaOH \xrightarrow{heat} \underset{(soluble)}{C_6H_5COONa} + \underset{(soluble)}{C_2H_5OH}$$

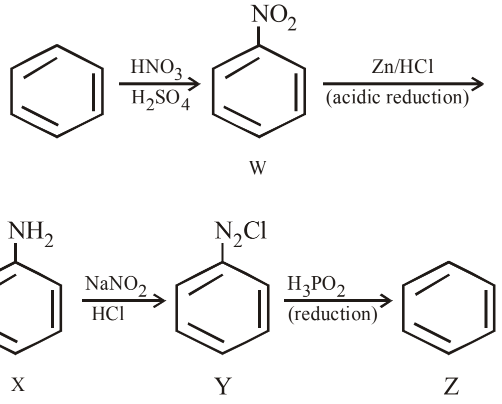
$$C_6H_5NH_2 + HCl \rightarrow \underset{(soluble)}{C_6H_5N^+H_3Cl^-} \xrightarrow{NaOH} \underset{(Insoluble)}{C_6H_5NH_2\downarrow}$$

11. **(c)**

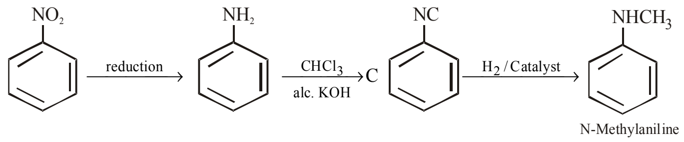
12. **(d)** Proceed backward ; tribromobenzene is produced by boiling compound Z with C_2H_5OH ; Z in turn is obtained by diazotisation of Y, so Y and Z should have $-NH_2$ and $-N_2Cl$ groups respectively, in addition to three Br atoms. Hence X should be $C_6H_5NH_2$



13. **(b)**



14. **(d)**

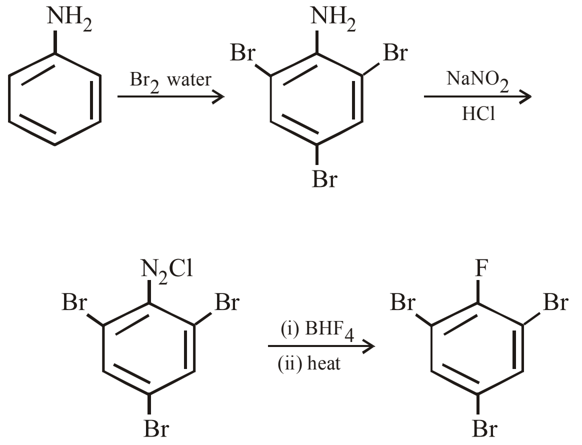


15. **(b)**

$$\underset{(C_7H_7NO)}{A} \xrightarrow{Br_2 / KOH} \underset{(amine)}{B} \xrightarrow[\text{ii) coupling with phenol}]{\text{i) diazotisation}} \text{Azo dye}$$

Given reactions indicate B as 1° aromatic amine, and A as an aromatic amide, $C_6H_5CONH_2$

16. **(c)**



17. **(c)** **18.** **(a)** **19.** **(c)**

20. **(d)** Tertiary amines have low boiling points due to absence of hydrogen bonding among isomeric amines the order is

$1° > 2° > 3°$

21. **(c)** Aliphatic amines are more basic than aromatic amines. Resonance decreases the basic character due to delocalisation of shared pair of electrons on nitrogen within benzene nucleus

22. **(c)** Enamine (ene for carbon-carbon double bond and amine for amine group). $>C=C-N<$

23. **(b)** (a) $C_6H_5COOC_2H_5 + (CH_3)_2NH \rightarrow$

$$C_6H_5CON(CH_3)_2 + C_2H_5OH$$

(b) $C_6H_5CONH_2 + CH_3MgI \rightarrow C_6H_5CONHMgI$

$$+ CH_4$$

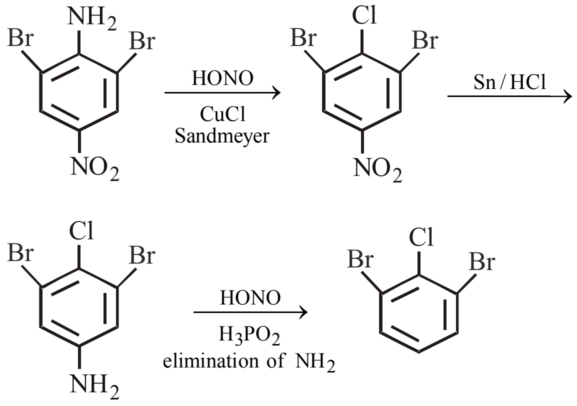
(c) $C_6H_5COCl + (CH_3)_2NH \rightarrow$

$$C_6H_5CON(CH_3)_2 + HCl$$

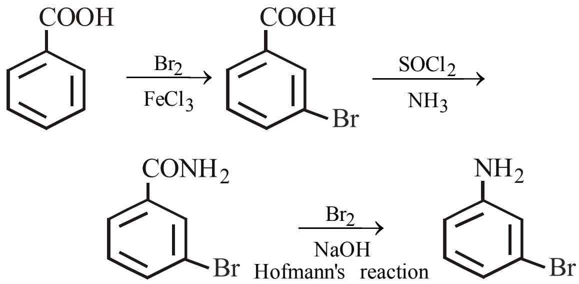
(d) $C_6H_5CO.O.COC_6H_5 + (CH_3)_2NH \rightarrow$

$$C_6H_5CON(CH_3)_2 + C_6H_5COOH$$

24 **(c)**



25. **(b)**

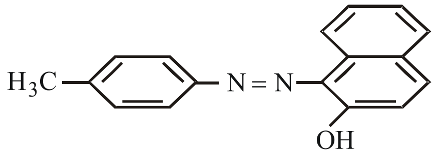


26. **(a)** The electrons withdrawing groups decrease the basic character and increase the acid character by inductive effect and resonance.

27. **(c)** The meta directing groups develop positive charge at o, p- positions and ortho-para directing groups develop negative charge at o, p positions – CHO is meta directing and $-NH_2$ is ortho-para directing.

28. **(c)**

29. **(c)** The first compound will give azo dye

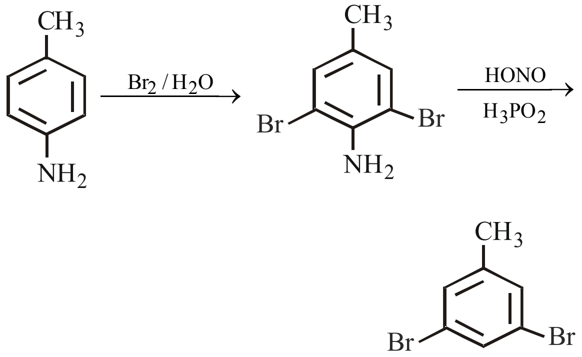


30. **(c)** $R-C\equiv N \xrightarrow[\text{Or Raney Ni}]{LiAlH_4 / ether} R-CH_2NH_2$

31. **(a)** See Gabriel's phthalimide synthesis for p-amines

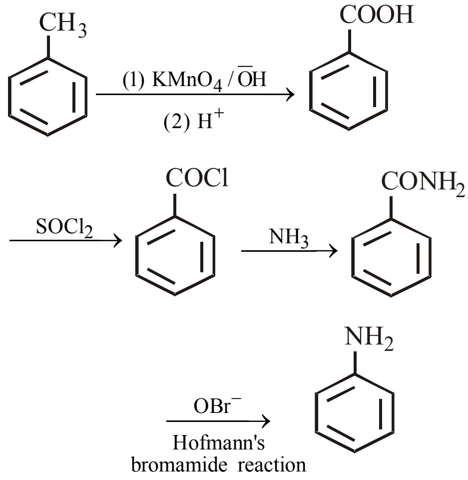
32. **(a)** 1° nitro alkanes give aldehyde and 2 ° nitro alkanes give Ketones.

33. **(a)**



34. **(b)** Aliphatic amines are stronger base than aromatic amines. Further the order $2° > 1° > 3° > NH_3$

35. **(d)**

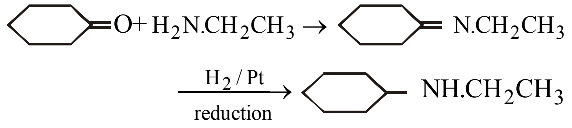


36. **(d)** $C_6H_5NH_2 + CS_2 \rightarrow C_6H_5NH.CS.SH \xrightarrow{HgCl_2}$

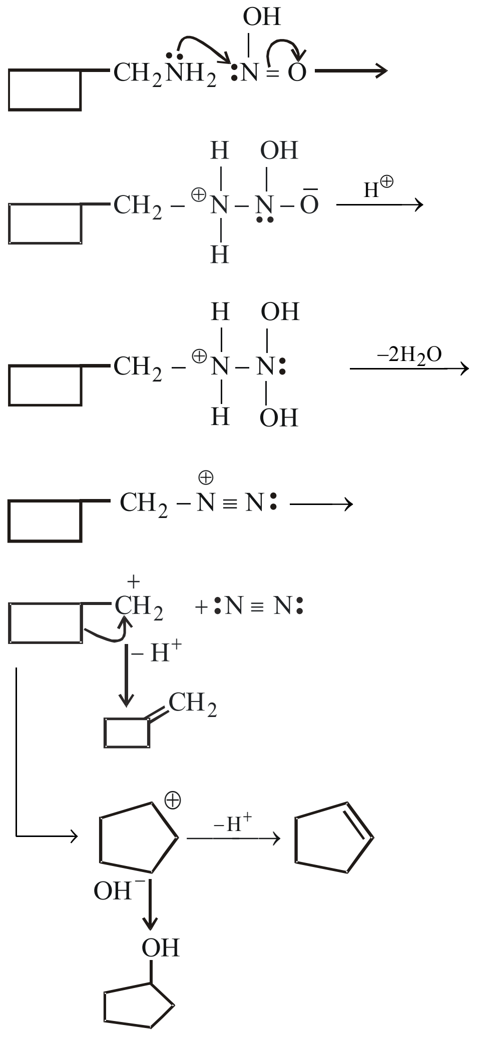
$C_6H_5N = C = S + HgS + 2HCl$

The reaction is called mustard oil reaction.

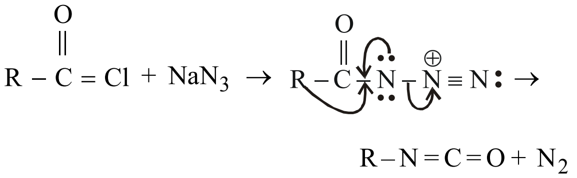
37. **(b)**



38. **(d)**

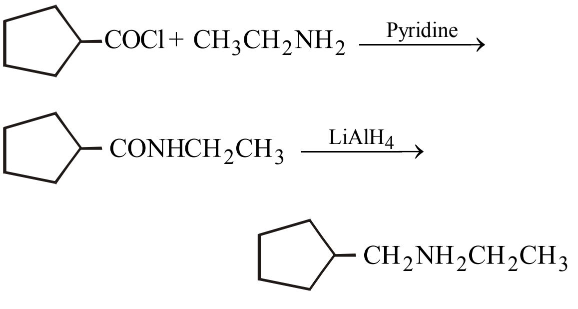


39. **(c)**



40. **(c)** Amides are hydrolysed to give acids and NH_3 or amines

41. **(c)**



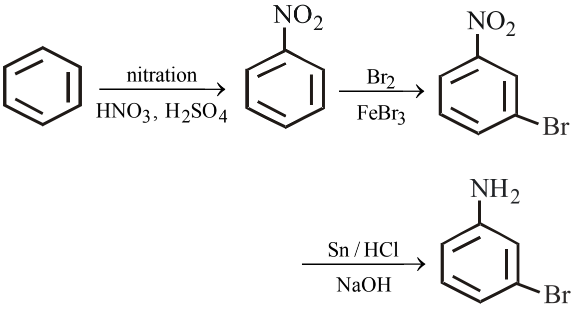
N-ethyl cyclopentyl methyl amine

42. **(c)** **43.** **(c)**

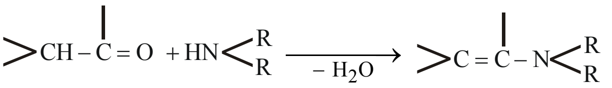
44. **(a)** Nitriles having α-hydrogen atom form alkyl derivatives with RBr in presence of $NaNH_2 / NH_3$.

45. **(b)**

46. **(b)**

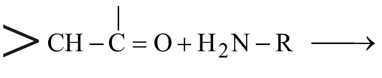


47. **(d)** Carbonyl compounds containing at least one α-hydrogen atom react with a secondary amine to give enamine

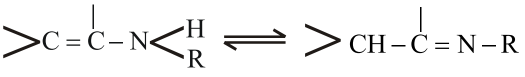


$$>CH-\overset{|}{C}=O + HN\begin{matrix}R\\R\end{matrix} \xrightarrow[-H_2O]{} >C=\overset{|}{C}-N\begin{matrix}R\\R\end{matrix}$$

Primary amines also form enamines



$$>CH-\overset{|}{C}=O+H_2N-R \longrightarrow$$



$$>C=\overset{|}{C}-N\begin{matrix}H\\R\end{matrix} \rightleftharpoons >CH-\overset{|}{C}=N-R$$

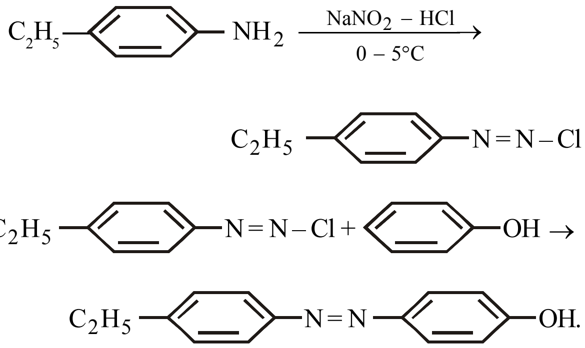
enamine imine

In Second case enamine – amine tautomerism is possible and equilibrium lies completely on the imine side

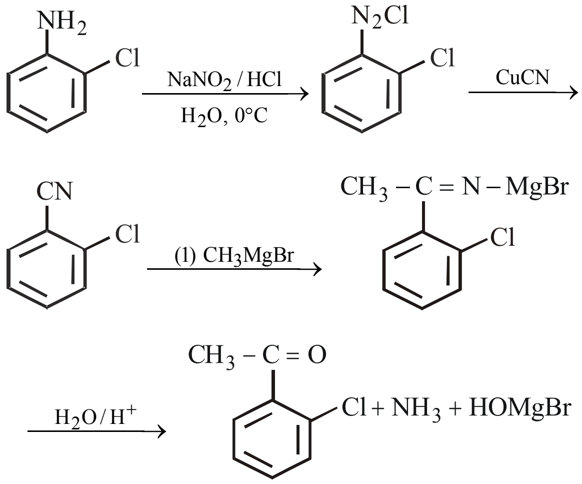
48. **(b)** Basic character of amines is

$2° > 1° > 3° > NH_3$

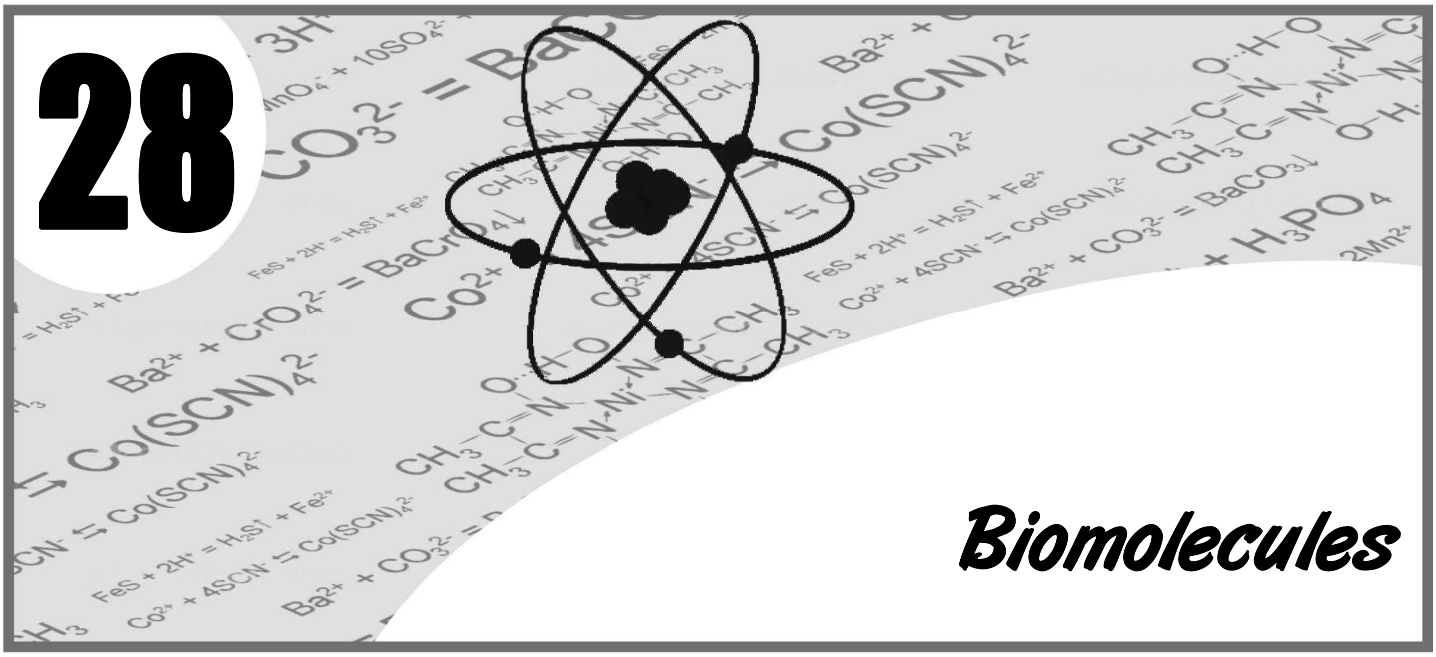
49. **(b)**


C2H5
NH2
NaNO2 – HCl
0 – 5°C
C2H5
N=N–Cl
C2H5
N=N–Cl +
OH →
C2H5
N=N
OH.

50. **(a)**


NH2
Cl
NaNO2 / HCl
H2O, 0°C
N2Cl
Cl
CuCN
CN
Cl
(1) CH3MgBr
CH3 – C = N – MgBr
Cl
H2O / H+
CH3 – C = O
Cl + NH3 + HOMgBr

❑❑❑



28

Biomolecules

CARBOHYDRATES:

Polyhydroxy aldehydes (Aldoses) or Ketones (Ketoses) or compounds which on hydrolysis give these and contain atleast one asymmetric carbon atom are known as carbohydrates. They are also called saccharides (Latin Saccharum = sugar) due to sweet taste of simpler members, the sugars.

The carbonyl group does not occur in the free form but forms intramolecular hemiacetal or acetal linkages with the - OH groups.

Classification: Carbohydrates are of three types.

Monosaccharides: These cannot be hydrolysed to simpler molecules and further subdivided into tetroses, pentoses or hexoses depending upon the number of carbon atoms.

Aldotetroses: Erythrose, Threose $CH_2OH.(CHOH)_2\ CHO$

Aldopentoses: Arabinose, xylose, Ribose, lyxose $CH_2OH(CH\ OH)_3\ CHO$

Aldohexoses: Glucose, Mannose, Allose, Galactose etc. $CH_2OH(CH\ OH)_4\ CHO$

Ketotetroses: Erythrulose $CH_2OH.CO.CHOH.CH_2OH$

Ketopentoses: Ribulose, xylulose $CH_2OH.CO(CHOH)_2\ CH_2OH$

Ketohexoses: Fructose, sorbose etc

$$CH_2OH.CO(CHOH)_3.CH_2OH$$

OLIGOSACCHARIDES :(Greek oligos, few).

On hydrolysis they generally give two to nine monosaccharides (same or different) and further classified as **Disaccharides** eg. sucrose, maltose, lactose etc. $C_{12}H_{22}O_{11}$ give two mono saccharides

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{D(+) glucose}}{C_6H_{12}O_6} + \underset{\text{D(–) Fructose}}{C_6H_{12}O_6}$$

- The bond formed between two monosaccharides is called a **glycosidic** bond and normally it is (1, 4) bond.
- Sucrose is most abundant in plants and known as cane sugar or table sugar.
- **Invert - sugar:** Equimolar mixture of glucose and fructose obtained by hydrolysis of sucrose.

Trisaccharides: Raffinose ($C_{18}H_{32}O_{16}$)

$$C_{18}H_{32}O_{16} + 2H_2O \xrightarrow{H^+} \text{Glucose + Fructose + Galactose}$$

Tetrasaccharides: Stachyose $C_{24}H_{42}O_{21}$

$$C_{24}H_{42}O_{21} + 3H_2O \xrightarrow{H^+} \text{Glucose + Fructose + 2 Galactose}$$

POLYSACCHARIDES:

These are polymers of monosaccharides. Examples are

Starch, cellulose, glycogen, inulin, pectin etc.

(i) **Starch** $(C_6H_{10}O_5)_n$ is a polymer of α - glucose and major reserve food in plants, turns blue with iodine. It is a mixture of two components (i) **amylose** (20%), an unbranched polymer water soluble (ii) **amylopectin** (80%), a branched polymer water insoluble. Sources of starch are potatoes, wheat; rice, maize, bananas etc.

(ii) **Cellulose** $(C_6H_{10}O_5)_n$. It is the most abundant and structural polysaccharide of plants. It is important food sources of some animals. It is polymer of D(+) β– glucose.

- The chief sources of cellulose are wood (contains 50% cellulose rest being lignin, resins etc.) and cotton (contains 90% cellulose rest being fats and waxes).

Useful materials obtained from cellulose.

- ***Mercerized cotton:*** Cellulose treated with conc. sodium hydroxide solution acquire silky lustre.
- ***Gun cotton or cordite:*** It is completely nitrated cellulose (cellulose nitrate), highly explosive in nature and used in the manufacture of smoke less gun powder **blasting gelatin**.

- ***Pyroxylin*** - It is partially nitrated cellulose. When dissolved in ether and alcohol it forms a transparent film called **collodion** which is used as covering for cuts and skin abrasions, manufacture of cellulose paints and lacquers.
- ***Cellulose acetate:*** It is used for making **Acetate Rayon** and motion picture films.
- ***Cellulose Xanthate:*** It is obtained by treating cellulose with sodium hydroxide and carbon disulphide and is the basic material for VISCOSE rayon.
- ***Celluloid*** - It is obtained by warming a mixture of camphor and pyroxylin in alcohol. It is used for making toys and photographic films.
- ***Cellophane*** - Cellulose xanthate film softened with glycerol.

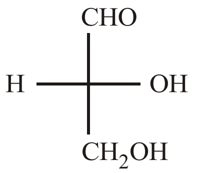
Homo polysaccharides - They give one kind of monosaccharides on hydrolysis e.g. starch, cellulose.

Hetero polysaccharides - They give two or more than two kind of monosaccharides e.g. Insulin.

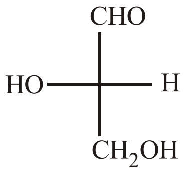
Reducing carbohydrates - Carbohydrates reducing Fehling reagent or Tollen'.s reagent are termed reducing carbohydrates. Examples - All monosaccharides and most of the disaccharides (except sucrose).

Sugars and non sugars - The monosaccharides and oligosaccharides having sweet taste are collectively known as sugars. Polysaccharides, insoluble in water are non sugars

D and L Configurations - Glyceraldehyde is optically active and has the following Fischer projections



D (+) Glyceraldehyde :



L (–) Glyceraldehyde

Sugars having the same configuration as D – glyceraldehyde at the most distant asymmetric carbon atom from the carbonyl group are designated as D - sugars and opposite to it L - sugars.

All naturally occurring monosaccharides belong to D - series.

Glucose - dextrose, grape sugar, corn sugar, blood sugar $C_6H_{12}O_6$

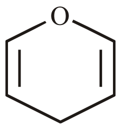
Manufacture - By hydrolysis of starch with hot dil. mineral acids

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \rightarrow \underset{\text{Dextron}}{(C_6H_{10}O_5)_n} H_2O \rightarrow$$

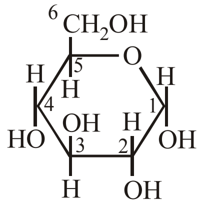
$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \rightarrow \underset{\text{Glu cos e}}{2C_6H_{12}O_6}$$

Structure : Glucose has pyranose structure i.e. ring structure consisting of 5C atoms and 10 hydrogen atoms.

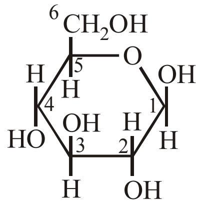
α and β glucose - In intermolecular hemiacetal formation (cyclic structure) CHO is converted into CHOH which can have two configurations shown below



Pyran



α-D-(+) – Glucopyranose



β-D-(+) – Glucopyranose

Glucose having (i) configuration about C_1 is the α - glucose and having (ii) configuration about C_1 is β -glucose. The carbon C_1 is known as **anomeric** carbon and α and β forms as **anomers**. Both the forms are optically active, α -D- glucose has specific rotation + 111.5° and β -D-glucose has specific rotation + 19.5°.

Mutarotation - When either of the two forms of glucose is dissolved in water there is change in rotation till the equilibrium value of + 52.5°. This is known as mutarotation

$$\underset{+111.5^\circ}{\alpha\text{–D(+)Glucose}} \rightleftharpoons \underset{+52.5^\circ}{\text{Equilibrium Mixture}}$$

$$\rightleftharpoons \underset{+19.5^\circ}{\beta\text{–D–(+)Glucose}}$$

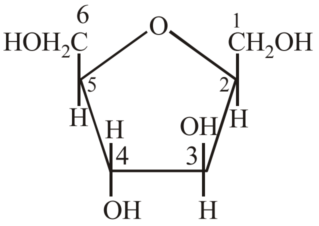
Fructose, Laevulose, fruit sugar $C_6H_{12}O_6$

Manufacture: By hydrolysis of inulin

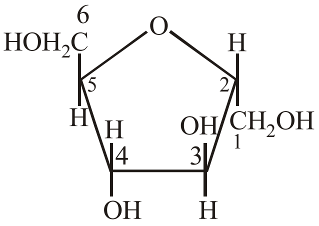
$$\underset{\text{Inulin}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H^+} \underset{\text{Fructose}}{nC_6H_{12}O_6}$$

Structure - Fructose has furanose structure i.e. ring structure consisting of 4C atoms and 1O atom.

α and β Fructose: The two forms have different configuration about C_2



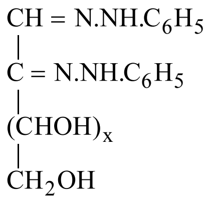
α-D-(–) – Fructofuranose



β-D-(–) – Fructofuranose

Epimers: Monosaccharides differing in configuration at a carbon other than anomeric carbon are called epimers e.g. glucose and galactose differ in configuration at C_4 hence called C_4 epimers

Osazones - Monosaccharides and reducing disaccharides react with excess of phenyl hydrazine to form crystalline substances of the structure

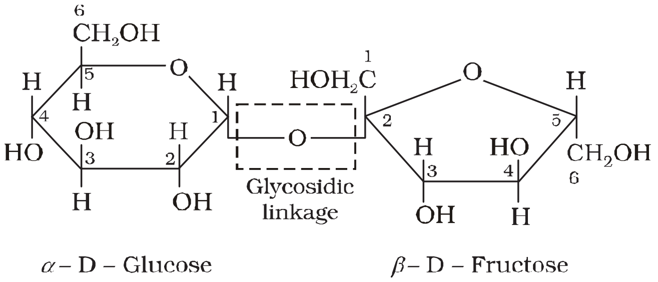


$$\begin{array}{l} CH = N.NH.C_6H_5 \\ | \\ C = N.NH.C_6H_5 \\ | \\ (CHOH)_x \\ | \\ CH_2OH \end{array}$$

Known as osazones. Glucose and Fructose give same osazone

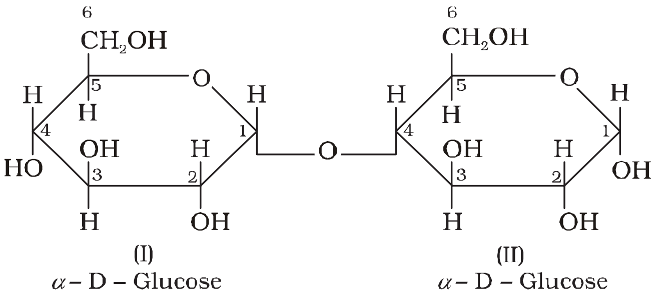
Disaccharides : These on hydrolysis with dil. acids or enzymes yield two molecules of same or different monosaccharides. The latter are joined together by an oxide linkage formed by the loss of water and is called **glycosidic linkage**.

(i) **Sucrose** $C_{12}H_{22}O_{11}$. It is non reducing sugar. It has glycosidic linkage between C1 of α-glucose and C2 of β-frucose. It is dextrorotatory but on hydrolysis give laevorotatary **inert sugar**. Fructose (– 92.4) and glucose (+ 52.5)



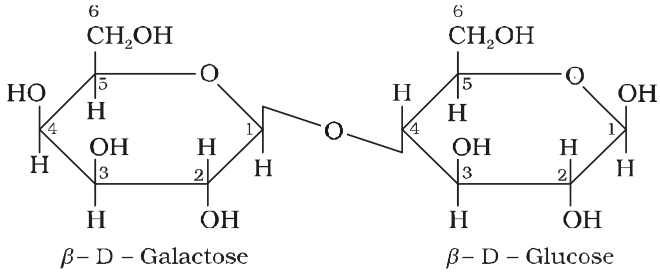
Sucrose

(ii) **Maltose** $C_{12}H_{22}O_{11}$. It is reducing sugar. On hydrolysis it gives two α-D-glocose units in which C1 of one glucose is linked to C4 of another glucose.



Maltose

(iii) **Lactose** $C_{12}H_{22}O_{11}$. It commonly known as milk sugar due to presence in milk. The linkage is between C1 of β-D-galactase and C4 of β-D-glucose. It is also reducing sugar.

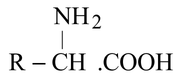


Lactose

AMINO ACIDS AND PROTEINS

Amino Acids - The compounds containing amino group ($-NH_2$) and carboxylic group (–COOH) are called amino acids.

General Formula



$$R-\underset{}{\overset{NH_2}{\overset{|}{C}H}}\ .COOH$$

α – Amino Acid

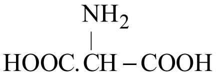
R = H, alkyl or aryl group. Except glycine ($H_2N.CH_2COOH$) others are optically active in nature.

Classification

(i) α, β, γ, δ ***amino acids*** depending upon the position of - NH_2 w.r.t. – COOH group.

(ii) ***Neutral*** - Having one $-NH_2$ and one –COOH e.g. $NH_2.CH_2.COOH$ glycine

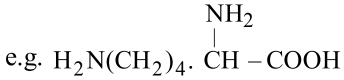
(iii) ***Acidic*** - Having one $-NH_2$ and two –COOH e.g.



$$HOOC.\overset{NH_2}{\overset{|}{C}H}-COOH$$

Aspartic acid.

(iv) ***Basic*** - Having two or more $-NH_2$ and one COOH



$$\text{e.g. } H_2N(CH_2)_4.\overset{NH_2}{\overset{|}{C}H}-COOH$$

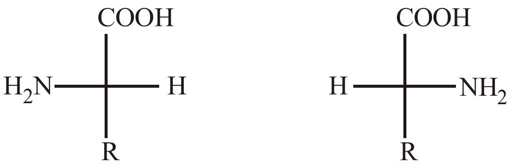
Lysine

Essential and non essential amino acids - Human body can synthesise ten amino acids called non essential amino acids. The remaining ten amino acids required for protein synthesis are called essential amino acids. They are

1. Phenylalanine	2. Histidine
3. Tryptophane	4. Valine
5. Methionine	6. Theonine
7. Arginine	8. Leucine
9. Isoleucine	10.Lysine

Nomenclature - They are known by their common names and abbreviated by first three letter of their common names eg. glycine is gly and alanine is ala.

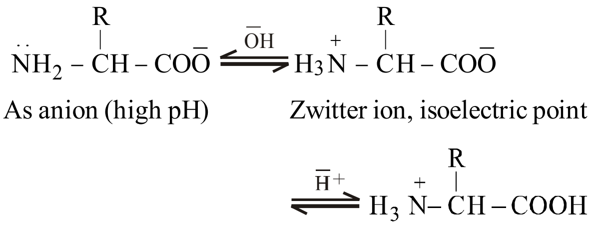
Configuration of α -amino acids



L - Amino acid (NH₂ on L.H.S.)
D - Amino acid (NH₂ on R.H.S.)

Naturally occuring α - amino acids are L - amino acids. D - Amino acids occur in some antibiotics and bacterial cell walls.

Structure :

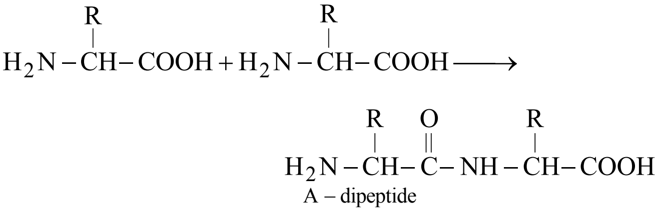


$$\ddot{N}H_2-\overset{R}{\overset{|}{C}H}-CO\bar{O}\ \underset{}{\overset{\bar{O}H}{\rightleftharpoons}}\ H_3\overset{+}{N}-\overset{R}{\overset{|}{C}H}-CO\bar{O}\ \overset{H^+}{\rightleftharpoons}\ H_3\overset{+}{N}-\overset{R}{\overset{|}{C}H}-COOH$$

As anion (high pH)
Zwitter ion, isoelectric point

As cation (low pH)

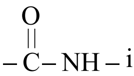
Peptides: Peptides are condensation products of two or more amino acids



$$H_2N-\overset{R}{\overset{|}{C}H}-COOH+H_2N-\overset{R}{\overset{|}{C}H}-COOH\longrightarrow$$

$$H_2N-\overset{R}{\overset{|}{C}H}-\overset{O}{\overset{||}{C}}-NH-\overset{R}{\overset{|}{C}H}-COOH$$

A – dipeptide



$$-\overset{O}{\overset{||}{C}}-NH-$$ is known as peptide linkage and C–N a peptide bond

Polypeptides - Condensation products of many amino acids.

Proteins - They are linear polymers of α - amino acid (Berzelius 1830)

Structure of Proteins

(i) ***Primary structure*** - It simply reveals the sequence of amino acids.

(ii) ***Secondary structure*** - α - helix structure maintained by hydrogen bonds or β - pleated sheet structure when size of R groups is small.

(iii) ***Tertiary structure*** - The folding and super imposition of polypeptide chains forms a compact globular shape, termed as tertiary structure. It is stabilised by covalent, ionic, hydrogen and disulphide bridge.

(iv) ***Quaternary structure-*** The precise arrangement constitutes the **quaternary** structure.

Classification on the basis of hydrolysis products

(i) ***Simple proteins***- Which yield only α - amino acids upon hydrolysis.

(ii) ***Conjugated proteins*** - Which yields α - amino acids and non protein called prosthetic group. (Gr prosthesis, an addition).

Protein	Prosthetic group
Nucleoproteins	Nucleic acid
Phospho proteins	Phosphoric acid
Glyco proteins	Carbohydrates
Metallo proteins	Metals
Chromo proteins	Pigment
Lipo proteins	Lipids

(iii) ***Derived proteins*** - They are obtained by partial hydrolysis of simple or conjugated proteins

Proteins $\rightarrow$ Proteoses $\rightarrow$ Peptones $\rightarrow$ Polypeptides

Classification according to functions

(i) ***Structural proteins :*** Fibrous proteins

(ii) ***Enzymes :*** Serve as catalyst pepsin, trypsin etc.

(iii) ***Harmones :*** Insulin

(iv) ***Contractile Proteins :*** Found in muscles eg myosin, actin.

(v) ***Anti bodies :*** Gamma globulins present in blood.

(vi) ***Blood protein :*** Albumins, haemoglobin and fibrinogen.

Denaturation of protein - The process that changes the three dimensional structure of native protein. It can be caused by change in pH, addition of electrolyte, heating or addition of solvent like water, alcohol or acetone.

Tests

(i) **Biuret** - Protein solution + NaOH + dil. $CuSO_4 \rightarrow$ Pink or violet colour

(ii) **Ninhydrin** - Protein solution + Ninhydrin $\rightarrow$ blue colour

(iii) **Hopkin's cole** - Protein solution + glyoxalic acid + conc. $H_2SO_4 \rightarrow$ Blue - violet

(iv) **Million's** - Protein solution + Millon's reagent $\rightarrow$ Pink colour.

Millon's reagent - Solution of mercuric nitrate and nitrite in nitric acid containing traces of nitrous acid.

(v) **Iodine reaction** - Protein solution + iodine in potassium iodide solution $\rightarrow$ yellow colour

(vi) **Xanthoproteic test** - Protein solution + conc $HNO_3 \rightarrow$ yellow colour $\xrightarrow{NaOH}$ orange colour

ENZYMES

Enzymes - A group of complex proteinoid organic compounds, elaborated by living organisms which catalyse specific organic reactions are called enzymes.

Coenzymes - Non proteinous components required for the activity of certain enzymes are known as coenzymes.

Coenzymes include metal ions like Mn^{2+}, Mg^{2+}, K^+, Na^+, Zn^{++}, Co^{++} etc. hetero cyclic ring systems (pyrrole, purine, pyidine etc), a sugar residue, phosphoric acid residue or vitamins like thiamine, riboflavin, niacin etc.

In such cases the protein part of enzymes is called **apoenzyme**

Endoenzyme - acts in the same cell in which it is synthesised.

Exoenzyme - acts outside the cell in which it is synthesised.

Nomenclature - They are usually named by adding the suffix - ase to the root name of the substrate eg urease, maltase.

Hydrolytic enzymes - Catalyse hydrolysis and are mostly simple proteins.

Oxidative enzymes - catalyse oxidation reduction reaction and are mostly conjugated proteins.

Some Common Enzymes

Name	*Substrate*	*Products*
Urease	Urea	$CO_2 + NH_3$
Maltase	Maltose	Glucose
Invertase	Sucrose	Glucose + Fructose
Amylase	Starch	Maltose
Lipase	Glycerides	Fatty acids + Glycerol
Trypsin	Proteins	Amino acids
Alcohol dehydrogenase	Ethanol	Acetaldehyde
Ascorbic acid oxidase	Ascorbic acid	Dehydro ascorbic acid

Characteristic features of Enzymes -

(i) ***Rate of reaction*** - They increase the rate of reaction upto 10 million times.

(ii) ***Specific nature -*** Urease catalyse the hydrolysis of urea and not methyl urea.

(iii) ***Optimum temperature*** - It is about 20 °C- 40° C.

(iv) ***pH of medium -*** It is about 7 but for Pepsin (1.8-2.2) Trypsin (7.5 - 8.3)

(v) ***Concentration -*** Dilute solutions

(vi) ***Amount*** - Very small amount can accelerate the reaction.

(vii) ***Exergonic reaction*** - Enzyme catalyse the exergonic reactions.

Enzyme inhibitors - The compounds which inhibit the enzyme action. With the help of such compounds the reaction can be controlled.

Mechanism of enzyme action

$$\begin{tikzcd} \text{Enzyme + Substrate} \arrow[r] & \text{[Enzyme substrate]} \arrow[d] \\ & \text{Product + Enzyme} \end{tikzcd}$$

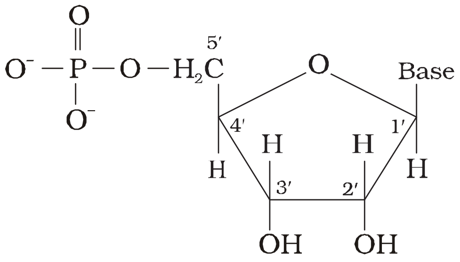
Applications

(i) ***Treatment of diseases*** - The congenital disease phenyl ketonurie caused by phenylalanine - hydroxylase can be cured by diet of low phenylalanine content. Albinism is caused by deficiency of tyrosinase. Enzyme streptokinase is used for blood cloting to prevent heart disease.

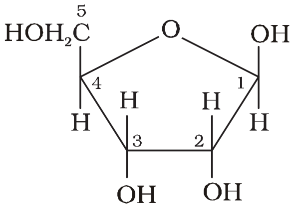
(ii) ***In industry*** - Tanning of leather, fermentation process.

NUCLEIC ACIDS

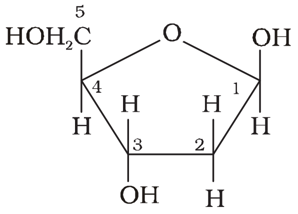
Nucleotides - Nucleotides consist of 5 - carbon sugar (pentose) + nitrogenous base + 1-3 phosphate groups.



Pentose - is either Ribose or deoxy Ribose (not having oxygen at C_2).

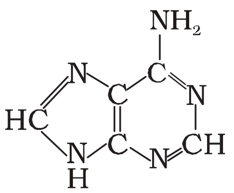


β–D–ribose

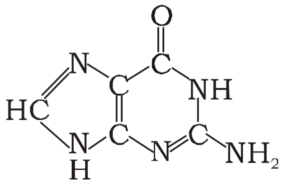


β–D–2–deoxyribose

Nitrogenous base - Derived from purines having two rings in their structure Examples are adenine (A) and Guanine (G).

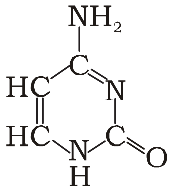


Adenine (A)

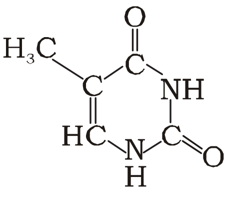


Guanine (G)

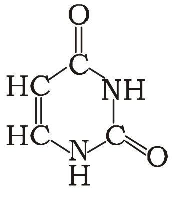
Derived from Pyrimidines having one ring in their structure . Examples
Thymine (T), Uracil(U) and Cytosine (C).



Cytosine (C)



Thymine (T)

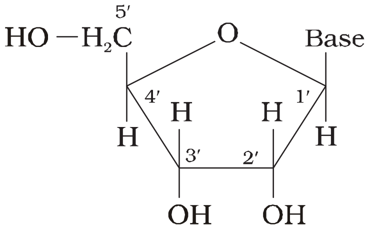


Uracil (U)

Ribonucleotide - Phosphate unit + Ribose + One base unit from AGC or U.

Deoxy Nucleotide - Phosphate unit + Deoxyribose + One base from AGC or T.

Nucleoside - Ribose + one base unit from AGCT or U



Nucleic acid - It is polynucleotide, present in the nucleus of the living cells or bacterial cells having no nucleus and in viruses having no cells.

DNA - Deoxy ribonucleic acid

DNA + $H_2O \rightarrow$ Phosphoric acid + Deoxy ribose + AGCT

RNA - Ribonucleic acid

RNA + $H_2O \rightarrow$ Phosphoric acid + Ribose + AGCU

Structure of DNA - It consists of two polynucleotide chains, each chain forms a right handed helical spiral with ten bases in one turn of the spiral. The two chains coil to double helix and run in opposite direction held together by hydrogen bonding.

DNA exists in five forms A,B,C,D and E.

Wang/ Rich (1979) reported DNA with left handed double helical configuration. It was named as Z - DNA.

Structure of RNA - It is usually a single strand of ribonucleotides and take up right handed helical conformation. Ribonucleotide consists of three different molecules - phosphate, ribose sugar and nitrogenous base. The latter may be purine (adenine or guanine) or pyrimidine (cytosine or uracil). Upto 12,000 nucleotides constitute as RNA.

It can pair with complementary strands of DNA or RNA according to standard base pairing rules - G pairs with C, A pairs with U or T. The paired strands in RNA - RNA or RNA - DNA are anti parallel as in DNA.

Messenger RNA (m-RNA). It is produced in the nucleus and carries information for the synthesis of proteins.

Ribosomal RNA (r - RNA) - Its role yet not known.

Transfer RNA (Soluble or Adoptive RNA) (S.RNA, t - RNA) - It is found in cytoplasm. Its function is to collect amino acids from cytoplasm for protein synthesis.

Function of Nucleic acids

(i) To direct the synthesis of proteins.

(ii) To transfer the genetic information (hereditary characters).

Replication - A molecule of DNA can exactly duplicate of itself. The process is called replication.

Template - It means pattern. In the process of replication of DNA the parent strand serves as template.

Gene - The portion of DNA carrying information about a specific protein is called gene.

Genetic Code - The relation between the amino acid and the nucleotide triplet is called genetic code.

Codons - The nucleotide bases in RNA function in groups of three (triplet) in coding amino acids. These base triplets are called codons.

Mutation - Error in genetic code is called mutation.

LIPIDS :

Lipids (Greek lipos = fat) - The constituents of animals and plants soluble in organic solvents (ether, chloroform, carbon tetra chloride, hexane, benzene etc.) but insoluble in water are called lipids.

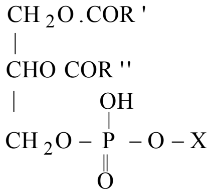
Classification of Lipids

(I) Simple lipids

- **(a)** ***Fats and oils*** on hydrolysis give long chain fatty acids + glycerol
- **(b)** ***Waxes*** - Long chain fatty acids + long chain alcohols. Vegetable and animal oils and fats have similar chemical structure and are triesters of glycerol called glycerides. Simple glycerides contain one type of fatty acids. Mixed glycerides contain two or three types of fatty acids.

(II) Complex lipids -

(i) Phospholipids - Phosphate + glycerol + fatty acids + a nitrogen containing base - General formula



$$\begin{array}{l} CH_2O.COR' \\ | \\ CHO\ COR'' \\ |\qquad\quad OH \\ \qquad\qquad | \\ CH_2O-\underset{\underset{O}{\|}}{P}-O-X \end{array}$$

$$X = \underset{\text{Ethanolamine}}{OHCH_2CH_2NH_2},$$

$$\underset{\text{Choline}}{[OHCH_2CH_2N^+(CH_3)_3]OH}, \underset{\text{L-Serine}}{OHCH_2CHNH_2COOH}$$

When X = chloline the phospholipid is called Lecithine. The latter is found in brain tissues, lever and egg yolk and an important component of nerve tissue membrane.

Function of Phospholipids -

- **(a)** As emulsifying agents since they carry hydrophilic polar groups and hydrophobic non polar groups.
- **(b)** They absorb fatty acids from the intestine and transport to blood cell.

(ii) Glycolipids - They contain one or more simple sugars and are important components of cell membranes and chloroplast membranes.

Common saturated fatty acids - $CH_3-(CH_2)_n\ COOH$

When n = 4 caproic acid; n = 6 caprylic acid; n = 8 capric acid, n = 10 lauric acid n = 12 myristic acid; n = 14 Palmitic acid, n = 16 stearic acid

Common unsaturated acids

$C_{17}H_{33}COOH$ oleic acid; $C_{17}H_{33}COOH$ Linoleic acid

Difference between oils and fats - Oils are liquids at ordinary temperature (below 20ºC) and contain lower fatty acids or unsaturated fatty acids

Fats are solids or semi solids above 20ºC and contain higher saturated fatty acids. Both oils and fats act as “energy reservoirs” for the cells.

Plant Waxes

Carnauba wax $C_{25}H_{51}.COO\ C_{31}H_{63}$ myricyl car otate. Ester of myricyl alcohol $C_{31}H_{63}OH$ and cerotic acid $C_{25}H_{51}.COOH$

They protect the plant from dehydration and invasion of harmful organism

Animal waxes

Beeswax $C_{13}H_{27}COOC_{26}H_{53}$ ceryl myristate, $C_{15}H_{31}COO\ C_{31}H_{63}$ mericyl palmitate, spermaceti wax cetyl palmitate $C_{15}H_{31}COO\ C_{16}H_{33}$

Bee’s wax is used in the manufacture of polishes, candles and water proof coating.

Steroids and Terpenes - Menthol, Camphor are common plant terpenes. Carotenoids and pigments are also terpenes.

Essential oils - The volatile, sweet smelling liquids obtained from flowers, leaves, stems etc. Example terpenes or esters of lower fatty acids eg clove oil, rose oil, Lemon oil.

Drying oils - The oils which are converted into tough, transparent mass when exposed to air by oxidation - polymerisation process are called drying oils.

Examples - Linseed oil, perilla, poppy seed oils. Cotton seed oil and til oil are semidrying oils.

Characterization of fats :

- **(i) Acid value** - The number of milligrams of KOH required to neutralise the free acid present in 1 gm of oil or fat.
- **(ii) Saponification value** - The number of milligrams of KOH required to saponify 1 gm of oil or fat.

  Or

  The number of milligrams of KOH required to neutralise the free acid resulting from the hydrolysis of 1 gm of an oil or fat.
- **(iii) Iodine value** - The number of gms of iodine absorbed by 100 gms of oil or fat.
- **(iv) Reichert - Meissel Value (R/M value)** - The number of cc of N/10 KOH required to neutralise the distillate of 5 gm of hydrolysed fat.

VITAMINS

Vitamins : The organic compounds that can not be produced by the body but are necessary for life, growth and health known as Accessory dietary factors or vitamins. The vitamins are neither structural building units nor supplier of energy. They simply transform energy into action.

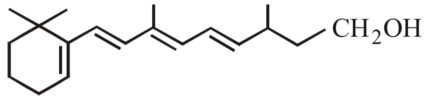
Classification : Vitamins are classified into two groups

- (a) **Water soluble vitamins :** Vitamin B, complex and vitamins C
- (b) **Fat soluble vitamins :** Vitamins A, D, E and K

The important Vitamins are as follows

VITAMIN A :

Its chemical name is Retinol. It has following structure



Sources of vitamins A : Milk, liver, butter, egg yolk, carrot spinach, cod liver and shark lever.

It is essential for growth and for vision. A lack of vitamin A results in, night blindness, loss of weight, hardening of cornea (Xerophthalmia), drying up and scale formation (Keratinization) of epithelial tissues.

VITAMIN B_1 :

Thiamine (aneurin)

Sources : Polished rice, yeast, egg, in all cells as its pyrophosphate ester, certain vegetables.

Its deficiency causes a disease beriberi. It also affects nervous system and the symptoms are weakness, headach loss of appetite.

VITAMIN B_2:

Riboflavin (lactoflavin) :- It is bright yellow powder showing a green fluorescence.

Sources : Yeast, green vegetables, milk, meat, liver, kidney. Its deficiency causes lips, mouth and tongue are usually sore, eyes burn.

VITAMIN B_6 :

(Pyridoxine, Adermin)

Sources : meat, fish, egg, yolk and whole cereals.

It causes nervous disturbances and convulusions.

VITAMIN B_{12} :

It contains the element cobalt.

Sources :- liver, meat, egg and rain water

Lack of B_{12} causes pernicious anaemia

VITAMIN C (ASCORBIC ACID) :

Sources : Fresh fruits, orange, lemons, graps, green vegetables and potatoes. During cooking the large proportion of it is destroyed and process is accelerated by traces of copper.

It helps in proper healing of cuts and abrasions. Its deficiency causes scurvy. Which is characterised by weakness, tendency for bleeding in the muscles.

VITAMIN D :

It consists about ten compounds which are designated as D_1, D_2, D_3 etc. The D_2 is calciferol, found in egg, milk, code liver oil. It is formed by U. V. irradiation of ergosterol.

Vitamin D regulates absorption of calcium and phosphate from intestine and promotes the formation of bones. A lack of vitamin D causes rickets (bones become soft; common in children) and osteomalacia modified form of rickets in adults, during pregnancy.

Vitamin D_3 is cholecalciferol.

VITAMIN E :

The three closely related compounds comprising vitamin E are α, β and γ - tocopherol.

Sources of α,β: wheat germ, seed germ oils, cotton seed oil, green leaves.

Sources of γ :- cotton seed oil.

The most potent is α - tocopherol. Its deficiency causes loss of reproductive sterility. Hence it is also known as "anti- sterility" vitamin.

VITAMIN K :

It is also known as coagulation or anti - haemorrhagic vitamin. It consists in compounds K_1 (phylloquinone) and K_2 (menaquinone - 6 ($K_{2(30)}$), menaquinone - 7 ($K_{2(35)}$) menaquinone - 9 ($K_{2(45)}$) indicating the number of isoprene units.

Sources :- green plants, fish, egg yolk and liver.

HORMONES

The chemical substances secreted by ductless glands such as thyroid, adrenals are called Hormones. They directly pass into the blood stream and regulate the function of other organs of the body. They are also called chemical messengers. The glands which produce hormones are called endocrine glands.

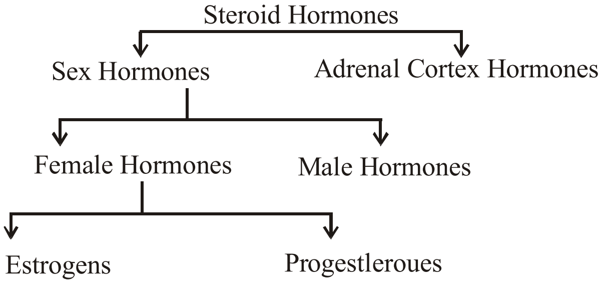
Classification of hormones:

On the basis of their chemical constitution the hormones have been classified into three types

1. Steroid hormones e.g. Cortisone, Androgens
2. Peptide hormones e.g. Oxytocino, Insulin
3. Amino acid hormones e.g. Epinephrine, Thyroxine

Classification of steroid of hormones

The steroid hormones have been divided into the types as follows



Types of Hormones and their functions

1. **Steroid hormones**
   - (i) Estrogens and Progesterones (from ovary/uterus). It maintains pregnancy and develops sex organs of female characteristic
   - (ii) Testosterone (Androgens) (from Testis) : Develops and maintains male sex organs.
   - (iii) Cortisone and related hormones (from Adrenal cortex). It regulates metabolism of fats, proteins, carbohydrates, water mineral acids and employed in the treatment of inflammatory diseases.
2. **Amino acid hormones :**
   - (i) Thyroxine (from thyroid). It stimutes oxidative metabolism and regulates general growth.
   - (ii) Adrenalino (epinephrine) (from Adrenal modulla). It releases glucose from glycogen and fatty acids from fats. It also increases blood pressure and pulse rate.
3. **Peptide Hormones :**
   - (i) Insulin (from pancreas): It Decreases blood glucose level.
   - (ii) Glucagon (from Pancreas): increases blood glucose level
   - (iii) Oxytocino (from Pituitary) It cause contraction of some smooth muscles.
   - (iv) Vasopressin (from Pituitary) : It Inhibits excretion of water from body by way of urine.

Exercise-1 | NCERT Based Questions

Very Short/Short Answer Questions

1. Why are carbohydrates generally optically active?

2. Give a polysaccharide which is stored in the liver of animals as food reserve.

3. Name the protein which stores oxygen in the muscle tissues.

4. How many tripeptides are possible if each alanine, glycine and tyrosine is used only once?

5. Deficiency of which vitamin causes scurvy?

6. Explain the structural difference between α-glucose and β-glucose. What effect does this difference make on utilisation of glucose molecules by the cell?

7. What are the differences between α-helix structure and β-pleated sheet structure?

8. Classify the following as monosaccharides, disaccharides or polysaccharides:

(a) Sucrose
(b) Fructose
(c) Starch
(d) Maltose,
(e) Glucose

9. Why does glucose reacts with Fehling's solution and phenyl hydrazine, but not with $NaHSO_3$?

10. Give the appropriate term to describe the following:

(a) A molecule with a full positive charge and a full negative charge on different parts of the molecules.
(b) A compound formed by condensing together of a number of 2-amino acid molecules.
(c) The change which occurs when a solution of a protein is heated.
(d) The class of proteins to which keratin belongs.

11. In an electric field, towards which electrode an amino acid would migrate at a

(a) pH < isoelectric point
(b) pH > isoelectric point
(c) pH = isoelectric point

12. What is hypervitaminoses and avitaminoses?

13. How can reducing and non-reducing sugars be distinguished? Mention the structural feature characterising reducing sugars.

14. What is essentially the difference between α-glucose and β-glucose? What is meant by pyranose structure of glucose

15. What are the different types of RNA found in cells of organisms? State the functions of each type.

16. After watching a programme on TV about the adverse effects of junk food and soft drinks on the health of schools children, Sonali, a student of Class XII, discussed the issue with the school principal. Principal immediately instructed the canteen contractor to replace the fast food with the fibre and vitamins rich food like sprouts, salad, fruits etc. This decision was welcomed by the parents and the students.

After reading the above passage, answer the following questions.

(a) What values are expressed by Sonali and the Principal of the school?
(b) Give two examples of water-soluble vitamins.

Long Answer Questions

17. How are glucose molecules joined together to make starch, glycogen and cellulose?

Multiple Choice Questions

18. Which of the following is a disaccharide ?

(a) Lactose (b) Starch
(c) Cellulose (d) Fructose

19. Complete hydrolysis of cellulose gives

(a) D-ribose (b) D-glucose
(c) L-glucose (d) D-fructose

20. The function of enzymes in the living system is to

(a) transport oxygen
(b) provide energy
(c) provide immunity
(d) catalyse biochemical reactions

21. Which of the following statements about vitamin B_{12} is incorrect ?

(a) It has a cobalt atom
(b) It also occurs in plants
(c) It is also present in rain water
(d) It is needed for human body in very small amounts

22. The pyrimidine bases present in DNA are

(a) cytosine and thymine (b) cytosine and uracil
(c) cytosine and adenine (d) cytosine and guanine

23. The cell membranes are mainly composed of

(a) fats (b) proteins
(c) phospholipids (d) carbohydrates

24. The commonest disaccharide has the molecular formula
(a) $C_{10}H_{18}O_9$ (b) $C_{10}H_{20}O_{10}$
(c) $C_{18}H_{22}O_{11}$ (d) $C_{12}H_{22}O_{11}$

25. The two forms of D–glucopyranose obtained from the solution of D–glucose are called
(a) Isomers (b) Anomers
(c) Epimers (d) Enantiomers

26. Proteins when heated with conc. HNO_3 give a yellow colour. This is
(a) Oxidizing test (b) Xanthoproteic test
(c) Hoppe's test (d) Acid base test

27. Chemically considering digestion is basically
(a) Anabolism (b) Hydrogenation
(c) Hydrolysis (d) Dehydrogenation.

Exercise-2 | CONCEPTUAL MCQs

1. Which of the following monosaccharides is a pentose?
(a) Glucose (b) Fructose
(c) Arabinose (d) Galactose

2. α-D- Glucose and β- D-glucose differ from each other due to difference in one carbon with respect to its
(a) size of hemiacetal ring (b) number of OH groups
(c) configuration (d) conformation

3. In fructose, the possible optical isomers are
(a) 12 (b) 8 (c) 16 (d) 4

4. Which of the following is the sweetest sugar?
(a) Sucrose (b) Glucose
(c) Fructose (d) Maltose

5. Assuming sweetness of the cane sugar to be 10, the sweetness of glucose is
(a) 15 (b) 1.5
(c) 12.5 (d) 7.5

6. The change in the optical rotation (with time) of freshly prepared solution of sugar is known as
(a) Specific rotation (b) Inversion
(c) Rotatory motion (d) Mutarotation

7. Glucose reacts with acetic anhydride to form
(a) monoacetate (b) tetra-acetate
(c) penta-acetate (d) hexa-acetate

8. Glucose molecule reacts with X number of molecules of phenylhydrazine to yield osazone. The value of X is
(a) three (b) two
(c) one (d) four

9. Which substance chars when heated with conc. H_2SO_4?
(a) Carbohydrate (b) Hydrocarbon
(c) Fat (d) Protein

10. What happens when H_2SO_4 is treated with sugar?
(a) Oxidation (b) Reduction
(c) Dehydration (d) Hydrolysis

11. Molisch test is answered by
(a) sucrose (c) fructose
(c) glucose (d) All carbohydrates

12. Which of the following does not reduce Benedict's solution?
(a) Glucose (b) Fructose
(c) Sucrose (d) Aldehyde

13. Table sugar is a
(a) disaccharide of d-glucose and d-fructose
(b) a monosaccharide
(c) a disaccharide containing two glucose units
(d) D-glucose

14. The common disaccharide has the molecular formula
(a) $C_{12}H_{22}O_{11}$ (b) $C_{10}H_{18}O_9$
(c) $C_{10}H_{20}O_{10}$ (d) $C_{10}H_{32}O_{11}$

15. Hydrolysis of sucrose gives
(a) two molecules of glucose
(b) two molecules of fructose
(c) one molecule each of glucose and fructose
(d) one molecule each of glucose and mannose

16. Hydrolysis of sucrose is called
(a) hydration (b) saponification
(c) esterification (d) inversion

17. The term invert sugar refers to an equimolar mixture of
(a) D-glucose and D-galactose
(b) D-glucose and D-fructose
(c) D-glucose and D-mannose
(d) D-glucose and D-ribose

18. Cellulose is a polymer of
(a) glucose (b) fructose
(c) ribose (d) sucrose

19. Complete hydrolysis of cellulose gives
(a) D-fructose (b) D-ribose
(c) D-glucose (d) L-glucose

20. Which carbohydrate is an essential constituent of plant cells?
(a) Starch (b) Cellulose
(c) Sucrose (d) Vitamins

21. Oleic, stearic and palmitic acids are
(a) nucleic acids (b) amino acids
(c) fatty acids (d) none of these

22. Which of the following is an unsaturated acid?
(a) Linoleic (b) Stearic
(c) Myristic (d) Lauric

23. Drying oil invariably contains
(a) linoleic acid (b) lauric acid
(c) stearic acid (d) butyric acid

24. A triglyceride can have how many different acyl groups?
(a) 3 (b) 2
(c) 1 (d) 4

25. Oils are converted into fats by
(a) hydration (b) decarboxylation
(c) hydrogenation (d) dehydrogenation

26. Saponification of coconut oil yields glycerol and
(a) palmitic acid (b) sodium palmitate
(c) oleic acid (d) stearic acid

27. Iodine value is related to
(a) fats and oils (b) alcohols
(c) esters (d) hydrocarbons

28. The best solvent for removing butter stain from cloth is
(a) $CHCl_3$ (b) C_2H_5OH
(c) $C_2H_5OC_2H_5$ (d) H_2O

29. Lipids are
(a) nucleic acids occurring in plants
(b) proteins occurring in animals
(c) carbohydrates occurring in plants
(d) fats of natural origin

30. Phospholipids are esters of glycerol with
(a) two carboxylic acid residues and one phosphate group
(b) one carboxylic acid residue and two phosphate groups
(c) three phosphate groups
(d) three carboxylic acid residues

31. Which of the following is not an amino acid?
(a) Glycine (b) Adenine
(c) Histidine (d) Benzidine

32. The segment of DNA which acts as the instruction manual for the synthesis of the protein is
(a) nucleoside (b) nucleotide
(c) ribose (d) gene

33. Imino acid among these compounds is
(a) serine (b) proline
(c) tyrosine (d) lysine

34. The structural feature which distinguishes proline from natural α-amino acids?
(a) Proline is optically inactive
(b) Proline contains aromatic group
(c) Proline is a dicarboxylic acid
(d) Proline is a secondary amine

35. Which amino acid is achiral?
(a) alanine (b) valine
(c) proline (d) None of these

36. Which is not a true statement?
(a) α- carbon of α-amino acid is asymmetric
(b) all proteins are found in L-form
(c) human body can synthesize all proteins they need
(d) at pH=7 both amino acids and carboxylic groups exist in the ionised form

37. The acid shows salt-like character in aqueous solution is
(a) acetic acid (b) benzoic acid
(c) formic acid (d) α-aminoacetic acid

38. Amino acids are the building blocks of
(a) carbohydrates (b) vitamins
(c) fats (d) proteins

39. What is the monomer of a polypeptide?
(a) Amino acid (b) Glucose
(c) Nucleoside (d) Nucleotide

40. The main structural feature of proteins is
(a) ester linkage (b) ether linkage
(c) peptide linkage (d) All of these

41. Peptides on hydrolysis give
(a) amines (b) amino acids
(c) ammonia (d) alcohols

42. The number of amino acids found in proteins that a human body can synthesize is
(a) 20 (b) 10
(c) 5 (d) 14

43. Which of the following is not a function of proteins?
(a) Nail formation
(b) Skin formation
(c) Muscle formation
(d) Providing energy for metabolism

44. Insulin, a hormone, chemically is a
(a) fat (b) steroid
(c) protein (d) carbohydrate

45. Which one of the following is not a protein?
(a) Wool (b) Nail
(c) Hair (d) DNA

46. The helical structure of proteins is stabilized by
(a) H-bonding (b) van der Waals forces
(c) ionic bond (d) peptide bond

47. Denaturation of proteins leads to loss of its biological activity by
(a) formation of amino acids
(b) loss of primary structure
(c) loss of both primary and secondary structures
(d) loss of both secondary and tertiary structures

48. Lack of essential amino acids in the diet leads to the disease called
(a) Night blindness (b) Pernicious anaemia
(c) Kwashiorkor (d) Sickel cell anaemia

49. Which one of the following is responsible for maintaining blood sugar level in human body?
(a) Riboflavin (b) Insulin
(c) Fats (d) Hormones

50. Iodine test is shown by
(a) polypeptides (b) glycogen
(c) starch (d) glucose

51. Enzymes are
(a) catalysts (b) proteins
(c) fatty acids (d) carbohydrates

52. Enzymes are made up of
(a) edible proteins
(b) proteins with specific structure
(c) nitrogen containing carbohydrates
(d) carbohydrates

53. Of the following statements about enzymes which ones are true?
(i) Enzymes lack in nucleophilic groups
(ii) Enzymes are highly specific both in binding chiral substrates and in catalysing their reactions
(iii) Enzymes catalyse chemical reactions by lowering the energy of activation
(iv) Pepsin is a proteolytic enzyme
(a) (i) and (iv) (b) (i) and (iii)
(c) (ii), (iii) and (iv) (d) (i)

54. Enzymes are essential as biocatalysts. They function in
(a) aqueous medium, temp = 30–35ºc; pH=7
(b) organic medium
(c) aqueous medium under extreme pH conditions
(d) None of these

55. The enzyme which converts glucose and fructose into ethyl alcohol is
(a) diastase (b) invertase
(c) sucrose (d) zymase

56. Enzyme which breaks down starch to maltose is
(a) maltase (b) zymase
(c) diastase (d) invertase

57. Which of the following is correct?
(a) Cycloheptane is an aromatic compound
(b) Diastase is an enzyme
(c) Acetophenone is an ether
(d) All of these

58. Enzymes in the living systems
(a) provide energy
(b) provide immunity
(c) transport oxygen
(d) catalyse biological reactions

59. Enzymes take part in a reaction and
(a) decrease the rate of a chemical reaction
(b) increase the rate of a chemical reaction
(c) both (a) and (b)
(d) None of these

60. The base adenine occurs in
(a) DNA only (b) RNA only
(c) DNA and RNA both (d) Protein

61. Purine derivative among the following bases is
(a) thymine (b) uracil
(c) guanine (d) cytosine

62. Which substance is not present in nucleic acids?
(a) Cytosine (b) Adenine
(c) Thymine (d) Guanidine

63. Adenosine is an example of
(a) nucleotide (b) nucleoside
(c) purine base (d) pyrimidine base

64. A nucleotide consists of
(a) carbon sugar
(b) nitrogen containing base
(c) phosphoric acid
(d) All of these

65. DNA has deoxyribose, a base and the third component which is
(a) phosphoric acid (b) ribose
(c) adenine (d) thymine

66. Which of the following is not present in a nucleotide?
(a) Guanine (b) Cytosine
(c) Adenine (d) Tyrosine

67. The pair of bases in DNA are held together by
(a) hydrogen bonds (b) ionic bonds
(c) phosphate groups (d) oxygen linkages

68. In nucleic acids, the nucleotides are linked to one another though
(a) Hydrogen bond (b) Peptide bond
(c) Glycosidic linkage (d) Phosphate groups

69. Chargaff's rule states that in an organism
(a) amount of adenine (A) is equal to that of guanine (G) and the amount of thymine (T) is equal to that of cytosine (C)
(b) amount of adenine (A) is equal to that of cytosine (C) and the amount of thymine (T) is equal to that of guanine (G)
(c) amount of adenine (A) is equal to that of thymine (T) and the amount of guanine (G) is equal to that of cytosine (C)
(d) amount of all bases are equal

70. The double helical structure of DNA was proposed by
(a) Watson and Crick (b) Meichers
(c) Emil Fischer (d) Khorana

71. α - Helix is found in
(a) DNA (b) RNA
(c) lipid (d) Carbohydrates

72. Which of the following compounds is responsible for the transmission of heredity characters?
(a) RNA (b) DNA
(c) Glucose (d) Haemoglobin

73. The latest discovery in cytology is that of
(a) respiration (b) genetic code
(c) enzyme (d) None of these

Exercise-3 | PAST COMPETITION MCQs

1. RNA and DNA are chiral molecules, their chirality is due to **[CBSE-PMT 2007]**
(a) chiral bases
(b) chiral phosphate ester units
(c) D-sugar component
(d) L-sugar component

2. Which one of the following is an amine hormone ? **[CBSE-PMT 2008]**
(a) Thyroxine (b) Oxypurin
(c) Insulin (d) Progesterone

3. In DNA, the complimentary bases are: **[CBSE-PMT 2008]**
(a) adenine and thymine; guanine and cytosine
(b) adenine and thymine ; guanine and uracil
(c) adenine and guanine; thymine and cytosine
(d) uracil and adenine; cytosine and guanine

4. The segment of DNA which acts as the instrumental manual for the synthesis of the protein is: **[CBSE-PMT 2009]**
(a) ribose (b) gene
(c) nucleoside (d) nucleotide

5. Which of the following hormones contains iodine? **[CBSE-PMT 2009]**
(a) Testosterone (b) Adrenaline
(c) Thyroxine (d) Insulin

6. Which one of the following does not exhibit the phenomenon of mutarotation ? **[CBSE-PMT 2010]**
(a) (+) – Sucrose (b) (+) – Lactose
(c) (+) – Maltose (d) (–) – Fructose

7. Fructose reduces Tollen's reagent due to: **[CBSE-PMT 2010]**
(a) enolisation of fructose followed by conversion to glucose (having aldehydic group) by the base present in Tollen's reagent
(b) asymmetric carbons
(c) primary alcoholic group
(d) secondary alcoholic group

8. Which one of the following statements is not true regarding (+) Lactose ? **[CBSE-PMT 2011]**
(a) On hydrolysis (+) Lactose gives equal amount of D(+) glucose and D(+) galactose.
(b) (+) Lactose is a β-glycoside formed by the union of a molecule of D(+) glucose and a molecule of D(+) galactose.
(c) (+) Lactose is a reducing sugar and does not exhibit mutarotation.
(d) (+) Lactose, $C_{12}H_{22}O_{11}$ contains 8-OH groups.

9. Which of the statements about "Denaturation" given below are correct ? **[CBSE-PMT 2011 M]**
(A) Denaturation of proteins causes loss of secondary and tertiary structures of the protein.
(B) Denturation leads to the conversion of double strand of DNA into single strand
(C) Denaturation affects primary structure which gets distorted
Options :
(a) (B) and (C) (b) (A) and (C)
(c) (A) and (B) (d) (A), (B) and (C)

10. Which one of the following statements is incorrect about enzyme catalysis? **[CBSE-PMT 2012 S]**
(a) Enzymes are mostly proteinous in nature.
(b) Enzyme action is specific.
(c) Enzymes are denaturated by ultraviolet rays and at high temperature.
(d) Enzymes are least reactive at optimum temperature.

11. Deficiency of vitamin B_1 causes the disease **[CBSE-PMT 2012 S]**
(a) Convulsions (b) Beri-Beri
(c) Cheilosis (d) Sterility

12. Which of the following acids does not exhibit optical isomerism ? **[CBSE-PMT 2012 S]**
(a) Maleic acid (b) α -amino acids
(c) Lactic acid (d) Tartaric acid

13. RNA is different from DNA because RNA contains **[AIEEE 2002]**
(a) ribose sugar and thymine
(b) ribose sugar and uracil
(c) deoxyribose sugar and thymine
(d) deoxyribose sugar and uracil.

14. Complete hydrolysis of cellulose gives **[AIEEE 2003]**
(a) D-ribose (b) D-glucose
(c) L-glucose (d) D-fructose

15. The reason for double helical structure of DNA is operation of **[AIEEE 2003]**
(a) dipole-dipole interaction
(b) hydrogen bonding
(c) electrostatic attractions
(d) van der Waals' forces

16. Identify the correct statement regarding enzymes [AIEEE 2004]

(a) enzymes are specific biological catalysts that cannot be poisoned

(b) enzymes are normally heterogeneous catalysts that are very specific in their action

(c) enzymes are specific biological catalysts that can normally function at very high temperatures (t~1000k)

(d) enzymes are specific biological catalysts that possess well-defined active sites

17. Which base is present in RNA but not in DNA ?

(a) Guanine (b) Cytosine [AIEEE 2004]

(c) Uracil (d) Thymine

18. Insulin production and its action in human body are responsible for the level of diabetes. This compound belongs to which of the following categories ? [AIEEE 2004]

(a) An enzyme (b) A hormone

(c) A co-enzyme (d) An antibiotic

19. In both DNA and RNA, heterocyclic base and phosphate ester linkages are at – [AIEEE 2005]

(a) C'_5 and C'_1 respectively of the sugar molecule

(b) C'_1 and C'_5 respectively of the sugar molecule

(c) C'_2 and C'_5 respectively of the sugar molecule

(d) C'_5 and C'_2 respectively of the sugar molecule

20. The term anomers of glucose refers to [AIEEE 2006]

(a) enantiomers of glucose

(b) isomers of glucose that differ in configuration at carbon one (C-1)

(c) isomers of glucose that differ in configurations at carbons one and four (C-1 and C-4)

(d) a mixture of (D)-glucose and (L)-glucose

21. The pyrimidine bases present in DNA are [AIEEE 2006]

(a) cytosine and thymine (b) cytosine and uracil

(c) cytosine and adenine (d) cytosine and guanine

22. The secondary structure of a protein refers to

(a) fixed configuration of the polypeptide backbone

(b) $\alpha-$helical backbone [AIEEE 2007]

(c) hydrophobic interactions

(d) sequence of $\alpha-$amino acids.

23. α - D-(+)-glucose and β-D-(+)-glucose are

(a) conformers (b) epimers [AIEEE 2008]

(c) anomers (d) enatiomers

24. The two functional groups present in a typical carbohydrate are: [AIEEE 2009]

(a) $-CHO$ and $-COOH$ (b) $>C=O$ and $-OH$

(c) $-OH$ and $-CHO$ (d) $-OH$ and $-COOH$

25. Biuret test is **not** given by [AIEEE 2010]

(a) carbohydrates (b) polypeptides

(c) urea (d) proteins

26. The presence or absence of hydroxyl group on which carbon atom of sugar differentiates RNA and DNA? [AIEEE 2011]

(a) 1st (b) 2nd

(c) 3rd (d) 4th

27. Which of the following compounds can be detected by Molisch's Test ? [AIEEE 2012]

(a) Nitro compounds (b) Sugars

(c) Amines (d) Primary alcohols

28. Which one of the following statements is correct? [AIEEE 2012]

(a) All amino acids except lysine are optically active

(b) All amino acids are optically active

(c) All amino acids except glycine are optically active

(d) All amino acids except glutamic acids are optically active

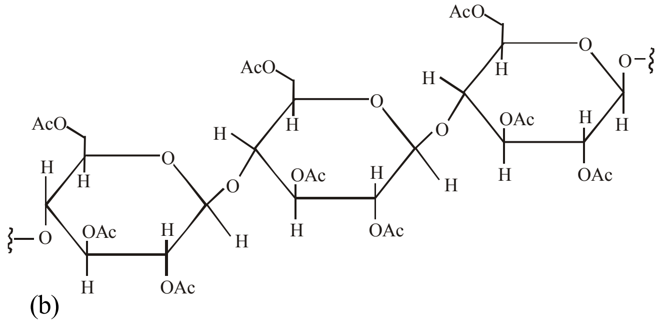
29. Synthesis of each molecule of glucose in photosynthesis involves : [JEE M 2013]

(a) 18 molecules of ATP (b) 10 molecules of ATP

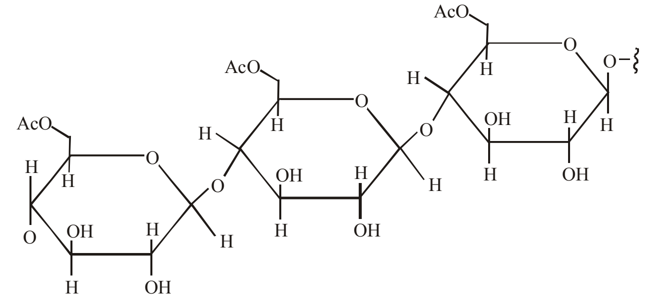
(c) 8 molecules of ATP (d) 6 molecules of ATP

30. Cellulose upon acetylation with excess acetic anhydride/ H_2SO_4 (catalytic) gives cellulose triacetate whose structure is [IIT-JEE 2007]

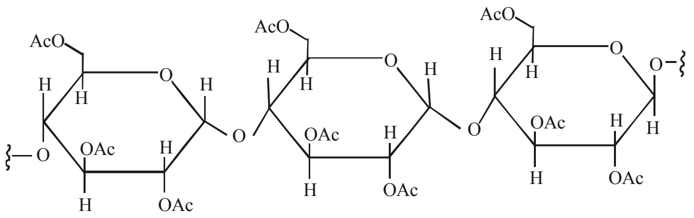
(a)



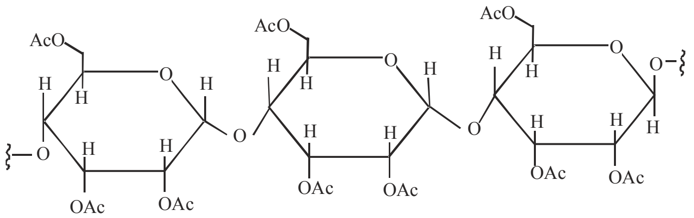
(b)



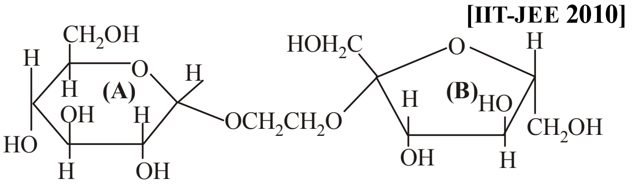
(c)



(d)

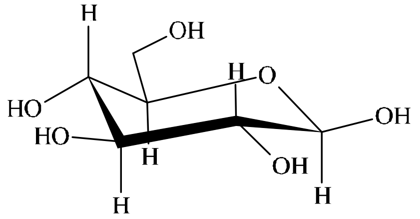


31. The correct statement about the following disaccharide is **[IIT-JEE 2010]**



(a) Ring (**A**) is pyranose with α - glycosidic link
(b) Ring (**A**) is furanose with α - glycosidic link
(c) Ring (**B**) is furanose with α - glycosidic link
(d) Ring (**B**) is pyranose with β - glycosidic link

32. The following carbohydrate is **[IIT-JEE 2011]**

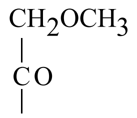


(a) a ketohexose (b) an aldohexose
(c) an α-furanose (d) an α-pyranose

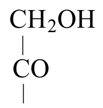
Exercise-4 | Applied MCQs

1. The rapid interconversion of α-D-glucose and β-D-glucose in solution is known as
(a) racemisation (b) asymmetric induction
(c) fluxional isomerism (d) mutarotation

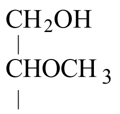
2. For osazone formation, the effective structural unit necessary is

(a) 

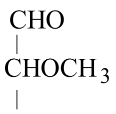
$$\begin{array}{c}CH_2OCH_3\\ |\\ CO\\ |\end{array}$$

(b) 

$$\begin{array}{c}CH_2OH\\ |\\ CO\\ |\end{array}$$

(c) 

$$\begin{array}{c}CH_2OH\\ |\\ CHOCH_3\\ |\end{array}$$

(d) 

$$\begin{array}{c}CHO\\ |\\ CHOCH_3\\ |\end{array}$$

3. An organic compound with the formula $C_6H_{12}O_6$ forms a yellow crystalline solid with phenylhydrazine and gives a mixture of sorbitol and mannitol when reduced with sodium. Which among the following could be the compound?
(a) fructose (b) glucose
(c) mannose (d) sucrose

4. Which is correct statement?
(a) Starch is a polymer of glucose
(b) Amylose is a component of cellulose
(c) Proteins are compounds of only one type of amino acid
(d) In cyclic structure of fructose, there are four carbons atoms and one oxygen atom.

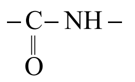
5. Which of the following reagents cannot distinguish between glucose and fructose?
(a) Tollen's regent (b) Fehling's solution
(c) Benedict's solution (d) All of these

6. In polysaccharides, the linkage connecting monosaccharides is called
(a) glycoside linkage (b) nucleoside linkage
(c) glycogen linkage (d) peptide linkage

7. The chemical change in DNA molecule that could lead to synthesis of protein with an altered amino acid sequence is called
(a) replication (b) lipid formation
(c) cellular membrane (d) mutation

8. In an amino acid, the carboxyl group ionises at pK_{a_1} =2.34 and ammonium ion at pK_{a_2} = 9.60. The isoelectric point of the amino acid is at pH
(a) 5.97 (b) 2.34
(c) 9.60 (d) 6.97

9. Which statement is incorrect about peptide bond?
(a) C–N bond length in proteins is longer than usual C–N bond length
(b) Spectroscopic analysis shows planar structure of



$$\begin{array}{c}-\underset{\displaystyle\overset{\|}{O}}{C}-NH-\end{array}$$ bond

(c) C–N bond length in proteins is smaller than usual C–N bond length
(d) None of these

10. Secondary structure of protein refers to

(a) mainly denatured proteins and structure of prosthetic groups

(b) three -dimensional structure, especially the bond between amino acid residues that are distinct from each other in the polypeptide chain

(c) linear sequence of amino acid residues in the polypetide chain

(d) regular folding patterns of continous portions of the polypeptide chain

11. Violet colour is obtained when dilute $CuSO_4$ is added in alkaline solution of protein. This test is known as

(a) Biuret test (b) Xanthoproteic test

(c) Hopkins-cole test (d) Millon's test

12. Which of the following statements is incorrect?

(a) Enzymes are organic catalysts

(b) Enzymes have a very large turnover number

(c) Enzymes action is specific

(d) Enzymes always require a coenzyme in their catalytic action.

13. In nucleic acids, the sequence is

(a) phosphate - base - sugar

(b) sugar- base-phosphate

(c) base- sugar - phosphate

(d) base- phosphate - sugar

14. If one strand of DNA has the sequence ATGCTTGA, the sequence in the complimentary strand would be

(a) TACGAACT (b) TCCGAACT

(c) TACGTACT (d) TACGTAGT

15. Which metal is present in vitamin B_{12}?

(a) Manganese (b) Iron

(c) Cobalt (d) Copper

16. Vitamin A is called

(a) retinol (b) ascorbic acid

(c) tocopherol (d) calciferol

17. Which of the following is fat soluble?

(a) Pyridoxine (b) Vitamin A

(c) Thiamine (d) Riboflavin

18. Which of the following compounds is not vitamin?

(a) guanine (b) Thiamine

(c) Riboflavin (d) Niacin

19. The hormone produced by pancreas

(a) Adrenaline (b) Glucogen

(c) Thyroxene (d) Cortisone

20. Which of the following is a male sex hormone

(a) Cortisone (b) Testosterone

(c) Progesterone (d) Estrone

21. Which is oil soluble vitamin

(a) B_1 (b) A

(c) B_{12} (d) B_6

22. Vitamin D is also known as

(a) sunshine vitamin (b) ascorbic acid

(c) growth vitamin (d) reproductive vitamin

23. Riboflavin is vitamin

(a) B_6 (b) B_1

(c) B_2 (d) B_{12}

24. Vitamin which contains cobalt is

(a) B_{12} (b) B_6

(c) A (d) E

25. Which of the following steroid is hormone?

(a) Progesterone (b) Adrenaline

(c) Insulin (d) Thyroxine

26. Deficiency of vitamin E causes

(a) loss of fertility (b) impaired clotting

(c) scurvy (d) night blindness

27. Scurvy is caused by the deficiency of vitamin

(a) D (b) C

(c) B_6 (d) A

28. The water soluble vitamin is

(a) B_1 (b) K

(c) E (d) D

29. Citrus fruits are rich in vitamin

(a) K (b) A

(c) C (d) B

30. Cod liver oil is rich in

(a) vitamin A (b) vitamin B_{12}

(c) vitamin B_6 (d) vitamin C

31. Night blindness is caused by deficiency of

(a) vitamin B_{12} (b) vitamin A

(c) vitamin C (d) vitamin E

32. Which of the following statements about vitamin B-12 is incorrect?

(a) It has a cobalt atom

(b) It also occurs in plants

(c) It is also present in rain water

(d) It is needed for human body in very small amounts

33. Match List I (name of vitamin) with List II (deficiency result/ disease) and select the correct answer using the codes given below the lists :

List I	***List II***
I. Ascorbic acid	A. Beri-beri
II. Retinol	B. Cracked lips
III. Riboflavin	C. Scurvy
IV. Thiamine	D. Night blindness

(a) I - B, II - A, III - C, IV - D (b) I - A, II - B, III - C, IV - D

(c) I - D, II - C, III - B, IV - A (d) I - C, II - D, III - B, IV - A

34. The hormone which controls the processes of burning of fats, proteins and carbohydrates to liberate energy in the body is

(a) cortisone (b) adrenaline

(c) thyroxine (d) insulin

35. Two vitamins absorbed from intestine along with fats are

(a) A, D (b) A, B

(c) A, C (d) D, B

36. A vitamin that contains both N and P is

(a) Vitamin C (b) Vitamin K

(c) Vitamin B_{12} (d) Vitamin D

37. Which is wrongly matched?

(a) Insulin - steroid hormone

(b) Estrone - control the uterine cycle in women

(c) Oxytocin - contraction of uterus

(d) Pot. metabisulphite - food preservative

Hints & Solutions

EXERCISE 1

1. Carbohydrates have at least one (or more) chiral carbon atom
2. Glycogen (a polymer of D-glucose).
3. Myoglobin.
4. $3 \times 2 \times 1 = 6$ tripeptides are possible.
5. Vitamin C.
8. (*a*) Disaccharide
   (*b*) Monosaccharide
   (*c*) Polysaccharide
   (*d*) Disaccharide
   (*e*) Monosaccharide
10. (*a*) Zwitter ion
   (*b*) Polypeptide
   (*c*) Denaturation
   (*d*) Fibrous proteins.
11. (*a*) it migrates to the cathode.
   (*b*) it migrates to the anode.
   (*c*) no migration occurs.
12. Excess intake of vitamin A and D causes hypervitaminoses while multiple deficiencies caused by lack of more than one vitamin is called avitaminoses.

18. **(a)** **19.** **(b)** **20.** **(d)** **21.** **(c)** **22.** **(a)**
23. **(c)** **24.** **(d)** **25.** **(b)** **26.** **(b)** **27.** **(c)**

EXERCISE 2

1. **(c)**

2. **(c)** α – and β-D-glucoses differ in the arrangement of groups around one carbon atom (C_1) i.e. they differ in configuration at C_1, hence these are also known as anomers

3. **(b)** Fructose has 3 chiral centres and hence number of optical isomers are $2^3 = 8$

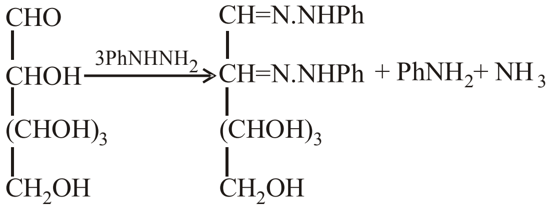
4. **(c)**

5. **(d)** Sweeetness of glucose is about 75% of cane sugar

6. **(d)**

7. **(c)** Glucose has 5 hydroxyl groups, hence it reacts with acetic anhydride to form a penta-acetate

8. **(a)**



$$\begin{array}{l} CHO \\ | \\ CHOH \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} \xrightarrow{3PhNHNH_2} \begin{array}{l} CH{=}N.NHPh \\ | \\ CH{=}N.NHPh \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} + PhNH_2 + NH_3$$

9. **(a)** Carbohydrates char on heating due to dehydration

10. **(c)** **11.** **(d)**

12. **(c)** Sucrose, being a non-reducing sugar, does not reduce Benedict's solution. Remember that fructose has an α-hydroxy ketonic group, which is also reducing group (different from ordinary ketonic group)

13. **(a)** **14.** **(a)** **15.** **(c)**

16. **(d)** Since sucrose is dextrorotatory while hydrolysis product of sucrose, having equimolar mixture of glucose and fructose, is laevorotatory. Hence the hydrolysed product of sucrose is known as invert sugar and the hydrolysis of sucrose is known as inversion.

17. **(b)** **18.** **(a)** **19.** **(c)** **20.** **(b)**

21. **(c)** **22.** **(a)**

23. **(a)** Drying oils contain unsaturated fatty acids such as linoleic and linolenic acids

24. **(a)** Since glycerol has three –OH groups, it can have three acyl (similar or different) groups

25. **(c)**

26. **(b)** Saponification (alkaline hydrolysis) of oils and fats gives glycerol and sodium salt of fatty acids, which is sodium palmitate in the present question

27. **(a)**

28. **(a)** Butter, being a lipid, dissolves in chloroform

29. **(d)** **30.** **(a)**

31. **(d)** Benzidine is 4,4'-diaminodiphenyl

32. **(d)**

33. **(b)** Proline contains imino (secondary amino), $>$NH group

34. **(d)**

35. **(d)** All are chiral

36. **(b)** All proteins are not found in L-form but they may be present in form of D or L.

37. **(d)** Only option (d) has $-NH_2$ and $-COOH$ groups in the same molecule

38. **(d)** **39.** **(a)** **40.** **(c)** **41.** **(b)**

42. **(b)** Human body can synthesize 10 of the 20 amino acids obtained by hydrolysis of various proteins

43. **(d)** Proteins do not provide energy for metabolism.

44. **(c)** **45.** **(d)** **46.** **(a)** **47.** **(d)**

48. **(c)** **49.** **(b)**

50. **(c)** Starch forms blue complex with iodine

51. **(b)** **52.** **(b)** **53.** **(c)** **54.** **(a)**

55. **(d)** **56.** **(c)** **57.** **(b)** **58.** **(d)**

59. **(b)** **60.** **(c)** **61.** **(c)**

62. **(d)** Guanidine, $H_2N-\overset{\overset{NH}{||}}{C}-NH_2$, is neither a purine nor a pyrimidine base

63. **(b)** **64.** **(d)** **65.** **(a)**

66. **(d)** Tyrosine is an α-amino acid, and neither a purine nor a pyrimidine base

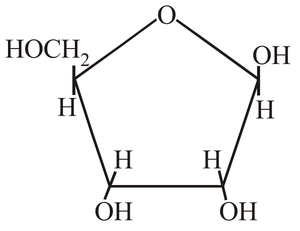
67. **(a)** **68.** **(d)** **69.** **(c)** **70.** **(a)**

71. **(a)** DNA has double stranded α-helical structure

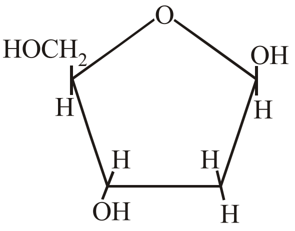
72. **(b)** **73.** **(b)**

EXERCISE 3

1. **(c)** Each nucleic acid consists of a pentose sugar a heterocyclic base, and phosphoric acid. The sugar present in DNA is 2-deoxy -D (–) ribose and the sugar present in RNA is D (–)- ribose. The chirality of DNA and RNA molecules are due to the presence of sugar components.



D(–)–ribose



2-deoxy–D(–)–ribose

2. **(a)** Thyroxine is an amine hormone.

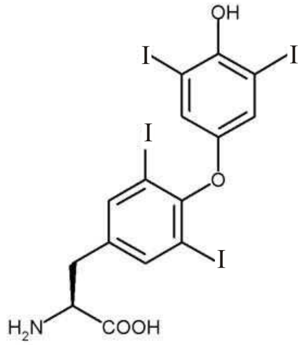
3. **(a)** In DNA the complimentary base are Adenine and thymine.

Guanine and cytosine

The genetic information for cell is contained in the sequence of bases A, T, G and C in **DNA** molecule.

4. **(b)** The DNA sequence that codes for a specific protein is called a Gene and thus every protein in a cell has a corresponding gene.

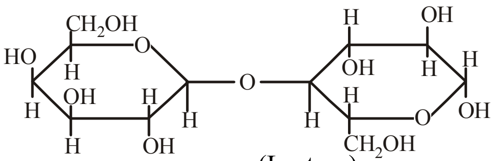
5. **(c)** Thyroxine is the only hormone among the given choices that contains iodine. Its structure is as follows:



6. **(a)** Sucrose does not have free — CHO or CO group, hence it does not undergo mutarotation.

7. **(a)**

8. **(c)**



(Lactose)

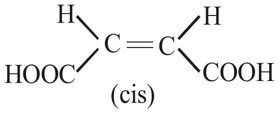
All reducing sugar shows mutarotation.

9. **(c)** When the proteins are subjected to the action of heat, mineral acids or alkali, the water soluble form of globular protein changes to water insoluble fibrous protein. This is called denaturation of proteins. During denaturation secondary and tertiary structures of protein destroyed but primary structures remains intact.

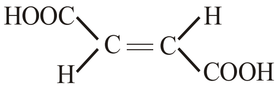
10. **(d)** Enzymes are most reactive at optimum temperature. The optimum temperature for enzyme activity lies between 40°C to 60°C.

11. **(b)** Beri-Beri.

12. **(a)**



(cis)
maleic acid



(Trans)

It shows geometrical isomerism but does not show optical isomerism.

13. **(b)**

14. **(b)** $(C_6H_{10}O_5)n + nH_2O \xrightarrow{H+} \underset{D-Glucose}{nC_6H_{12}O_6}$

15. **(b)** Hydrogen bonding

16. **(d)** Enzymes are very specific biological catalysts possessing well - defined active sites

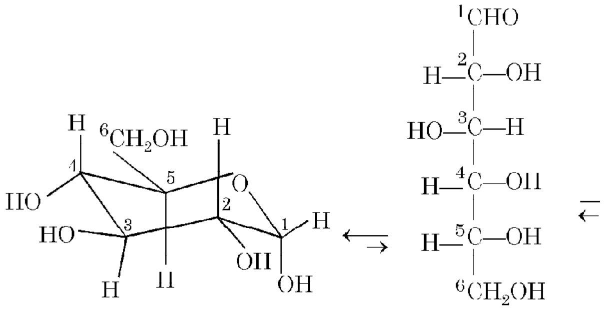
17. **(c)** RNA contains cytosine and uracil as pyrimidine bases while DNA has cytosine and thymine.

Both have the same purine bases i.e., Guanine and adenine.

18. **(b)** Insulin is a biochemically active peptide harmone secreted by pancreas.

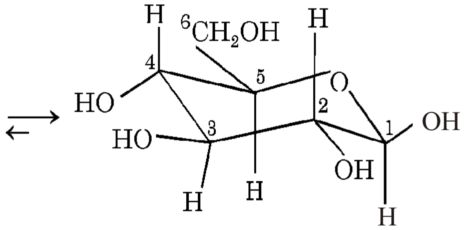
19. **(b)** In DNA and RNA heterocyclic base and phosphate ester are at C_1' and C_5' respectively of the sugar molecule.
Each corners is shared by 8 cubes and each face is shared by 2 faces

20. **(b)** Cyclisation of the open chain structure of D-(+)-glucose has created a new stereocenter at C_1 which explains the existence of two cyclic forms of D-(+)-glucose, namely α– and β–. These two cyclic forms are *diasteromers, such diastereomers which differ only in the configuration of chiral carbon developed on hemiacetal formation* (it is C_1 in glucose and C_2 in fructose) *are called* **anomers** and the hemiacetal carbon (C_1 or C_2) is called the **anomeric carbon.**



α–D-(+)-Glucopyranose
m.p. 146°C ; $[\alpha]_D = +112.2°$
(36% at equilibrium)

Open chain form
of D-(+)-glucose
(negligible % at equbilibrium)



β–D-(+)-Glucopyranose
m.p. 150°C ; $[\alpha]_D = +18.7°$
(64% at equilibrium)

21. **(a)** The pyrimidine bases present in DNA are cytosine and thymine.

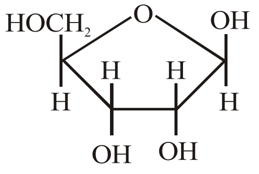
22. **(b)** The secondary structure of a protein refers to the shape in which a long peptide chain can exist. There are two different conformations of the peptide linkage present in protein, these are α-helix and β-conformation. The α-helix always has a right handed arrangement. In β-conformation all peptide chains are stretched out to nearly maximum extension and then laid side by side and held together by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as β-pleated sheet.

23. **(c)** Since $\alpha - D - (+) -$ glucose and $\beta - D - (+)$ glucose differ in configuration at C – 1 atom so they are anomers. Anomers are those diastereomers that differ in configuration at C – 1 atom.

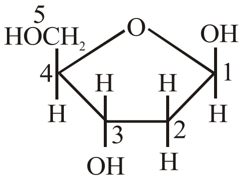
24. **(c)** Glucose is considered as a typical carbohydrate which contains –CHO and –OH group.

25. **(a)** Biuret test produces violet colour on addition of dilute $CaSO_4$ to alkaline solution of a compound containing peptide linkage.

26. **(b)** RNA has D (–) – Ribose and the DNA has 2–Deoxy D (–) – ribose as the carbohydrate unit.



ribose

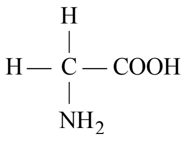


2-deoxy ribose

From the structures it is clear that 2nd carbon in DNA do not have OH group.

27. **(b)** **Molisch's Test :** This is a general test for carbohydrates. One or two drops of alcoholic solution of α-naphthol is added to 2 ml glucose solution. 1 ml of conc. H_2SO_4 solution is added carefully along the sides of the test-tube. The formation of a violet ring at the junction of two liquids confirms the presence of a carbohydrate or sugar.

28. **(c)** With the exception of glycine all the 19 other common amino acids have a uniquely different functional group on the central tetrahedral alpha carbon.



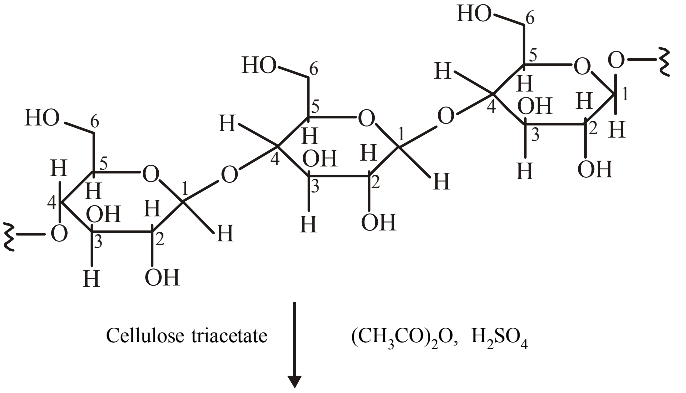
$$H-\overset{\displaystyle H}{\underset{\displaystyle NH_2}{C}}-COOH$$

glycine

29. **(a)** $6CO_2 + 12NADPH + 18ATP \rightarrow C_6H_{12}O_6 + 12NADP + 18ADP$

30. **(a)** Cellulose is a polysaccharide composed of only D-glucose units. Every adjacent glucose units are joined by β-glycosidic linkage between C_1 of one glucose and C_4 of the next.

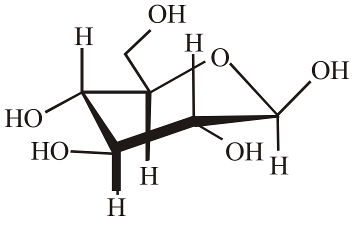
Thus in every glucose units only three –OH groups are free to form triacetate.



(–OH = –OCOCH$_3$)

31. **(a)**

32. **(b)**



It is a β-pyranose hence it is an aldohexose.

EXERCISE 4

1. **(d)** **2. (b)**

3. **(a)** Since the compound forms a yellow crystalline solid, i.e. osazone with phenylhydrazine, it may be an aldohexose or a ketohexose. Further, since on reduction, compound forms a mixture of sorbitol and mannitol, it must be a ketohexose, i.e. fructose. Recall that glucose on reduction gives only one alcohol glucitol (Sorbitol)

4. **(a)**

5. **(d)** All the three reagents reduce both glucose and fructose and hence cannot be used to distinguish between them

6. **(a)**

7. **(d)**

8. **(a)** Isoelectric point (pH)

$$= \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{2.34 + 9.60}{2} = 5.97$$

9. **(c)** Due to resonance,  $-\overset{\overset{\ddot{O}}{\|}}{C}-\ddot{N}H- \longleftrightarrow -\overset{\overset{O^-}{\|}}{C}=\overset{+}{N}H-$, C – N bond acquires some double bond character, hence shorter in length

10. **(d)**

11. **(a)**

12. **(d)** Enzymes may or may not require a coenzyme for their catalytic action

13. **(c)**

14. **(a)** On the basis of structure of guanine and complementary bases present in them, we can say that if the sequence of bases in one strand of DNA is I, then the sequence in the second strand should be II

A : T : G : C : T : T : G : A I
T : A : C : G : A : A : C : T II

15. **(c)** Vit. B_{12} contains cobalt.

16. **(a)** Retinol is the name of Vitamin A

17. **(b)** Vitamin A is fat soluble.

18. **(a)** Guanine is not vitamine while others are

19. **(b)** Glucogen is produced by pancreas

20. **(b)** Testosterone is male sex harmone

21. **(b)** Vitamin A is oil soluble

22. **(a)** Vitamin D is also known as sunshine vitamin

23. **(c)** B_2 is Riboflavin

24. **(a)** B_{12} contains cobalt

25. **(a)** Progesterone is a hormone

26. **(a)** Loss of fertility is caused by vitamin E

27. **(b)** Scurvy is caused by the deficiency of vitamin C

28. **(a)** B_1 is water soluble vitamin

29. **(c)** Citrus fruits are rich in vitamin C

30. **(a)** Cod liver oil is rich in vitamin A

31. **(b)** Vitamin A.

32. **(b)** Vitamin B_{12} does not occur in plants

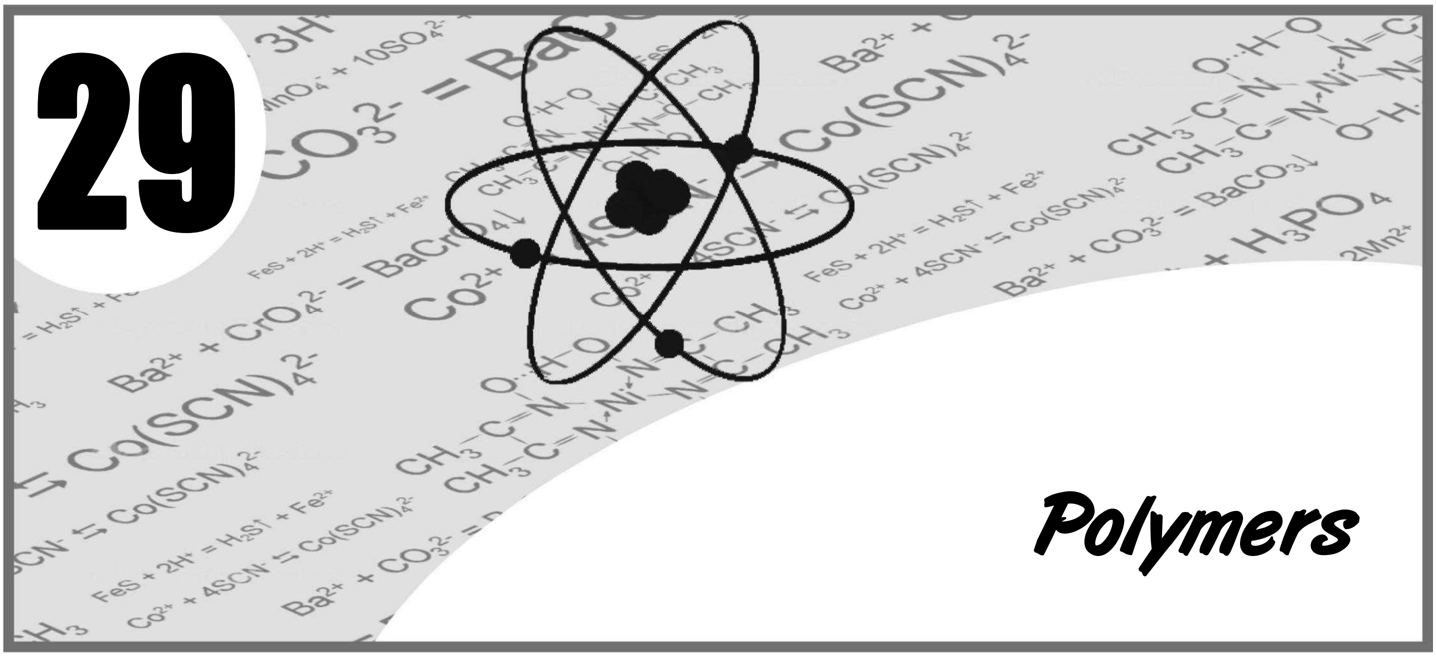
33. **(d)** Ascorbic acid - Scurvy
Retinol - Night blindness
Riboflavin - Cracked lips
Thiamine - Beri-Beri
Thus option (d) is correct.

34. **(d)** Insulin

35. **(a)** Vitamin A, D are absorbed from the intestine by fats.

36. **(c)** Vitamin B_{12} contains both N and P

37. **(a)**



29

Polymers

POLYMERS :

The macromolecules formed by the union between same or different molecules are known as polymers.

POLYMERISATION :

The process of joining together the simple molecules is known as polymerisation.

MONOMERS :

Small molecules which are joined together to form polymers are known as monomers.

DEGREE OF POLYMERISATION :

The number of monomolecules (n) which combine to form a given macromolecule is called the degree of polymerisation.

HIGH POLYMERS :

Such polymers have high degree of polymerisation.

OLIGOMERS :

They have low degree of polymerisation.

DISTINCTION BETWEEN POLYMERS AND MACROMOLECULES :

Polymers have repeat units and a macromolecule may or may not have repeat units eg chlorophyll and polythene.

HOMOPOLYMERS :

Polymers containing one type of monomer units.

COPOLYMERS :

Polymers containing two or more types of monomer units.

CLASSIFICATION :

They may be divided into two categories.

(i) ***Natural polymers -*** They are obtained from natural sources eg **poly saccharides** (starch, cellulose), **Proteins** (polymers of amino acids), gums, resins (cross linked polymers formed by compounds containing double or triple bonds slowly oxidised by atmospheric oxygen). **natural rubber** (polymer of isoprene), **Nucleic acids** (polymers of nucleotides) silk and wool (polymers of amino acids).

(ii) ***Synthetic polymers -*** Polymers prepared by synthesis (man made), are known as synthetic polymers eg. polystyrene, nylon, PVC etc.

CLASSIFICATION BASED ON STRUCTURE :

(i) ***Linear polymers -*** Polymers containing the monomeric units linked together to form long straight chains stacked over one another to give packed structure.

Such polymers have high tensile strength, high densities, high m.p. and b.p. Examples - fibres and plastics.

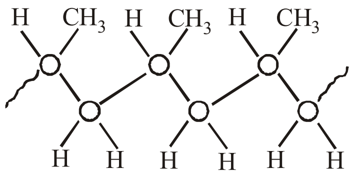
(ii) ***Branched polymers -*** Long chain of monomer units containing side chains of different length forms branched polymers. The chains are loosely packed, hence polymers have low density, low m.p. and low tensite strength. Examples - Amylopectin and glycogen.

(iii) ***Cross - linked*** or three dimensional polymers - Such polymers have three dimensional network and are hard, brittle and rigid. Examples - Bakelite, melamine.

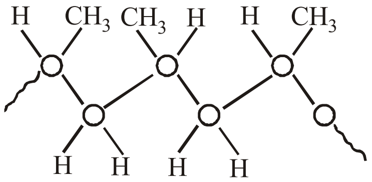
STEREOCHEMICAL CLASSIFICATION :

Polymers of propylene can be classified into

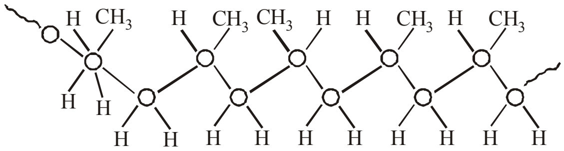
(i) *Isotactic* - with all methyl groups on one side of extended chain



(ii) ***Syndiotactic,*** with methyl groups alternating regularity side to side



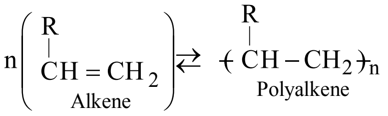
(iii) ***Atactic***-with random distribution of methyl groups



(Above polymers are obtained by coordination polymerisation)

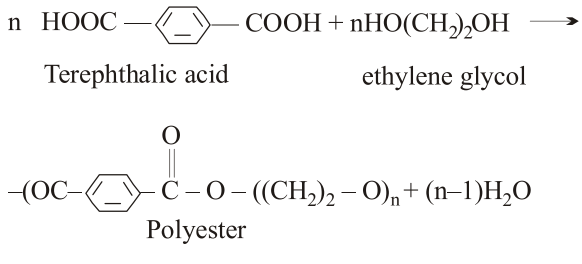
CLASSIFICATION BASED UPON MODE OF SYNTHESIS :

(i) ***Addition polymers*** **-** Polymers formed without the elimination of any elements and the molecular weight of the polymer is the exact multiple of the monomer unit are known as addition polymers



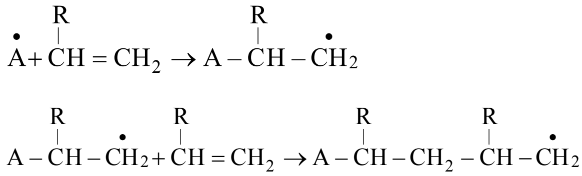
$$n\left(\underset{\text{Alkene}}{\overset{\overset{R}{|}}{C}H=CH_2}\right) \rightleftarrows \underset{\text{Polyalkene}}{\left(\overset{\overset{R}{|}}{C}H-CH_2\right)_n}$$

(ii) ***Condensation polymers*** - They are formed with elimination of certain elements in the form of H_2O, C_2H_5OH, NH_3 etc. and molecular weight of polymer is not exact multiple of monomer unit eg. terephthalic acid condenses with ethylene glycol to give polyester



CHAIN GROWTH AND STEP GROWTH POLYMERS :

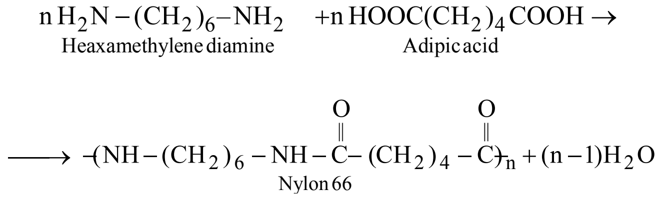
(i) ***Chain growth polymers-*** In chain growth polymerisation each step consumes a reactive particle and produces another similar particle.



$$\dot{A}+\overset{\overset{R}{|}}{C}H=CH_2 \rightarrow A-\overset{\overset{R}{|}}{C}H-\dot{C}H_2$$

$$A-\overset{\overset{R}{|}}{C}H-\dot{C}H_2+\overset{\overset{R}{|}}{C}H=CH_2 \rightarrow A-\overset{\overset{R}{|}}{C}H-CH_2-\overset{\overset{R}{|}}{C}H-\dot{C}H_2$$

(ii) ***Step growth polymers -*** Polymerisation proceeds through various steps independent of each other and it happens when monomer units contain more than one functional group. For example formation of nylon 66, bakelite etc proceed by step growth polymerisation.



$$n\underset{\text{Heaxamethylene diamine}}{H_2N-(CH_2)_6-NH_2} + n\underset{\text{Adipic acid}}{HOOC(CH_2)_4COOH} \rightarrow$$

$$\longrightarrow \underset{\text{Nylon 66}}{\left(NH-(CH_2)_6-NH-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}\right)_n} + (n-1)H_2O$$

CLASSIFICATION ON THE BASIS OF PHYSICAL PROPERTIES AND INTERPARTICLE FORCES :

(i) ***Elastomers*** **-** They can be easily stretched and can be made rigid to some extent by adding cross linking agents eg vulcanised rubber. They possess weakest intermolecular forces.

(ii) ***Thermoplastics*** - They become soft on heating and harden on cooling. eg polythene, polystyrene. They can be worked up again and again. Forces between molecules are intermediate of elastomers and fibers.

(iii) ***Thermosetting*** - Such polymers undergo chemical changes when heated and set to hard mass when cooled eg Bakelite. Such polymers can not be reworked. There is excessive cross linking on heating and three dimensional net work of bonds.

(iv) ***Fibres*** - Linear polymers containing polymeric units joined by hydrogen bonding. They can be woven into fabrics. Rayons, nylons are the examples.

FORMATION OF ADDITION POLYMERS :

They can be obtained by

(i) Free radical polymerisation

(ii) Cationic polymerisation

(iii) Anionic polymerisation

(iv) Ziegler - Natta polymerisation or coordination polymerisation

VULCANIZATION OF RUBBER :

Heating of rubber with sulphur which causes formation of sulphur bridges between molecules which are then cross linked is known as vulcanization of rubber. The vulcanised rubber is more elastic than natural rubber.

Vulcanization may be brought about by free radical generators (peroxides, azo compounds) and metal oxides (ZnO or MgO) also.

ANTIOXIDANTS :

Natural rubber is very sensitive to oxidation by air and ozone which can be inhibited by adding anti oxidants. They undergo easy oxidation and prevent the oxidative degradation of rubber.

Examples are N - phenyl - β - naphthylamine and

Di - β - naphthyl - p - phenylenediamine.

MOLECULAR MASS OF POLYMERS :

It is of two types

(i) Number average molecular mass (M_n^-) is given by

$$\overline{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 + ...}{N_1 + N_2 + N_3 + ...} = \frac{\Sigma N_iM_i}{\Sigma N_i}$$

Where N_1 number of molecules having molecular mass M_1 and so on. It is measured by osmotic pressure measurement.

(ii) Mass - average molecular mass $(\overline{M}_w)$ is given by

$$\overline{M}_w = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + ...}{N_1M_1 + N_2M_2 + N_3M_3 + ...} = \frac{\Sigma N_iM_i^2}{\Sigma N_iM_i}$$

It is determined by ultra centrifugation or sedimentation.

POLYDISPERSITY INDEX :

It is the ratio of mass average molecular mass $\overline{M}_w$ to the number average molecular mass $\overline{M}_n$

$$PDI = \frac{\overline{M}_w}{\overline{M}_n}$$

When PDI = 1 or nearly 1, we have monodisperse system in which all molecules have identical molecular mass. Natural polymers are monodisperse and synthetic polymers are polydisperse i.e. PDI > 1 for such polymers

IMPORTANT ADDITION POLYMERS :

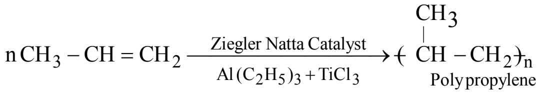
(i) ***Polyethylene***

$$nCH_2 = CH_2 \xrightarrow[1500\,atm;150-250°C]{Traces\ of\ O_2} \left(CH_2 - CH_2 \right)_n$$

Polythene or Polyethylene

Free radical initiator gives low density polythene and ionic catalyst gives high density polythene. It is white, transluscent, rigid, linear, used for making tubes, pipes, coated wires, insulator parts. etc.

(ii) ***Polypropylene***

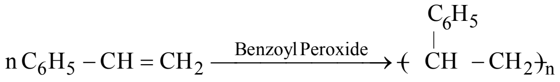


$$nCH_3 - CH = CH_2 \xrightarrow[Al(C_2H_5)_3 + TiCl_3]{Ziegler\ Natta\ Catalyst} \left(\underset{}{\overset{CH_3}{\overset{|}{CH}}} - CH_2 \right)_n$$

Polypropylene

It has good hardness, stiffness, resistance. Used for making ropes, carpets, washing machine parts etc.

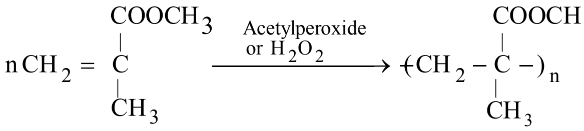
(iii) ***Polystyrene***



$$nC_6H_5 - CH = CH_2 \xrightarrow{Benzoyl\ Peroxide} \left(\overset{C_6H_5}{\overset{|}{CH}} - CH_2 \right)_n$$

It is transparent, light, moisture resistant used for battery cases, refrigerator parts, electric insulators, combs, buttons TV cabinets. Its trade name is **Styrofoam** or **styron**.

(iv) Polymethylmeth acrylate, **Lucite** or **Plexiglass**.

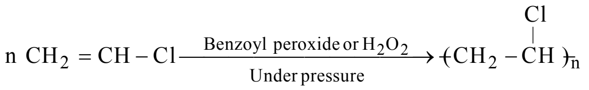


$$nCH_2 = \underset{\underset{CH_3}{|}}{\overset{\overset{COOCH_3}{|}}{C}} \xrightarrow{\substack{Acetylperoxide\\ or\ H_2O_2}} \left(CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{COOCH_3}{|}}{C}} - \right)_n$$

Methylmeth acrylate (MMA) PMMA

It is hard, fairly rigid. It is used for making lenses, artificial eyes, dentures, aircraft windows.

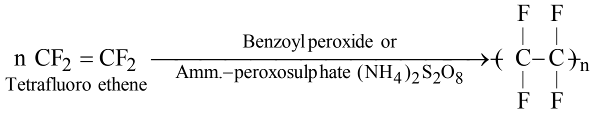
(v) ***Polyvinyl chloride (PVC)***



$$n\ CH_2 = CH - Cl \xrightarrow[Under\ pressure]{Benzoyl\ peroxide\ or\ H_2O_2} \left(CH_2 - \overset{\overset{Cl}{|}}{CH} \right)_n$$

It is resistant to light, atmopheric oxygen, chemically inert. It is used for electrical insulators, floor covering, safety helmets etc.

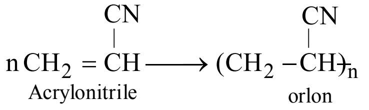
(vi) ***Teflon, Polytetrafluoroethylene (PTFE) of Fluon***



$$\underset{Tetrafluoro\ ethene}{n\ CF_2 = CF_2} \xrightarrow[Amm.-peroxosulphate\ (NH_4)_2S_2O_8]{Benzoyl\ peroxide\ or} \left(\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}} - \underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}} \right)_n$$

It is extremely tough, resistant to heat and chemicals. It is used for making gaskets, pump parts, coating utensils, high frequency insulator

(vii) ***Polyacrylonitrile (PAN), acrilon or orlon***

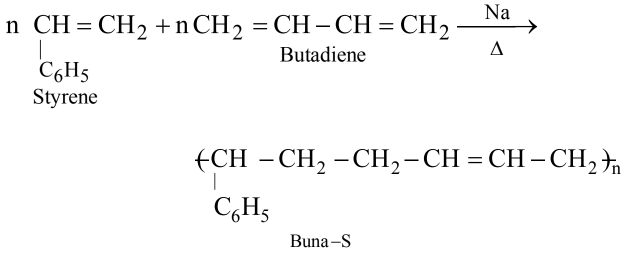


$$\underset{Acrylonitrile}{nCH_2 = \overset{\overset{CN}{|}}{CH}} \longrightarrow \underset{orlon}{\left(CH_2 - \overset{\overset{CN}{|}}{CH} \right)_n}$$

It is hard used in preparing cloths, carpets

RUBBERS

(i) ***Buna - S*** **or SBR or GSR (Government styrene rubber)**

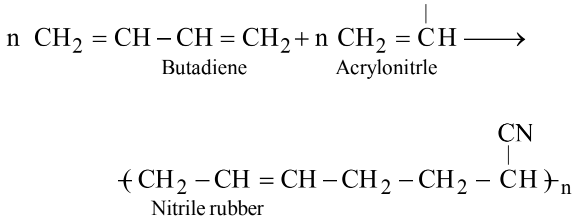


$$n\ \underset{\underset{Styrene}{\underset{C_6H_5}{|}}}{CH} = CH_2 + n\underset{Butadiene}{CH_2 = CH - CH = CH_2} \xrightarrow[\Delta]{Na}$$

$$\underset{Buna-S}{\left(\underset{\underset{C_6H_5}{|}}{CH} - CH_2 - CH_2 - CH = CH - CH_2 \right)_n}$$

It is used for manufacture of tyres, floor tiles, gaskets, cable insulators etc.

(ii) ***Nitrile rubber*** (GR-A or Buna - N)

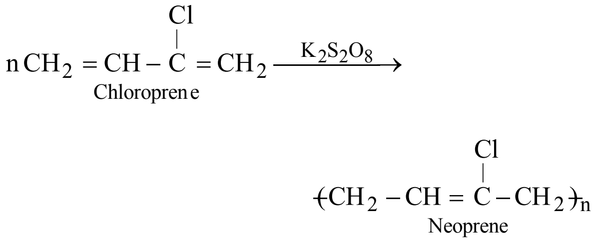


$$n\ \underset{Butadiene}{CH_2 = CH - CH = CH_2} + n\ \underset{Acrylonitrle}{CH_2 = \overset{\overset{CN}{|}}{CH}} \longrightarrow$$

$$\underset{Nitrile\ rubber}{\left(CH_2 - CH = CH - CH_2 - CH_2 - \overset{\overset{CN}{|}}{CH} \right)_n}$$

Excellent resistant to heat and chemicals. It is used for making conveyer belts, printing rollers, automobile parts.

(iii) *Neoprene*



$$n\,\underset{\text{Chloroprene}}{CH_2=CH-\overset{\overset{Cl}{|}}{C}=CH_2}\xrightarrow{K_2S_2O_8}$$

$$\underset{\text{Neoprene}}{\left(CH_2-CH=\overset{\overset{Cl}{|}}{C}-CH_2\right)_n}$$

It is resistant to heat and chemicals. It is used for making protective clothing, reaction vessels, floor tiles etc.

(iv) ***Heavy rubber*** - It is cis poly isoprene having length of repeat unit 8.1 A°.

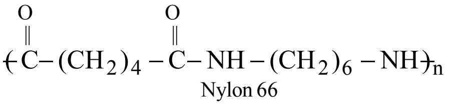
(v) ***Gutta percha*** - It is trans poly isoprene having length of repeat unit 4.72A°.

IMPORTANT CONDENSATION POLYMERS :

(A) **Nylons** - Synthetic polyamids are known as Nylons

(i) ***Nylon 66:*** Copolymer of adipic acid (6C) and hexamethylene diamine (6C).

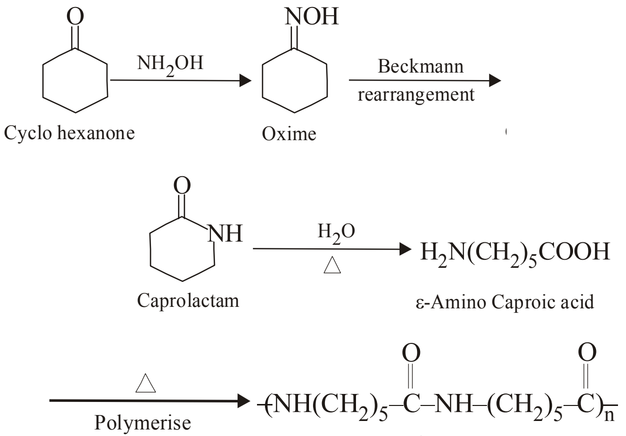
$$n\ \underset{\text{Adipic acid}}{HOOC(CH_2)_4COOH}+n\underset{\text{Hexamethyl ene diamine}}{H_2N(CH_2)_6NH_2}\rightarrow$$



$$\underset{\text{Nylon 66}}{\left(\overset{\overset{O}{||}}{C}-(CH_2)_4-\overset{\overset{O}{||}}{C}-NH-(CH_2)_6-NH\right)_n}$$

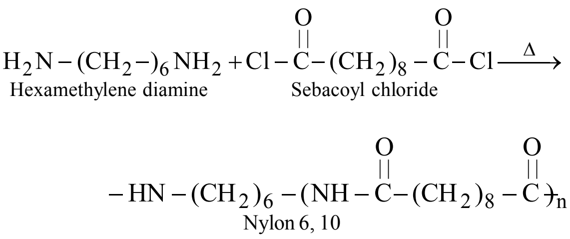
It has high tenacity and elasticity. It is resistant to abrasion and not affected by sea water. It is used for reinforcement of rubber tyres, manufacture of parachute, safety belts, carpets and fabrics.

(ii) ***Nylon 6:*** Homopolymer of caprolactam (6C)



Nylon-6

(iii) ***Nylon 6, 10*** - Copolymer of hexamethylene diamine (6C) and sebacoyl chloride (10C)

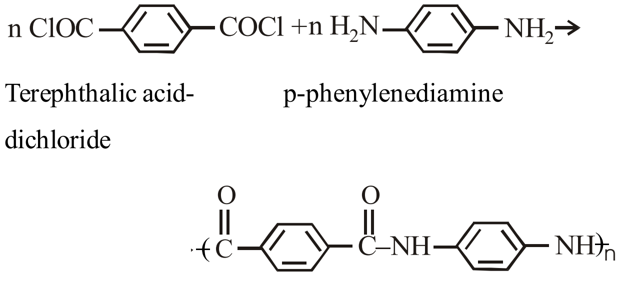


$$\underset{\text{Hexamethylene diamine}}{H_2N-(CH_2-)_6NH_2}+\underset{\text{Sebacoyl chloride}}{Cl-\overset{\overset{O}{||}}{C}-(CH_2)_8-\overset{\overset{O}{||}}{C}-Cl}\xrightarrow{\Delta}$$

$$\underset{\text{Nylon 6, 10}}{-HN-(CH_2)_6-\left(NH-\overset{\overset{O}{||}}{C}-(CH_2)_8-\overset{\overset{O}{||}}{C}\right)_n}$$

It is used for making brush bristlers

(iv) ***Kevlar:*** It is aromatic polyamide resembling nylons

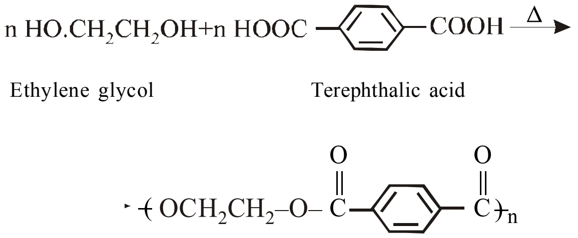


Kevlar

It is used in aircraft industries, bullet proof vests, helmets, ropes cables.

(B) **Polyesters:** Condensation polymers of a dibasic acid and a diol

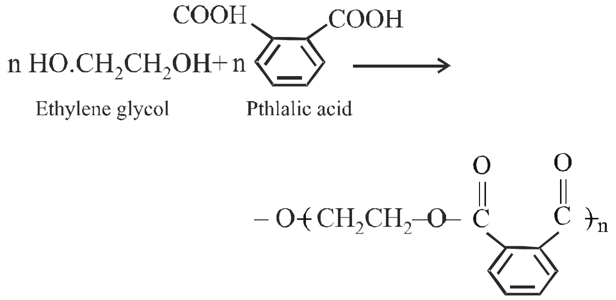
(i) ***Terylene*** (dacron) / Polyethylene Terephthalate (PET)



Terylene

It is resistant to mineral and organic acids. It is used for blending with wool to provide better crease, in safety helmets and aircraft battery boxes.

(ii) ***Glyptal or Alkyd resin*** (general name) **:** Condensation polymers of dibasic acids and polyhydroxy alcohols

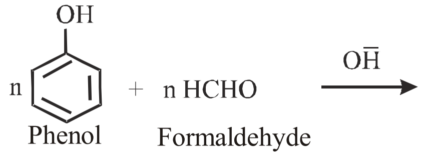


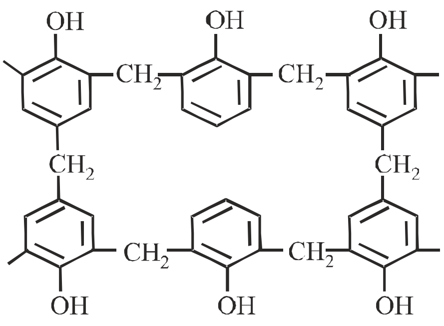
Glyptal

Cross linked copolymer; For making good insulators, sheets, rods, switches, lacquers and adherant paints.

(C) **Thermosetting resins:**

(i) ***Bakelite:*** Phenol formaldehyde resin





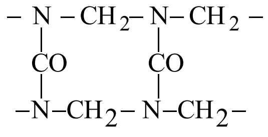
Bakelite

High degree polymerisation leads to rigid, hard, scratch resistant, infusible, attacked by alkalies phenolic resins. They are used for making switches, plugs telephone parts. Sulphonated bakelites are used as ion - exchange resins in water softening.

Low degree polymerisation gives bonding glue, preparation of varnishes and lacquers.

(ii) ***Urea formaldehyde resin***

$$\underset{\text{Urea (2 parts)}}{H_2N.CO.NH_2} + \underset{\substack{\text{form aldehyde}\\ \text{(1 part)}}}{HCHO} \xrightarrow{\text{basic medium}}$$

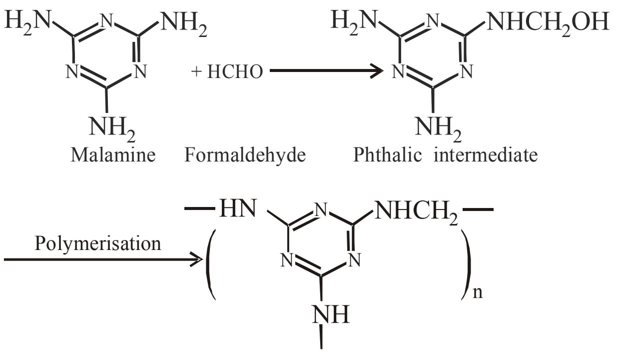


Urea formaldehde resin

(Crosslinked polymer)

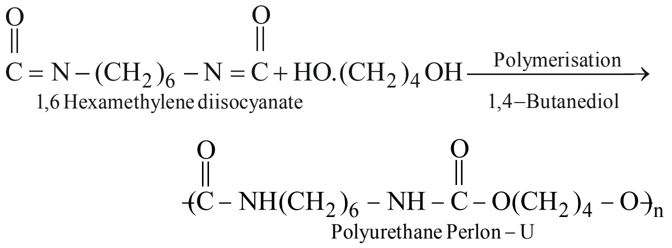
It is used for bonding grinding wheels, insulation, cation exchanger and decorative articles.

(iii) ***Melamine formaldehyde resins*** (MF resin)*:*



It is better than UF resin and used in making decorative laminates crockery under the trade name melmac, plywood industry as adhesive.

(iv) ***Polyuresthanes -*** Polymers of diisocyanate and diol eg. : Perlon-U



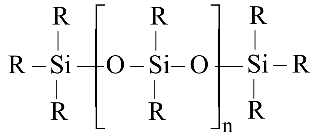
$$\underset{\text{1,6 Hexamethylene diisocyanate}}{\overset{O}{\overset{\|}{C}} = N-(CH_2)_6-N=\overset{O}{\overset{\|}{C}}} + \underset{\text{1,4–Butanediol}}{HO.(CH_2)_4OH} \xrightarrow{\text{Polymerisation}}$$

$$\underset{\text{Polyurethane Perlon – U}}{\left(\overset{O}{\overset{\|}{C}}-NH(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-O(CH_2)_4-O\right)_n}$$

It is substitute of leather. They are used as foams, films adhesives, gaskets etc.

SILICON RESINS :

Different organo-silicon chlorides can be polymerised by carefully controlled hydrolysis giving silicon resins. They contain alternate silicon oxygen structure.



where R = alkyl or phenyl radical

Silicones may be (a) liquid silicones or silicone oils (b) silicon greases (c) silicon rubbers (d) solid silicones.

RESIN :

Resin is a low molecular weight polymer used as binder, fusible and mouldable. It changes into infusible cross - linked form during moulding in presence of catalyst.

RAYON :

It is artificial silk. Actually the term includes all synthetic fibres manufactured from cellulose. The manufacturing can be carried out by

(i) Acetate process

(ii) Viscose process.

PLASTICIZERS :

The substances added to resins to increase their plasticity and flexibility are known as plasticizers. Examples are, vegetable oils (non drying), phosphates (tributyl phosphate, triphenyl phosphate etc), esters of oleic, stearic or phthalic acids and camphor etc.

RECLAIMED RUBBER:

Rubber obtained from waste rubber articles.

REINFORCED RUBBER OR PLASTIC:

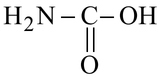
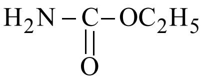
They are obtained by adding solid fillers. They are also known as filled plastics or rubbers.

Exercise-1 | NCERT BASED QUESTIONS

Very Short/Short Answer Questions

1. What does 'PMMA' stand for?
2. Give two examples of biopolymers.
3. Which of the following is a branched polymer:
4. Write the expression for number average molecular mass $(\overline{M}_n)$ (and weight average molecular mass $(\overline{M}_w)$.
5. Which is a better material for making PVC pipes — a thermoset plastic or a thermoplastic ?
6. Name a polymer that is used for making
   (*i*) non-stick wares (*ii*) non-breakable crockery
7. Write equations for the synthesis of (*a*) neoprene and (*b*) glyptal. Which one of the two is condensation polymer?
8. Write the information asked for the following polymers:
   (*a*) Bakelite – Materials used for preparation.
   (*b*) PVC – Monomer unit
   (*c*) synthetic rubber – Material required for preparation.
   (*d*) Nylon – 66 – Materials required for preparation.
9. PVC is quite a strong polymer in comparison to polyethene and polypropylene. Assign a suitable reason.
10. Why do the densities of low density polythene and high density polythene differ?
11. Give structures of monomers of the following polymers:
    (*i*) PVC (*ii*) Teflon (*iii*) PMMA
12. Differentiate between linear polymers and branched chain polymers.
13. How do double bonds in rubber molecules influence their structure and reactivity?
14. Distinguish between addition polymers and condensation polymers. Classify the following into addition and condensation polymers:
    (i) Polythene
    (ii) PTFE
    (iii) Polybutadiene
    (iv) Bakelite
15. Explain the following terms giving a suitable example for each:
    (i) Elastomers
    (ii) Condensation polymers
    (iii) Addition polymers
16. (a) What are the differences between thermosetting and thermoplastic polymers? Give one example of each.
    (b) Write down the structure of monomer and one use of the polymer polystyrene.
17. Write the names and structures of the monomers of the following polymers : 3
    (i) Buna-S
    (ii) Neoprene
    (iii) Nylon-6, 6
18. Write the names and structures of monomers of the following polymers: 3
    (i) Polystyrene
    (ii) Dacron
    (iii) Teflon

Multiple Choice Questions

19. Which is not true about polymers?
    (a) Polymers do not carry any charge
    (b) Polymers have high viscosity
    (c) Polymers scatter light
    (d) Polymers have low molecular weight
20. An example of biopolymer is
    (a) Teflon (b) Neoprene
    (c) Nylon-66 (d) DNA
21. The turbidity of a polymer solution measures
    (a) the light scattered by solution
    (b) the light absorbed by a solution
    (c) the light transmitted by a solution
    (d) none of the above
22. Which one of the following is not an example of chain growth polymer?
    (a) Neoprene (b) Buna-S
    (c) PMMA (d) Glyptal
23. Dimethyl phthalate and ethylene glycol react to form
    (a) Nylon-6 (b) Nylon-66
    (c) Dacron (d) Neoprene
24. Urethane is
    (a) $H_2N-C\equiv N$
    (b) 
    $H_2N-\underset{\underset{O}{\|}}{C}-OH$
    (c) $HO-C\equiv N$
    (d) 
    $H_2N-\underset{\underset{O}{\|}}{C}-OC_2H_5$
25. Rayon is :
    (a) synthetic plastic (b) natural rubber
    (c) natural silk (d) artificial silk

Exercise-2 | CONCEPTUAL MCQs

1. Which is not true about polymers?
(a) Polymers do not carry any charge
(b) Polymers have high viscosity
(c) Polymers scatter light
(d) Polymers have low molecular weight

2. Which is not a macromolecule?
(a) DNA (b) Starch
(c) Palmitate (d) Insulin

3. The turbidity of a polymer solution measures
(a) the light scattered by solution
(b) the light absorbed by a solution
(c) the light transmitted by a solution
(d) None of these

4. An example of biopolymer is
(a) teflon (b) rubber
(c) nylon-66 (d) DNA

5. On the basis of mode of formation, polymers can be classified
(a) as addition polymers only
(b) as condensation polymers only
(c) as copolymers
(d) Both as addition and condensation polymers

6. Which of the following polymers do not involve cross linkages?
(a) Melmac (b) Bakelite
(c) Polythene (d) Vulcanised rubber

7. The catalyst used for the polymerization of olefins is
(a) Ziegler-Natta catalyst (b) Wilkinson's catalyst
(c) Pd-catalyst (d) Zeise's salt complex

8. Polymer obtained by condensation polymerization is
(a) polythene (b) teflon
(c) phenol-formaldehyde (d) nitrile rubber

9. A condensation polymer among the following is
(a) dacron (b) pvc
(c) polystyrene (d) teflon

10. Which of the following is used in paints?
(a) Terylene (b) Nylon
(c) Glyptal (d) Chloroprene

11. Which of the following is not an example of addition polymer ?
(a) Polystyrene (b) Nylon
(c) PVC (d) Polypropylene

12. Which one of the following is not an example of chain growth polymer?
(a) Neoprene (b) Buna-S
(c) PMMA (d) Glyptal

13. Which of the following is an example of themosetting polymer?
(a) Polythene (b) PVC
(c) Neoprene (d) Bakelite

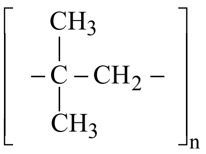
14. The process involving heating of rubber with sulphur is called
(a) galvanisation (b) vulcanization
(c) bessemerisation (d) sulphonation

15. Ebonite is
(a) natural rubber
(b) synthetic rubber
(c) highly vulcanized rubber
(d) polypropene

16. Natural rubber is a polymer of
(a) butadiene (b) ethyne
(c) styrene (d) isoprene

17. Teflon and neoprene are
(a) copolymers (b) condensation polymers
(c) homopolymers (d) monomers

18. $F_2C = CF_2$ is a monomer of
(a) teflon (b) glyptal
(c) nylon-6 (d) buna-s

19. Monomer of  is

$$\left[-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - CH_2 - \right]_n$$

(a) 2-Methylpropene (b) Styrene
(c) Propylene (d) Ethene

20. PVC is formed by polymerisation of
(a) 1-Chloroethene (b) Ethene
(c) Propene (d) 1-Chloropropene

21. Polyvinylalcohol can be prepared by
(a) polymerization of vinyl alcohol
(b) alkaline hydrolysis of polyvinyl acetate
(c) polymerization of acetylene
(d) reaction of acetylene with H_2SO_4 in presence of $HgSO_4$

22. Orlon is a polymer of
(a) styrene (b) tetrafluoroethylene
(c) vinyl chloride (d) acrylonitrile

23. Caprolactam polymerises to give
(a) terylene (b) teflon
(c) glyptal (d) Nylon-6

24. Which of the following is a polyamide molecule?
(a) Terylene (b) Rayon
(c) Nylon – 6 (d) Polystyrene

25. Polymer used in bullet proof glass is
(a) PMMA (b) Lexan
(c) Nomex (d) Kevlar

26. Interparticle forces present in nylon-66 are
(a) van der Waal's
(b) hydrogen bonding
(c) dipole-dipole interactions
(d) None of the above

27. Terylene is a condensation polymer of ethylene glycol and
(a) benzoic acid (b) phthalic acid
(c) salicyclic acid (d) terephthalic acid

28. Dimethyl phthalate and ethylene glycol react to form
(a) Nylon-6 (b) Nylon-66
(c) Dacron (d) Neoprene

29. Glyptal polymer is obtained from glycol by reacting with
(a) malonic acid (b) phthalic acid
(c) maleic acid (d) acetic acid

30. Bakelite is prepared by the reaction between
(a) phenol and formaldehyde
(b) ethylene glycol and dimethyl phthalate
(c) urea and formaldehyde
(d) tetramethylene glycol and hexamethylenediamine

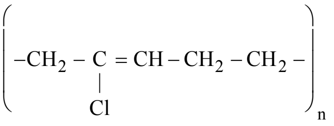
31. Soft drinks and baby feeding bottles are generally made up of
(a) Polystyrene (b) Polyurethane
(c) Polyurea (d) Polyamide

Exercise-3 | PAST COMPETITION MCQs

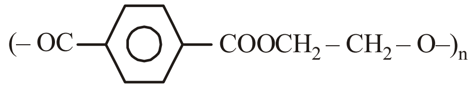
1. Which one of the following polymers is prepared by condensation polymerisation? **[CBSE PMT 2007]**
(a) Teflon (b) Natural rubber
(c) Styrene (d) Nylon-66

2. Which one of the following statements is *not true*? **[CBSE PMT 2008]**
(a) In vulcanization the formation of sulphur bridges between different chains make rubber harder and stronger.
(b) Natural rubber has the *trans* -configuration at every double bond
(c) Buna-S is a copolymer of butadiene and styrene
(d) Natural rubber is a 1, 4 - polymer of isoprene

3. Structures of some common polymers are given. Which one is **not** correctly presented? **[CBSE PMT 2009]**

(a) Neoprene; 
$\left(-CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2-CH_2-\right)_n$

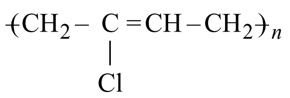
(b) Terylene;

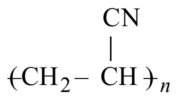


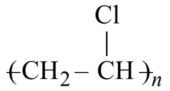
(c) Nylon 66; $[-NH(CH_2)_6NHCO(CH_2)_4CO-]_n$

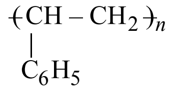
(d) Teflon; $(-CF_2-CF_2-)_n$

4. Which of the following structures represents neoprene polymer? **[CBSE PMT 2010]**

(a) 
$-\!\!(CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2)\!\!-_n$

(b) 
$-\!\!(CH_2-\overset{\overset{CN}{|}}{CH})\!\!-_n$

(c) 
$-\!\!(CH_2-\overset{\overset{Cl}{|}}{CH})\!\!-_n$

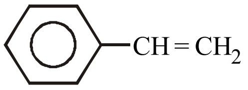
(d) 
$-\!\!(\underset{\underset{C_6H_5}{|}}{CH}-CH_2)\!\!-_n$

5. Of the following which one is classified as polyester polymer ? **[CBSE PMT 2011]**
(a) Terylene (b) Bakelite
(c) Melamine (d) Nylon-66

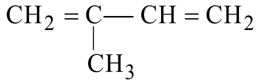
6. Which one of the following is not a condensation polymer ? **[CBSE PMT 2012 S]**
(a) Melamine (b) Glyptal
(c) Dacron (d) Neoprene

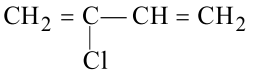
7. Which of the following statements is false? **[CBSE PMT 2012 S]**
(a) Artificial silk is derived from cellulose.
(b) Nylon-66 is an example of elastomer.
(c) The repeat unit in natural rubber is isoprene.
(d) Both starch and cellulose are polymers of glucose.

8. Which one of the following sets forms the biodegradable polymer? **[CBSE PMT 2012 M]**
(a) $CH_2=CH-CN$ and $CH_2=CH-CH=CH_2$
(b) H_2N-CH_2-COOH and $H_2N-(CH_2)_5-COOH$
(c) $HO-CH_2-CH_2-OH$ and

(d)  and $CH_2=CH-CH=CH_2$

9. Which is the monomer of Neoprene in the following ? [NEET 2013]

(a) 
$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2$

(b) 
$CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-CH=CH_2$

(c) $CH_2=CH-C\equiv CH$

(d) $CH_2=CH-CH=CH_2$

10. Nylon is an example of: [NEET 2013]

(a) Polysaccharide	(b) Polyamide
(c) Polythene	(d) Polyester

11. Polymer formation from monomers starts by [AIEEE 2002]

(a) condensation reaction between monomers

(b) coordinate reaction between monomers

(c) conversion of monomer to monomer ions by protons

(d) hydrolysis of monomers.

12. Nylon threads are made of [AIEEE 2003]

(a) polyester polymer	(b) polyamide polymer
(c) polyethylene polymer	(d) polyvinyl polymer

13. Which of the following is a polyamide? [AIEEE 2005]

(a) Bakelite	(b) Terylene
(c) Nylon-66	(d) Teflon

14. Which of the following is fully fluorinated polymer ? [AIEEE 2005]

(a) PVC	(b) Thiokol
(c) Teflon	(d) Neoprene

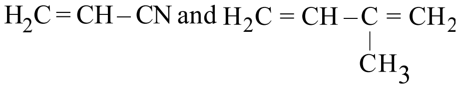
15. Bakelite is obtained from phenol by reacting with [AIEEE-2008]

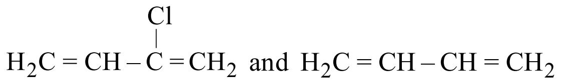
(a) $(CH_2OH)_2$	(b) CH_3CHO
(c) CH_3COCH_3	(d) HCHO

16. Buna-N synthetic rubber is a copolymer of: [AIEEE-2009]

(a) $H_2C=CH-CH=CH_2$ and $H_5C_6-CH=CH_2$

(b) $H_2C=CH-CN$ and $H_2C=CH-CH=CH_2$

(c) 
$H_2C=CH-CN$ and $H_2C=CH-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$

(d) 
$H_2C=CH-\overset{\displaystyle Cl}{\overset{|}{C}}=CH_2$ and $H_2C=CH-CH=CH_2$

17. The polymer containing strong intermolecular forces e.g. hydrogen bonding, is [AIEEE-2010]

(a) teflon	(b) nylon 6, 6
(c) polystyrene	(d) natural rubber

18. Among cellulose, poly (vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is [IIT-JEE 2009S]

(a) nylon	(b) poly (vinyl chloride)
(c) cellulose	(d) natural Rubber

Exercise-4 | Applied MCQs

1. Formation of polyethylene from calcium carbide takes place as follows

$$CaC_2+2H_2O\longrightarrow Ca(OH)_2+C_2H_2$$

$$C_2H_2+H_2\longrightarrow C_2H_4$$

$$nC_2H_4\longrightarrow(-CH_2-CH_2-)_n$$

The amount of polyethylene obtained from 64.1 kg of CaC_2 is

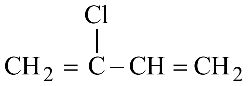
(a) 7 kg	(b) 14 kg
(c) 21 kg	(d) 28 kg

2. Ziegler-Natta catalyst is

(a) $K[PtCl_3(C_2H_4)]$	(b) $(Ph_3P)_3RhCl$
(c) $Al_2(C_2H_5)_6+TiCl_4$	(d) $Fe(C_5H_5)_2$

3. Which one of the following monomers gives the polymer neoprene on polymerization?

(a) $CCl_2=CCl_2$

(b) 
$CH_2=\overset{\displaystyle Cl}{\overset{|}{C}}-CH=CH_2$

(c) $CF_2=CF_2$

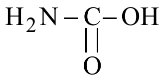
(d) $CH_2=CHCl$

4. Plexiglas (PMMA) is a polymer of

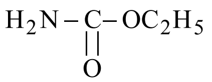
(a) acrylic acid	(b) methyl acrylate
(c) methyl methacrylate	(d) None of these

5. Urethane is

(a) $H_2N-C\equiv N$

(b) 
$H_2N-\underset{\displaystyle O}{\underset{||}{C}}-OH$

(c) $HO-C\equiv N$

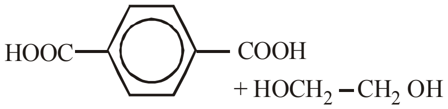
(d) 
$H_2N-\underset{\displaystyle O}{\underset{||}{C}}-OC_2H_5$

6. Which compound/set of compounds is used in the manufacture of nylon-66?

(a) $HOOC(CH_2)_4COOH+H_2N(CH_2)_6NH_2$

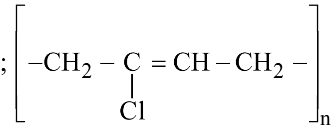
(b) $CH_2=CH-C(CH_3)=CH_2$

(c) $CH_2=CH_2$

(d) 

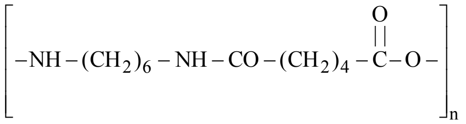
7. Which of the following is not correctly matched?

(a) Neoprene;



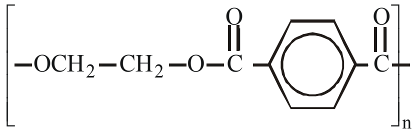
$$\left[-CH_2-\underset{Cl}{\underset{|}{C}}=CH-CH_2-\right]_n$$

(b) Nylon-66:

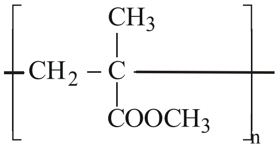


$$\left[-NH-(CH_2)_6-NH-CO-(CH_2)_4-\overset{O}{\overset{||}{C}}-O-\right]_n$$

(c) Terylene;



(d) PMMA :



$$\left[-CH_2-\overset{CH_3}{\overset{|}{\underset{COOCH_3}{\underset{|}{C}}}}-\right]_n$$

8. Match List-I (Monomer) with List II (Polymer) and select the correct answer using the codes given below the lists:

	List I	**List II**
I.	Hexamethylenediamine	A. Bakelite
II.	Phenol	B. Dacron
III.	Phthalic acid	C. Glyptal
IV.	Terephthalic acid	D. Melamine
		E. Nylon

Codes:

(a) I-E, II-A, III-B, IV-C
(b) I-E, II-A, III-C, IV-B
(c) I-D, II-C, III-A, IV-B
(d) I-D, II-C, III-A, IV-B

9. Which one of the following is used to make 'non-stick' cookware?

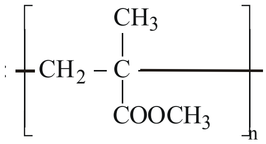
(a) PVC
(b) Polystyrene
(c) Poly (ethylene terephthalate)
(d) Polytetrafluoroethylene

10. Synthetic human hair wigs are made from a copolymer of vinyl chloride and acrylonitrile and is called

(a) PVC
(b) Polyacrylonitrile
(c) Cellulose
(d) Dynel

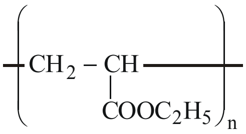
11. Acrilan is a hard, horny and a high melting material. Which of the following represents its structure?

(a)



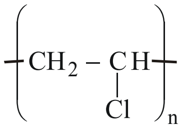
$$\left[-CH_2-\overset{CH_3}{\overset{|}{\underset{COOCH_3}{\underset{|}{C}}}}-\right]_n$$

(b)



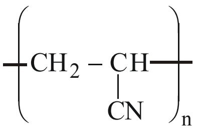
$$\left(-CH_2-\underset{COOC_2H_5}{\underset{|}{CH}}-\right)_n$$

(c)



$$\left(-CH_2-\underset{Cl}{\underset{|}{CH}}-\right)_n$$

(d)

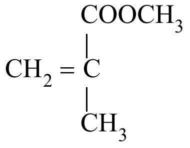


$$\left(-CH_2-\underset{CN}{\underset{|}{CH}}-\right)_n$$

Hints & Solutions

EXERCISE 1

1. PMMA stand for ‘poly methyl methacrylate’.
2. Starch and cellulose.
3. Low density polythene is a branched polymer.
4. $$\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \; ; \quad \overline{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$
5. Thermoplastic.
6. (*i*) Teflon (also known as PTFE).
   (*ii*) Melamine-formaldehyde resin.
8 (*a*) Phenol and formaldehyde
   (*b*) Vinyl chloride
   (*c*) chloroprene
   (*d*) Adipic acid and hexamethylene diamine.
9. The polarity of $C^{\delta+} — Cl^{\delta-}$ bond is responsible for its high strength.
11. (*i*) $CH_2=CHCl$ (*ii*) $F_2C=CF_2$ (*iii*)



$$CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle COOCH_3}{C}}$$

19. (d) **20. (d)** **21. (a)** **22. (d)** **23. (c)**
24. (d) **25. (d)**

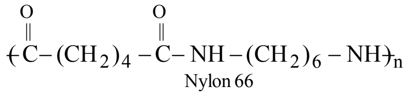
EXERCISE 2

1. (d)
2. (c) Palmitate is just a salt or an ester of palmitic acid (a fatty acid of the formula, $C_{15}H_{31}COOH$)
3. (a) Molecules of a polymer, being large in size, scatter light
4. (d) Deoxyribonucleic acid is a polymer found in living being
5. (d)
6. (c) Polythene is a linear polymer
7. (a)
8. (c) All other three polymers are obtained by addition polymerisation
9. (a)
10. (c)
11. (b) Nylon is a condensation polymer
12. (d) Glyptal is an example of a step growth polymer
13. (d)
14. (b)
15. (c) Ebonite is a hard highly vulcanized rubber, containing 20-30%, rubber
16. (d) **17. (c)** **18. (a)**
19. (a) Formula of the monomer indicated in bracket, $(CH_3)_2C=CH_2$, corresponds to 2-methylpropene
20. (a) P.V.C. (Polyvinyl chloride) is formed by polymerisation of vinyl chloride, $CH_2=CHCl$, whose IUPAC name is 1-chloroethene
21. (b) Vinyl alcohol, $CH_2=CHOH$, monomer of polyvinyl alcohol exists mainly as CH_3CHO ; hence polyvinyl alcohol is best prepared by the alkaline hydrolysis of polyvinyl acetate which in turn is prepared by the polymerisation of vinyl acetate
22. (d) Orlon is a trade name of polyacrylonitrile
23. (d) **24. (c)** **25. (b)**
26. (b) Nylon-66 is a polyamide having –CONH– ; oxygen of **CO** of amide linkage is linked to H of NH of the other –CO**NH**– linkage
27. (d) **28. (c)** **29. (b)** **30. (a)**
31. (a)

EXERCISE 3

1. (d) Copolymer of adipic acid (6C) and hexamethylene diamine (6C).

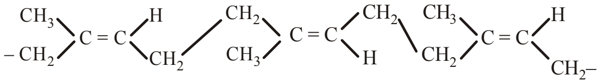
$$n\,\underset{\text{Adipic acid}}{HOOC(CH_2)_4COOH} + n\underset{\text{Hexamethylene diamine}}{H_2N(CH_2)_6NH_2} \rightarrow$$



$$\underset{\text{Nylon 66}}{\left(\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_4-\overset{\displaystyle O}{\overset{\|}{C}}-NH-(CH_2)_6-NH\right)_n}$$

It has high tenacity and elasticity. It is resistant to abrasion and not affected by sea water. It is used for reinforcement of rubber tyres, manufacture of parachute, safety belts, carpets and fabrics.

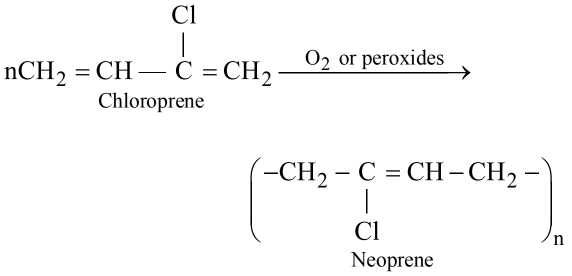
2. (b)



Natural rubber
(All cis configuration)

All statements except (b) are correct

3. (a) Neoprene is a polymer of chloroprene. Hence, correct representation is

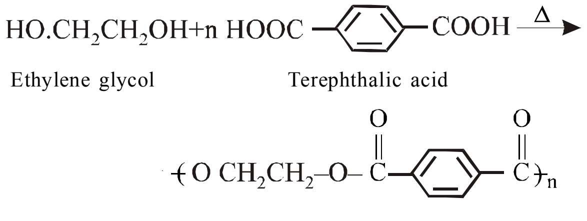


$$n\underset{\text{Chloroprene}}{CH_2=CH—\overset{\displaystyle Cl}{\overset{|}{C}}=CH_2} \xrightarrow{O_2 \text{ or peroxides}}$$

$$\underset{\text{Neoprene}}{\left(-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}=CH-CH_2-\right)_n}$$

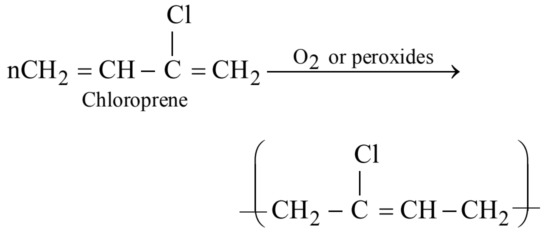
4. **(a)** Neoprene is a polymer of chloroprene (2 – chloro – 1, 3 – butadiene).

5. **(a)** Polyesters are condensation polymers of a dibasic acid and a diol. e.g., Terylene



Terylene

6. **(d)** Neoprene is an addition polymer of isoprene.



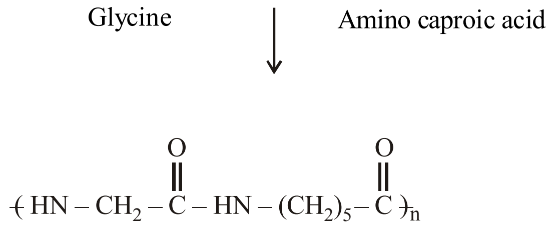
$$\underset{\text{Chloroprene}}{nCH_2 = CH - \overset{\overset{Cl}{|}}{C} = CH_2} \xrightarrow{O_2 \text{ or peroxides}} \left(CH_2 - \overset{\overset{Cl}{|}}{C} = CH - CH_2 \right)$$

Neoprene

7. **(b)** Nylon (polyamides) are fibres.

8. **(b)** Biodegradable polymer is Nylon-2- Nylon-6 which is copolymer of glycine ($H_2N - CH_2 - COOH$) and amino caproic acid ($H_2N{-}(CH_2)_5 - COOH$).

$nH_2N - CH_2 - COOH + nH_2N - (CH_2)_5 - COOH$

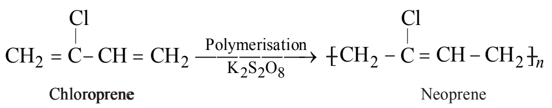


$$\underset{\text{Glycine}}{} \quad \downarrow \quad \underset{\text{Amino caproic acid}}{}$$

$$\left(HN - CH_2 - \overset{\overset{O}{\|}}{C} - HN - (CH_2)_5 - \overset{\overset{O}{\|}}{C} \right)_n$$

nylon – 2 – nylon – 6

9. **(b)** $\overset{\overset{Cl}{|}}{CH_2 = C} - CH = CH_2$ (chloroprene) is the monomer of neoprene.



$$\underset{\text{Chloroprene}}{CH_2 = \overset{\overset{Cl}{|}}{C} - CH = CH_2} \xrightarrow[K_2S_2O_8]{\text{Polymerisation}} \underset{\text{Neoprene}}{\left[CH_2 - \overset{\overset{Cl}{|}}{C} = CH - CH_2 \right]_n}$$

10. **(b)** Nylon is a synthetic polyamide polymer.

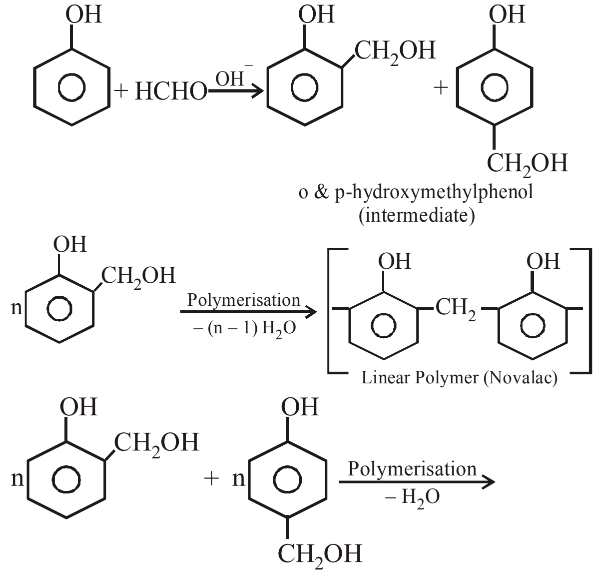
11. **(a)** Polymerisation starts either by condensation or addition reactions between monomers

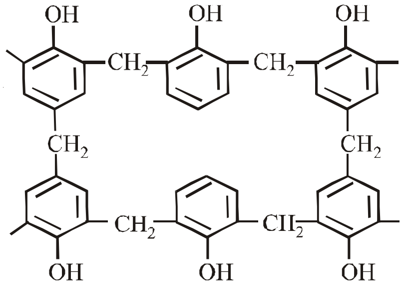
12. **(b)** Nylon is a polyamide polymer

13. **(c)** Nylon is a general name for all synthetic fibres forming polyamides.

14. **(c)** Teflon is polymer of $CF_2 = CF_2$.

15. **(d)** Phenol and formaldehyde undergo condensation polymerisation under two different conditions to give a cross linked polymer called bakelite.





Bakelite

16. **(b)** Buna – N is a copolymer of butadiene ($CH_2{=}CH{-}CH{=}CH_2$) and acrylonitrile ($CH_2 = CHCN$).

17. **(b)** Nylon 6, 6 has amide linkage capable of forming hydrogen bonding.

18. **(d)** Nylon and cellulose, both have intermolecular hydrogen bonding, polyvinyl chloride has dipole-dipole interactions, while natural rubber has van der Waal forces which are weakest.

EXERCISE 4

1. **(d)** The concerned chemical reactions are

(i) $\underset{64\,kg}{CaC_2} + 2H_2O \to Ca(OH)_2 + \underset{\text{Ethyne, 26kg}}{C_2H_2}$

(ii) $C_2H_2 + H_2 \to \underset{\text{Ethylene, 28 kg}}{C_2H_4}$

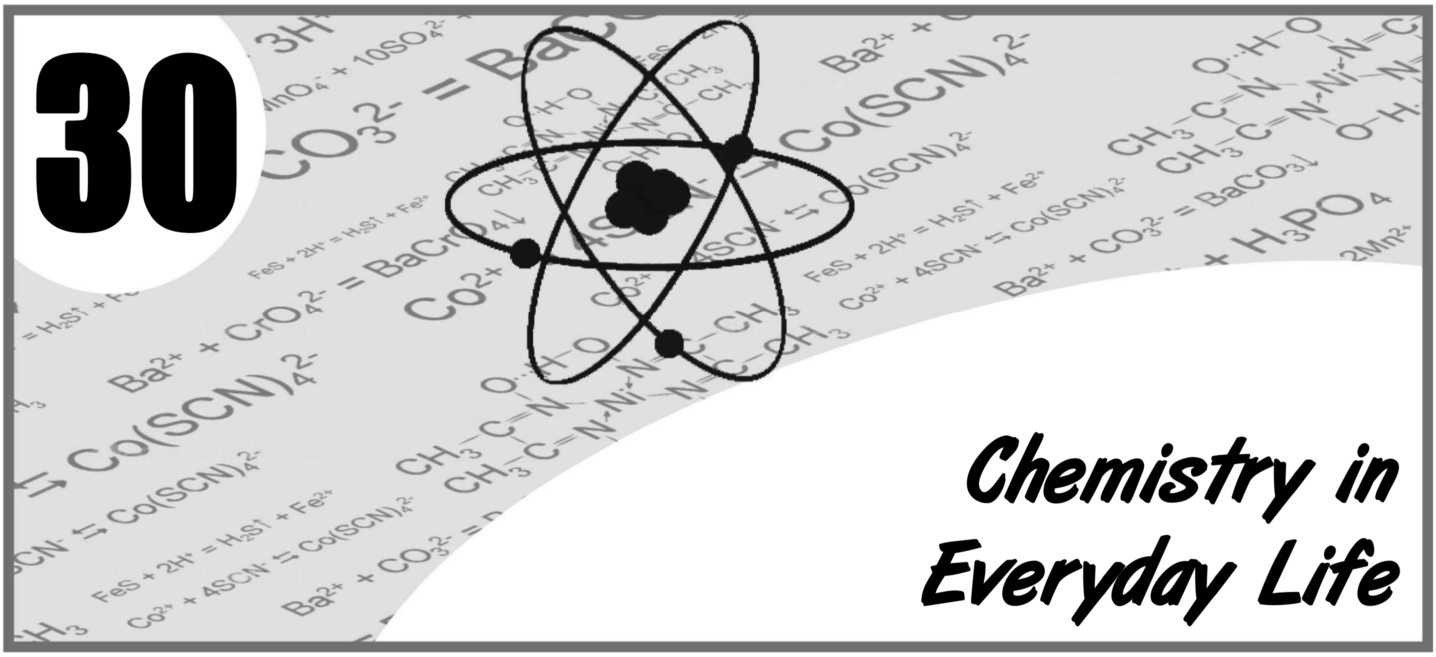
(iii) $\underset{\substack{n \times 28\,kg \\ \text{or } 28\,kg}}{nC_2H_2} \to \underset{\substack{n \times 28\,kg \text{ polythene} \\ \text{or } 28\,kg}}{[-CH_2 - CH_2-]_n}$

Thus 64 kg of CaC_2 gives 26 kg of acetylene which in turn gives 28 kg of ethylene whose 28 kg gives 28 kg of the polymer, polythene.

2. **(c)** 3. **(b)** 4. **(c)** 5. **(d)** 6. **(a)**

7. **(b)** Nylon-66 is a polyamide, hence it has only –CONH– linkage and no –COO– linkage

8. **(b)** 9. **(d)** 10. **(d)** 11. **(d)**



30

Chemistry in Everyday Life

DYES

DYE :

A synthetic or natural colouring matter to colour fabrics, plastics etc. The colour must be fast to the action of water, acid, alkalies, soap, light or friction. Every coloured substance is not a dye.

CHROMOPHORES :

The groups with multiple bonds responsible for the colour of the compounds eg. NO_2, NO, N = N, quinonoid structure etc.

AUXOCHROMES :

The groups that intensify the colour of the dye and confer the salt forming property to it eg - OH, $-NH_2$, $-SO_3H$, –COOH, OR, –NHR, $-NR_2$.

BATHOCHROMES :

The groups that deepen the colour.

HYPSOCHROMES:

The groups that lighten the colour.

ORDER OF DEEPENING THE COLOUR :

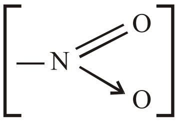
Yellow → Orange → Red → Purple → Blue → Green → Black.

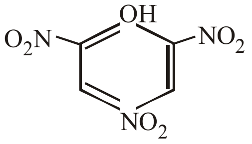
MORDANT :

A metal ion or a metal oxide that binds the fabric and the dye.

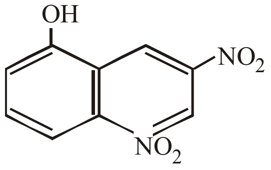
CLASSIFICATION ON THE BASIS OF CHEMICAL STRUCTURE :

(I) Nitro dyes





Picric acid

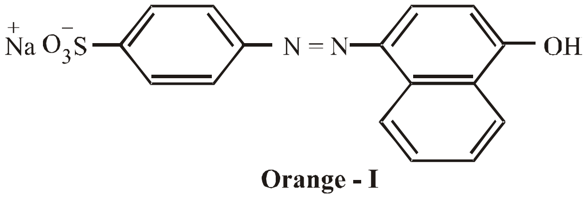


Martius yellow

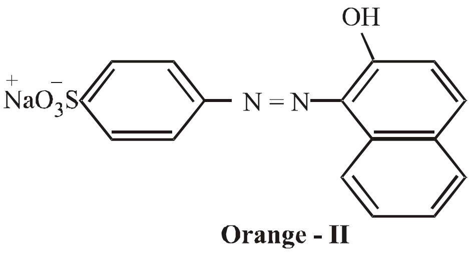
Prepared by the action of nitric acid on phenols, Naphthols and amines.

(II) Azodyes (– N = N –)

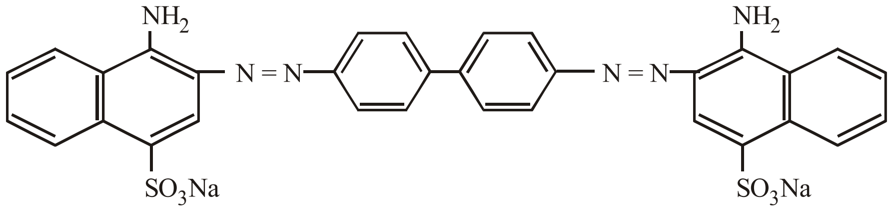
(a) Acidic azo dyes :



Orange - I

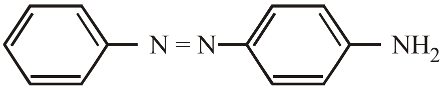


Orange - II

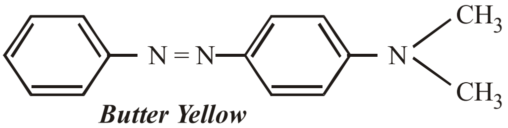


Congo Red

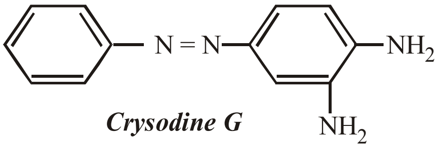
(b) ***Basic azo dyes***



Aniline Yellow

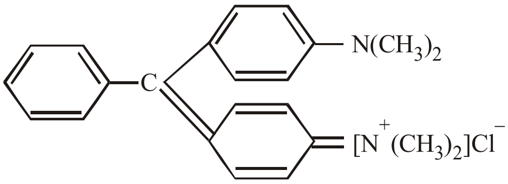


Butter Yellow

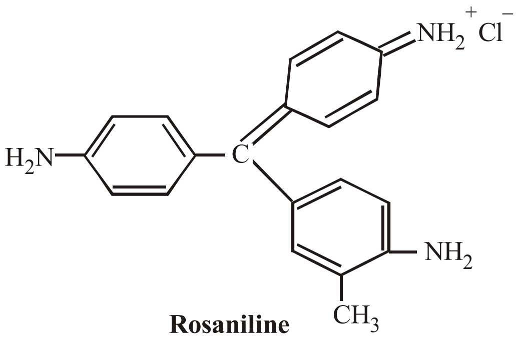


Crysodine G

(III) Triphenyl methane dyes :

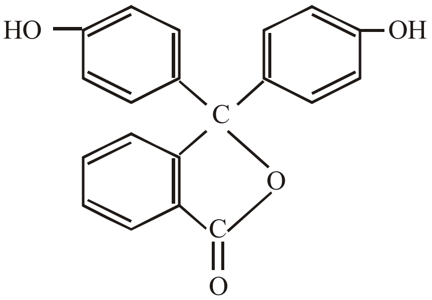


Malachite Green



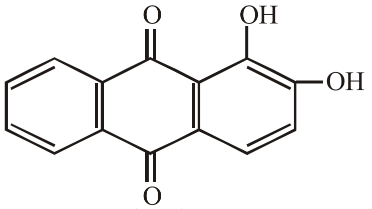
Rosaniline

(IV) Phthalein Dyes :



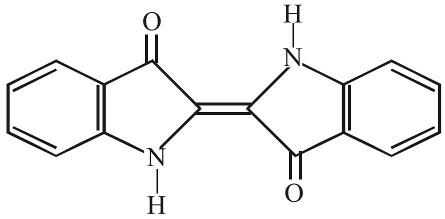
Phenolphthalein (indicator)

(V) Anthraquinone dyes :



Alizarin

(VI) Indigoid :



Indigo

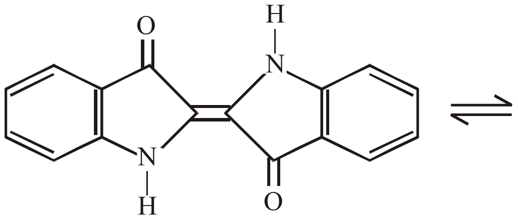
CLASSIFICATION ON THE BASIS OF APPLICATION:

(I) **Direct dyes:** Generally acidic and basic dyes directly applied to a fabric.

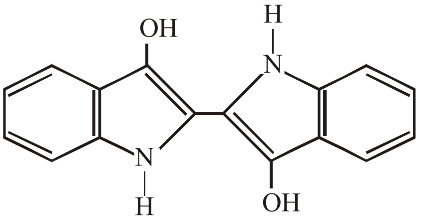
$$\text{Fibre} - NH_2 + HO - \text{Dye} \longrightarrow \text{Fibre} - NH_3^+ ....O^- - \text{Dye}$$

Congo red dyes cotton full red. Another example is Martius yellow.

(II) **Vat dyes :** They are used in their reduced state (leuco compound) and after application to the fabric, are oxidised to the dye e.g. Indigo.



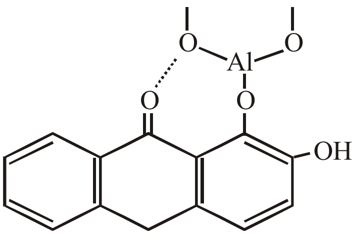
Indigo (blue)



Indigo white (Colourless)

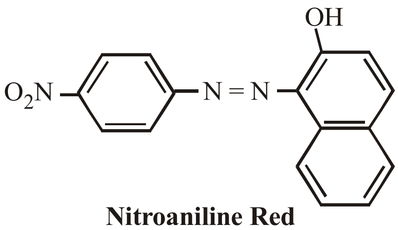
It binds to the cotton through H-bonding.

(III) Mordant dyes : Do not dye fabric directly, they require a mordant. For acidic dyes, a metal hydroxide and for basis dyes tannin (tannic acid) is required. The metal salts have been referred to as lakes.



Alizarin for Wool and nylon

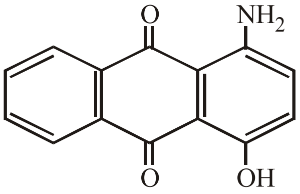
(IV) Ingrain dyes (Azoic dyes) : These are insoluble azo dyes and directly produced on the fibre. (Cotton or cellulosic). e.g. Nitro aniline red.



Nitroaniline Red

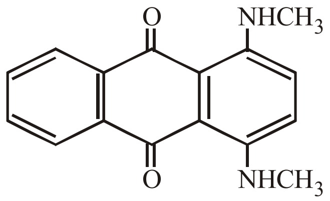
(V) Disperse dyes : These are water insoluble dyes and can be dispersed in colloidal form in water by suitable reagents. The fine dye particles are absorbed into the crystal structure of the fabric. These are used with synthetic fabrics Nylon, Polyester etc. Examples.

(a)



Celliton fast pink B

(b)



Celliton fast blue B

CHEMOTHERAPY

CHEMOTHERAPY :

Treatment of diseases by Chemicals having specific toxic effect upon the disease producing micro organisms without affecting the tissues of the host is called chemotherapy.

ANTISEPTICS :

The chemicals which prevent or check the sepsis of wounds. Examples are : ***dettol*** (chloroxylenol + terpeneol), ***Bithional*** (added to soaps). ***Salol, Acriflavin, Savlon, Gention violet, Mercuro Chrome, Salicylic acid, picric acid, resorcinol, phenol, iodoform, boric acid, iodine, methylene blue, potassium permanganate***.

DISINFECTANTS :

The chemical substances which completely destroy the micro organisms or stop their growth but are harmful to human tissues are called disinfectants. Examples are : ***1.0% phenol, SO_2*** in very low concentrations and chlorine in 0.2 to 0.4 ppm. They are used to disinfect floors, clothes, utensils etc.

ANTIPYRETICS :

They lower the body temperature i.e. fever reducing. Examples are : ***aspirin, paracetamol, phenacetin, analgin***.

ANALGESICS :

They are pain releiving. Examples are : ***Aspirin*** and ***analgin***, both are antipyretic and analgesics. **Novalgin** is most widely used analgesic.

Certain narcotics like ***Codeine, morphene, pethidine hydrochloride, methadone*** and ***heroin*** etc. are also used as analgesics.

TRANQUILIZERS :

Also called psycho-therapeutic drugs, reduce anxiety, induce sleep, and cure mental diseases. Examples are : ***Barbituric acid*** and its derivatives, ***seconal, luminal, Methyldopa*** and ***Hydralazine, Equanil, Chlordiozepoxide***.

SEDATIVES AND HYPNOTICS :

They are central nervous system depressants reduce restlessness, emotional tension and induce sleep. Examples are : ***Phenobarbital, Glute thimide, Valium, Veronal, Serotonen*** etc.

ANTIANXIETY AGENTS :

Examples are : ***Meprobamate*** and ***Diazepam, Iproniazid, Phenolzine*** (Nardic)

Tranquilizers, Sedatives & Hypnotics and **Antianxiety agents** are central nervous system stimulants.

ANAESTHETICS :

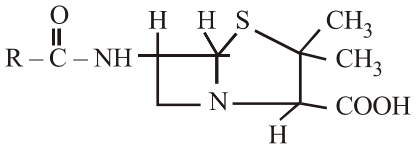
The chemical substances which produce insensibility to the vital functions of all types of cell especially of nervous system temporarily are called anaesthetics. Examples are, **General anaesthetics** - ***Chloroform, Fluothane***, **Local anaesthetics** - ***Cocaine, α-Eucaine, β-Eucaine***.

NARCOTICS :

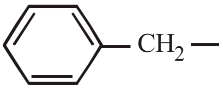
The chemical substances which act as depressant and analgesic. Examples : ***Heroin, Opium*** and ***Pethedine***.

ANTIBIOTICS :

The chemical substances produced by micro-organisms or by chemical synthesis that inhibit the growth of bacteria (bacteriostatic)or even destroy (bacteriocidal) them are called antibiotics. Examples : Penicillin is the first antibiotic discovered by Alexander Fleming. It is effective against pneumonia, bronchitis and sore throat etc.



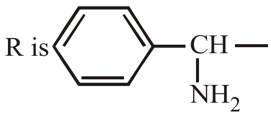
when R is

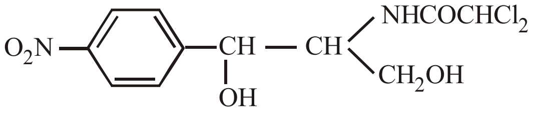


Penicillin G or Benzyl penicillin

R is $CH_3CH_2.CH = CH - CH_2 -$ Penicillin F

R is $CH_3 - (CH_2)_6 -$ Penicillin K


Ampicillin



Chloramphenicol.

Spectrum : The complete range of micro organism that can be killed by a particular antibiotic is known as spectrum. These are of following types:

(i) **Narrow Spectrum antibiotics :** Streptomycin, Chloromycetin.

Streptomycin tuberculosis is used in treatment

(ii) **Broad Spectrum antibiotics :** Chloramphenicol, Tetracyclin

Chloramphenicol is used in the treatment of ***typhoid, dysentry, whooping cough,*** certain primary infections and ***meningitis***.

Ampicillin though works against large number of diseases, induces allergy. Hence allergy test is must before its administration.

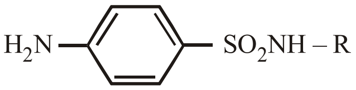
Examples of the types of antibiotics are

(i) Bacteriocial (Killing) – Aminoglycosides, Ofloxacin and Penicillin.

(ii) Bacteriostatic (inhibitory) – Tetracyclin, Erythromycin and chloramphenical

SULPHA DRUGS :

Sulpha drugs possess powerful bacteriostatic property due to Sulphanylamido group.



Sulphadiazine (Sulpha pyrimidine) : For pneumonia, rheumatic fever and bacillary dysentery etc.

Sulphanilamide : For pneumonia, urinary and respiratory infections.

Sulphathiazole (Cibazole) : For staphylococci infections, bubonic plague.

Sulpha acetamide : For urinary tract infections.

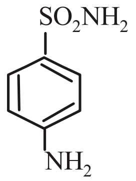
ANTIMALARIALS :

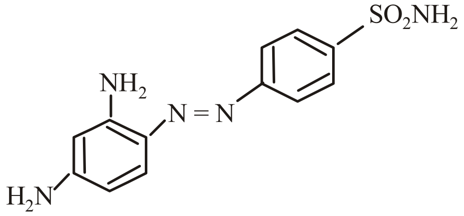
These are the drugs which cure malaria. Examples are : ***Plasmoquin (Plasmochin),*** **Atebrin** (Mepacrine), **Chloroquine**.

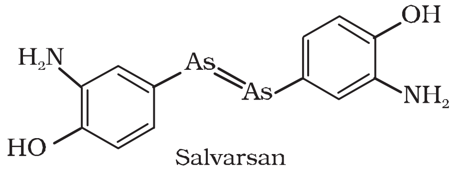
ANTIMICROBIALS

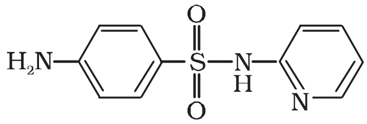
Antimicrobials are the drugs which are used to cure diseases caused by microbes or micro- organisms. An antimicrobial may control the microbials diseases as a bactericidal drug (kill the micro-organisms in the body) or as a bacteriostatic drug (inhibit the growth of micro-organiasms) or by increasing resistance of the body to infections.

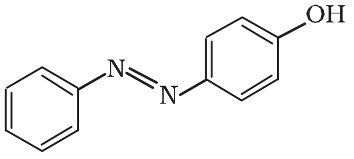
Examples are:


Sulphanilamide


Prontosil


Salvarsan


Sulphapyridine

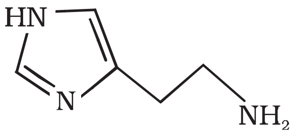

Azodye

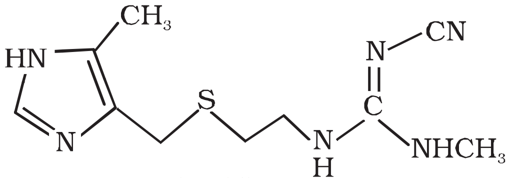
ANTACIDS

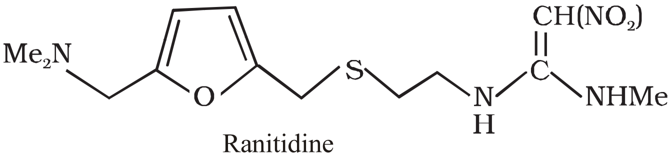
Antacids are the drugs which neutralize excess acid in the gastric Juices and give relief from acid indigestion. They remove the excess acid and raise the pH to appropriate level in stomach. There are mainly weak bases.

Examples– $Mg(OH)_2$, $KHCO_3$

Omeprazole, Lansoprazole, Histamine, Cimetidine and Ranitidine.

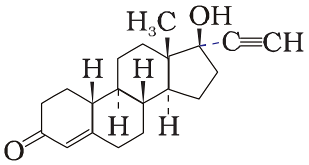

Histamine

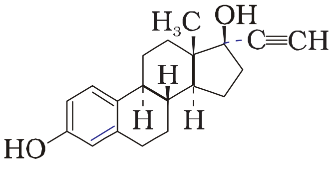

Cimetidine


Ranitidine

ANTIFERTILITY DRUG

The drugs which are used to control the pregnancy are known as Antifertility drugs or oral Contraceptives. These are essentially a mixture of estrogen and progesterone derivatives. *Examples* – Ormeloxifene, mixpristone, Norethindrone, Ethynylestrodiol (nonvestrol).


Norethindrone


Ethynylestradiol (novestrol)

ANTIHISTAMINES

Antihistamines are the drugs which diminsh the main action of histamine (Chemical substance which cause allergic reactions in body) released in the body and thus prevent the allergic reactions. These are also anti-allergic drugs. Examples diphenydramine (Banadry) hydiochlorid, Pheniramine maleate (Avil), Brompheniramine (Dimetapp); terfenadine (seldane), etc.

ROCKET PROPELLANTS

ROCKET PROPELLANTS :

Rocket propellant is a combination of a fuel and an oxidiser which when ignited generates a large volume of hot gases at a predetermined rate.

SOLID PROPELLANTS :

(I) **Composite propellants :** Fuel is a synthetic rubber or resin such as polyurethane or polybutadiene with additives such as Al or Mg. Oxidiser is Ammoniumperchlorate, potassiumperchlorate or Amm. nitrate.

(II) **Double base propellant :** Mixture of nitroglycerine and nitro cellulose.

In solid propellants ignition can not be controlled.

LIQUID PROPELLANTS :

(I) **Biliquid propellants :** Fuel is Kerosene, Alcohol, Hydrazine, Monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH), liquid hydrogen. Oxidiser is liquid oxygen, dinitrogen tetraoxide or nitric acid.

(II) **Monopropellants :** Nitromethane, methyl nitrate hydrazine, and hydrogen peroxide. They act as fuel as well as oxidiser.

Advantages : (i) They provide higher thrust than solid propellants. (ii) Thrust can be controlled.

HYBRID PROPELLANTS :

Fuel is solid acrylic rubber and oxidiser is dinitrogen tetraoxide.

REQUIREMENTS OF GOOD PROPELLANT :

Production of large volume of gases per gm of fuel and no residue left.

SOAPS AND DETERGENTS

DETERGENT :

(Lo detergere = to wipe clean). Any cleansing agent including soap as well.

SYNDETS :

Synthetic detergents.

SOAPS :

Metallic salts of higher fatty acids. Common higher fatty acids are palmitic acid $C_{15}H_{31}COOH$, stearic acid $C_{17}H_{35}COOH$ and oleic acid $C_{17}H_{33}COOH$.

HARD SOAPS :

Sodium salt of higher fatty acids prepared from cheap oils contain free alkali also.

SOFT SOAPS :

Potassium-salts of higher fatty acid.

TRANSPARENT SOAPS :

They contain glycerol and prepared by dissolving toilet soaps in ethanol.

MEDICATED SOAPS :

Soaps containing antiseptics, germicides etc.

MARINE SOAPS :

Prepared from coconut oil and gives lather with sea water.

CLEANING ACTION OF SOAPS :

It may be due the following two factors

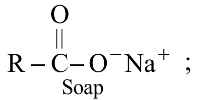
(i) Solubilisation of grease into the micelle

(ii) Emulsification of grease

When soap is applied on to a fabric, the tails of the soap anions are pegged ino the grease stains and polar head form a charged layer around it. By mutual repulsion the grease droplets are suspended in water (formation of emulsion) and are washed away with water.

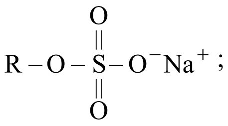
DETERGENTS :

Sodium salts of alkyl hydrogen sulphates or long chain alkyl benzene sulphonic acids.



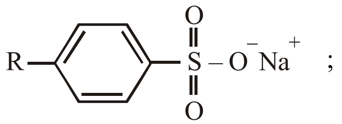
$$R-\overset{\overset{O}{\|}}{C}-O^-Na^+ \;;$$

Soap
Sodium Carboxylate

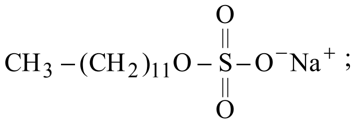


$$R-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O^-Na^+ \;;$$

Sodium alkyl Sulphate
Detergent

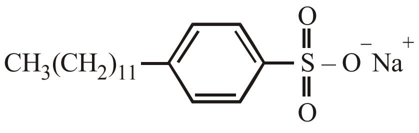

Sodium alkyl benzene sulphonate
Detergent

ANIONIC DETERGENTS :



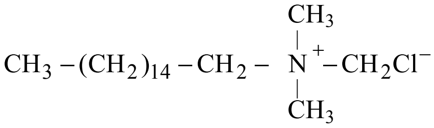
$$CH_3-(CH_2)_{11}O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O^-Na^+ \;;$$

Sodium lauryl sulphate


Sodium p-n-dodecyl benzene-Sulphonate

CATIONIC DETERGENTS / INVERT DETERGENTS :

Soluble cation.



$$CH_3-(CH_2)_{14}-CH_2-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_2Cl^-$$

n–hexadecyl–trimethyl ammonium chloride

NONIONIC DETERGENTS :

Monoesters of polyhydroxy alcohols or polyethens.

SUPERIORITY OF DETERGENTS TO SOAPS :

With hard water soaps form insoluble Ca and Mg carboxylates. Detergents form Ca and Mg soluble salts.

CLEANSING ACTION OF DETERGENTS:

The cleansing action of detergents are same as that of soaps. For example. A detergents, Sodium lauryl sulphate, $CH_3(CH_2)OSO_3Na$, Contains the polar group OSO_3^- alongwith the long hydrocarbon chains. It is an animic detergent in which anions associate together to form an ionic micelle. Similarly, Cationic detergent also forms micelle.

CHEMICALS IN COSMETICS

Cosmetics : Cosmetics are the substances used to improve a persons appearance by beautifying and improving complexion of skin. Cosmetics include :

CREAMS :

Creams are semi-solid preparations applied on the face to prevent the skin from drying and to provide necessary moisture, nutrients and vitamins to keep it healthy.

The creams are of the following types :

(i) ***Cold Creams :*** These are water in oil type emulsions containing vegetable or mineral oil, fat, bees wax, lanolin (perfume), borax and emulsifier. They serve as moisturiser, lubricate the skin and protect it against wind.

(ii) ***Vanishing Creams :*** These contain stearic acid, alkali water and humecant (glycerine). These keep the skin cool and oily. Vanishing cream provides a thin film on the skin having higher melting point than skin temperature and it seems to disappear (vanish).

(iii) ***Cleansing Creams :*** These remove facial make up, surface grime (sooty dirt) and oil.

(iv) ***Bleach cream :*** These bleach the skin to make it appear fair.

(v) ***Sunburn creams :*** These save the skin from sun burn in summer.

(vi) ***Foundation creams :*** These provide a base for powder and make-up.

TALCUM POWDERS :

Talc is a soft mineral having form of magnesium silicate $3MgO.4SiO_2.H_2O$. In the powder form it is used on the skin to make it feel smooth, dry and irritation free which is known as talcum powder. Modern face powders and baby powder protect skin from heat, absorb perspiration and impart brightness to skin by covering blemishes and imperfections.

The important ingredients of the talcum powders are:

(i) ***Talc*** or ***talcum*** which is hydrated magnesium silicate $3MgO.4SiO_2.H_2O$. Since talcum causes inflammation to skin by forming silicic acid, therefore aluminium hydrolicate is prefered.

(ii) ***Adherants :*** Zn and Mg soaps e.g. Zinc stearate

(iii) ***Absorbents :*** Chalk (Ca and Mg Carbonates) absorbs perspiration without any sign of absorption.

(iv) ***To provide apacity :*** ZnO, TiO_2 and collidal clay and used. These mask the enlarged pores and minor blemishes and protect the skin from UV radiations.

(v) ***Specific ingredients :*** Cooling agents and antiseptics *eg.* boric acid, etc.

Baby powders generally contain Zinc stearate as adhesive and boric acid as antiseptic. The particle size of good talcum should be more than 70 micron.

DEODORANTS :

The substances which remove or conceal unpleasant bodily smells are known as deodorants. They generally possess antibacterial properties and prevent bacterial decomposition of sweat by inhibiling, killing or removing the bacteria responsible for unpleasant body odours. Some deodorants mask the unpleasant body odours with more pleasant fragrances. Aluminium salts such as aluminium sulphate, aluminium chloride, aluminium hydroxy chloride, aluminium alcoholate, aluminium chlorohydroxy acetate possess excellant antibacterial properties.

In addition to aluminium salts zinc oxides (ZnO, ZnO_2) and zinc strearate are used since they are astringents (check bleeding) and antiseptics.

Phenolic antibacterials viz. p-chlorometaxylenol, dichlorometaxylenol and bithional are used in soaps, creams, baby powders, shaving lotions as body deodorants.

PERFUMES:

A perfume may be defined as a mixture of pleasant smelling substances incorporated in a suitable solvent. It is composed of three ingredients given as follows :

(i) ***Vehicle or solvent -*** To keep the pleasant smelling substances together a solvent is required which is also known as vehicle. Water-ethanol mixture is the most common vehicle which is volatile, odourless and non irritant.

(ii) ***Fixative :*** The substance which equalise the rate of evaporation of various adouriferous or odour producing components of the perfume. The fixatives may be

   (a) *Essential oil fixatives :* Sandal wood (most common), orris patchouli, vetine etc.

   (b) *Animal fixatives :* Musk, civet, ambegris castor etc.

   (c) *Resinous fixatives :* Benzoin, tolublasam, perublasam, terpenoids etc.

   (d) *Synthetic fixatives* : Glyceryl diacetate, benzyl benzoate, ethyl phthalate etc.

(iii) ***Odouriferous substances :*** These may be natural or synthetic.

NATURAL PERFUMES :

They are obtained from plants and animals. eg. essential oils (terpenes) linalool, limonene, camphor, pinene, geraniol, citronellol eugenol, cineole, citral, bantalol. The perfumes derived from animal sources are muscone, civet, caster musk, ambegris, musk zibata etc.

SYNTHETIC OR SEMISNYTHETIC PERFUMES :

(i) ***Esters :*** Esters of benzyl alcohol, cinnamic acid, salicylic acid. Common are benzyl propionate, isobutyrate, methyl salicylate (oil of wintergreen), benzyl cinnamate

(ii) ***Alcohols :*** 2-hexenol, 3-hexenol, phenyl ethyl alcohol.

(iii) ***Nitro*** compounds such as musk xylene and musk ambrette.

(iv) ***Aldehydes :*** Anisaldehyde (p-methoxy benzaldehyde) and cinnamaldehyde etc.

(v) ***Biphenyls :*** Biphenyl ether, biphenyl methane.

(vi) ***Ketones :*** Exaltone, benzophenone.

CHEMICALS IN FOOD :

Food additives :

The chemicals, synthetic or natural substances added to food preparations for different purposes as given below are known as food additives.

(i) ***Nutrients :*** To increase the nutritive value of the food eg. carbohydrates, proteins etc.

(ii) ***Preservatives :*** To retard spoilage from bacterial action. eg. $NaNO_2$ and $NaNO_3$ (in meat), C_6H_5COONa (in tomato katchup, fruit juices), Sodium metabisulphite (in pickles), Citric acid (fruit drinks), Sodium propionate (in bread and chease) and SO_2 (in wine and juices).

(iii) ***Flavour agents :*** To enhance the flavour or to develop flavour eg. alkyl alkanoates (esters), mono-sodium glutamate (MSG), vanillin, cinnamaldehyde.

(iv) ***Antioxidants :*** To exclude oxygen to retard or prevent spoilage eg. BHT (Butylated hydroxy toluene) and BHA (Bulylated hydroxy anisole).

(v) ***Sweetners :*** To add sweet taste eg. saccharin aspartame, sucralose.

(vi) ***Colourants :*** To give colour eg. Amarnath, Kesar etc.

CERAMICS :

They are inorganic, non metallic materials made of clay that is permanently hardned by heat at high temperature.

CLAY :

Certain earths, which are highly plastic when wet and converted to hard mass when heated which is unaffected by water. Clay is essentially hydrated aluminium silicate ($Al_2O_3.2SiO_2.2H_2O$). Clay with a low content of iron is usually white, so it burns white and is called *Kaolin* or *China Clay*.

TYPES OF CERAMICS :

broadly they are of three types:

(i) ***Clay products :*** porcelain, pottery, sanitary fittings, tiles, sewer pipes etc.

(ii) ***Refractories :*** Refractory bricks used as furnance linings

(iii) ***Glasses :*** Kitchenware

REFRACTORY :

Any material that can withstand high temperature without softening or suffering from deformation in shape.

CLASSIFICATION OF REFRACTORIES :

They have been classified into three main types

(i) ***Acid refractories :*** Which consists of acidic material like SiO_2, Al_2O_3. They are attacked by basic materials.

(ii) ***Basic refractories :*** Which consists of basic materials like CaO, MgO and attacked by acidic materials.

(iii) ***Neutral refractories :*** They are made from weakly acid/base materials like Zirconia ZrO_2, Carbon, Chromite (FeO, CrO_2).

(iv) ***Abrasive Ceramics :*** The silicon and tungsten carbides are very hard and used as cutting and grinding tools.

(v) ***Super conducting ceramics :*** These consists of mixture of oxides of metals eg. Yttrium Oxide, barium oxide, copper oxide, etc. They are used to electrical power transmission, building powerful magnets, navigation transportation, nuclear fusion experiments.

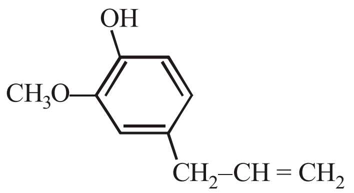
INSECT ATTRACTANTS/REPELLENTS

Sex attractants / pheromones :

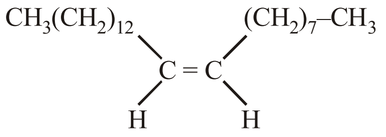
These are chemical substances secreted by insects used as signals (peculiar odour, colour etc.) by the other members of the same family. These are very powerful and required in very small amount (10^{-10}–10^{-20}g/cm^3). Some common sex attractants are as follows :

(a) **Bomby Kol** (1-hydoxy-trans 10-cis-12-hexadecane-diene). It is secreted by the abdominal cells of the silk worm moth.

(b) **Eugenol**



(c) **Muscaline** or (Z)-9-Tricosene

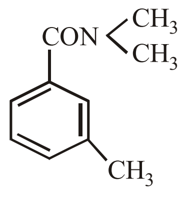


(d) **9-oxo-trans-2-decenoic acid.**
It is queen-bee sex attractant.

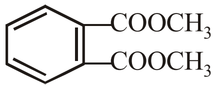
(e) **Dispariline :** secreted by female gypsy moth.

INSECT REPELLENTS :

These are chemical substances used to drive out the troublesome insects rather than killing them. The following are common mosquito repellent



N, N-dimethyl-3-methylbenzamide



Dimethyl phthalate

Di-n-propyl-2. S-pyridinedicarboxylate is used or housefly repellent.

Pest control : By the use of sex attractants particular insects can be collected at one place and later killed by usual insecticides without killing the desired insects which are otherwise useful.

Exercise-1 | NCERT BASED QUESTIONS

Very Short/Short Answer Questions

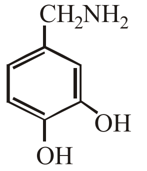
1. Name the antibiotic used specifically for treatment of typhoid fever.
2. Pick out the odd one from among the following compounds on the basis of their medicinal properties mentioning the reason:
   Luminal, seconal, phenacetion, equanil.
3. What type of drugs are omeprazole and lansoprazole?
4. Name a drug used for relieving pains and also for the prevention of heart attack.
5. Name the chemicals responsible for the antiseptic properties of dettol.
6. Sulpha drugs work like antibiotics but they are not antibiotics. Is this a valid statement and why? Give one example each of sulpha drugs and antibiotics.
7. What do you understand by 'broad spectrum antibiotics'? Is penicillin a broad spectrum antibiotic? Name a place in India where penicillin is manufactured.
8. Give IUPAC name of aspirin. Why should it not be taken on an empty stomach? Suggest a substitute of aspirin.
9. Classify the following as analgesic, tranquilizer or antiseptic: Valium, hydrogen peroxide, chlorodiazepoxide, ibuprofen, diclofenac, luminal.
10. Sleeping pills are recommended by doctors to the patients suffering from sleeplessness but it is not advisable to take its doses without consultation with the doctor. Why?
11. Why do drugs designed to cure ailments in one body organ not affect other body parts?
12. What are the consequences of using non-biodegradable detergents?
13. (a) Differentiate between a disinfectant and an antiseptics. Give one example of each.
    (b) What is tincture of iodine and what is it used for?
14. Explain the following terms giving one example of each type.
    (i) Antacids (ii) Disinfectants (iii) Enzymes
15. What are the following substances? Give one example of each.
    (i) Analgesics
    (ii) Antibiotics
    (iii) Tranquilizers.
16. (a) Which one of the following is a food preservative? Equanil, Morphine, Sodium benzoate
    (b) Why is bithional added to soap?
    (c) Which class of drugs is used in sleeping pills?
17. (i) What class of drugs in Ranitidine?
    (ii) If water contains dissolved Ca^{2+} ions, out of soaps and synthetic detergents, which will you use for cleaning clothes?
    (iii) Which of the following is an antiseptic? 0.2% phenol, 1% phenol

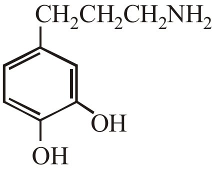
Long Answer Questions

18. What are tranquilizers? Give examples. How do they act on body? What precautions are kept in view for their use?
19. Name the three important antipyretics and write their structural formulae.
20. What are biodegradable and non-biodegradable detergents? What are the consequences of using latter class of detergents?
21. What are detergents? How are they classified? Why are detergents preferred over soap?

Multiple Choice Questions

22. Antiseptic chloroxylenol is
    (a) 4-chloro-3, 5-dimethylphenol
    (b) 3-chloro-4, 5-dimethylphenol
    (c) 4-chloro-2, 5-dimethylphenol
    (d) 5-chloro-3, 4-dimethylphenol
23. The bacteriostatic antibiotic among the following is
    (a) Erythromycin (b) Penicillin
    (c) Aminoglycoside (d) Ofloxacin
24. The drug used as an antidepressant is
    (a) Luminol (b) Tofranil
    (c) Mescaline (d) Sulphadiazine
25. Parkinson's disease is linked ot abnormalities in the levels of dopamine in the body. The structure of dopamine is

(a)


(b)


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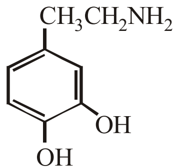
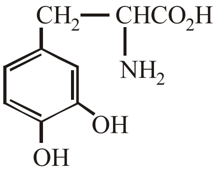
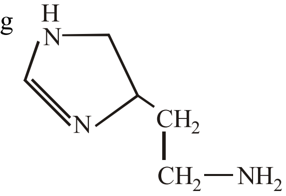


(d)


26. Arsenic drugs are mainly used in the treatment of
    (a) Jaundice (b) Typhoid
    (c) Syphilis (d) Cholera
27. Which of the following is not a broad spectrum antibiotic
    (a) Tetracycline (b) Chloromycetin
    (c) Penicillin (d) None of these
28. The drug



is used as
    (a) Antacid (b) Analgesic
    (c) Antimicrobial (d) Antiseptic
29. An example of a psychedelic agent is
    (a) DNA (b) LSD (c) DDT (d) TN

Exercise-2 | CONCEPTUAL MCQs

1. Detergents are prepared by the action of H_2SO_4 followed by neutralization by starting with
(a) chloesterol (b) lauryl alcohol
(b) cyclohexanol (d) p- nitrophenol

2. During the deepening of the colour of a dye, the absorption shifts towards red. This shifting is called
(a) bathochromic shift (b) hypsochromic shift
(c) hyperchromic shift (d) auxochromic shift

3. 2, 4, 6-Trinitrophenol is a/an
(a) acid dye (b) basic dye
(c) azo dye (d) vat dye

4. Which of the following is a basic dye ?
(a) alizarin (b) phthalein
(c) aniline yellow (d) orange-I

5. The substance used in the preparation of malachite green is
(a) formaldehyde (b) acetaldehyde
(c) benzaldehyde (d) acetone

6. The indicator used in the titration of a strong acid and a strong base is
(a) phenolphthalein (b) methyl orange
(c) alizarin yellow (d) red litmus

7. Diazo coupling is useful to prepare some
(a) pesticides (b) dyes
(c) proteins (d) vitamins

8. Which of the following is an azo dye ?
(a) methyl orange (b) phenolphthalein
(c) malachite green (d) methylene blue

9. An example of anthraquinone dye is
(a) alizarin (b) basic red
(c) methylene blue (d) phenolphthalein

10. Alum is used by dyers for cloth
(a) for fire- proofing fabrics (b) as first aid for cuts
(c) for softening hard water (d) as mordant

11. Alizarin belongs to the class of
(a) vat dyes (b) mordant dyes
(c) substantive dyes (d) reactive dyes

12. The use of chemicals for the treatment of diseases is called as
(a) homeotherapy (b) isothermtherapy
(c) chemotherapy (d) physiotherapy

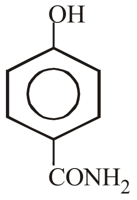
13. 2-Acetoxybenzoic acid is called
(a) antiseptic (b) aspirin
(c) antibiotic (d) mordant dye

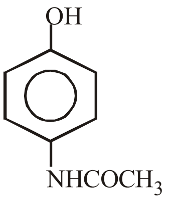
14. Aspirin is a/an
(a) antibiotic (b) antipyretic
(c) antiseptic (d) None of these

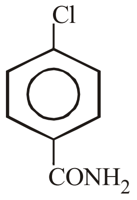
15. Substances which bring body temperature down are known as
(a) antipyretic (b) analgesics
(c) antibiotics (d) hypnotics

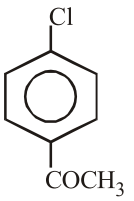
16. A drug that is antipyretic as well as analgesic is
(a) chloropromazine hydrochloride
(b) para- acetamidophenol
(c) chloroquin
(d) penicillin

17. The correct structure of the drug paracetamol is

(a)


(b)


(c)


(d)


18. Which of the following can possibly be used as analgesic without causing addiction and modification?
(a) Morphine
(b) N-acetyl-para-aminophenol
(c) Diazepam
(d) Tetrahydrocatenol

19. Which of the following is used for inducing sleep ?
(a) Paracetamol
(b) Chloroquine
(c) Bithional
(d) Barbituric acid derivatives

20. Which of these is a hypnotic ?
(a) Metaldehyde (b) Acetaldehyde
(c) Paraldehyde (d) None of these

21. Drug which helps to reduce anxiety and brings about calmness is
(a) tranquillizer (b) diuretic
(c) analgesic (d) antihistamine

22. Tranquillizers are substances used for the treatment of
(a) cancer (b) AIDS
(c) mental diseases (d) physical disorders

23. Arsenic drugs are mainly used in the treatment of
(a) jaundice (b) typhoid
(c) syphillis (d) cholera

24. Which of the following is an antidiabetic drug?
(a) Insulin (b) Penicillin
(c) Chloroquine (d) Aspirin

25. Amoxillin is semi-synthetic modification of
(a) penicillin (b) streptomycin
(c) tetracycline (d) chloramphenicol

26. Streptomycin, well known antibiotic, is a derivative of
(a) peptides
(b) carbohydrates
(c) purines
(d) terpenes

27. An ester used as medicine is
(a) ethyl acetate (b) methyl acetate
(c) methyl salicylate (d) ethyl benzoate

28. Parathion is
(a) an orgnic phosphorus compound
(b) chlorinated aromatic compound
(c) chlorinated aliphatic compound
(d) benzene derivative

29. SLV -3 uses ______ propellants
(a) solid (b) liquid
(c) solid-liquid (d) biliquid

Exercise-3 | PAST COMPETITION MCQs

1. Commonly used antiseptic 'Dettol' is a mixture of **[CBSE-PMT 1996]**
(a) *o*-chlorophenozylenol + terpeneol
(b) *o*-cresol + terpeneol
(c) phenol + terpeneol
(d) chloroxylenol + terpeneol

2. Which one of the following can possibly be used as analgesic without causing addiction and mood modification ? **[CBSE PMT-1997]**
(a) Diazepam
(b) Morphine
(c) N-Acetyl-para-aminophenol
(d) Tetrahydrocannabinol

3. Which one of the following is employed as a tranquilizer? **[CBSE PMT-2009]**
(a) Naproxen (b) Tetracycline
(c) Chlorpheninamine (d) Equanil

4. Which one of the following is employed as a tranquilizer drug? **[CBSE PMT-2010]**
(a) Promethazine (b) Valium
(c) Naproxen (d) Mifepristone

5. Which one of the following is employed as Antihistamine ? **[CBSE PMT-2011]**
(a) Chloramphenicol
(b) Diphenylhydramine
(c) Norothindrone
(d) Omeprazole

6. Chloroamphenicol is an : **[CBSE PMT-2012M]**
(a) antifertility drug
(b) antihistaminic
(c) antiseptic and disinfectant
(d) antibiotic-broad spectrum

7. Antiseptics and disinfectants either kill or prevent growth of microorganisms. Identify which of the following statements **is not true:** **[NEET 2013]**
(a) Chlorine and iodine are used as strong disinfectants.
(b) Dilute solutions of Boric acid and Hydrogen Peroxide are strong antiseptics.
(c) Disinfectants harm the living tissues.
(d) A 0.2% solution of phenol is an antiseptic while 1% solution acts as a disinfectant.

8. Which of the following could act as a propellant for rockets ? **[AIEEE 2003]**
(a) Liquid oxygen + liquid argon
(b) Liquid hydrogen + liquid oxygen
(c) Liquid nitrogen + liquid oxygen
(d) Liquid hydrogen + liquid nitrogen

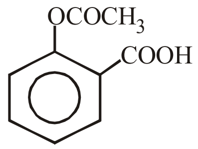
9. Which one of the following types of drugs reduces fever ? **[AIEEE 2005]**
(a) Tranquiliser (b) Antibiotic
(c) Antipyretic (d) Analgesic

10. Aspirin is known as : **[AIEEE-2012]**
(a) acetyl salicylic acid
(b) phenyl salicylate
(c) acetyl salicylate
(d) methyl salicylic acid

Exercise-4 | Applied MCQs

1. Structurally biodegradable detergent should contain
(a) normal alkyl chain (b) branched alkyl chain
(c) phenyl side chain (d) cyclohexyl side chain

2. Which among the following is not the correct match ?
(a) silk (polyamide) (b) indigo (azo dye)
(c) lipase (ester) (d) keratin (protein)

3. The compound  is used as

(a) antiseptic (b) antibiotic
(c) analgesic (d) pesticide

4. Phenol is used as
(a) an antiseptic (b) a disinfectant
(c) Both (a) and (b) (d) Neither (a) nor (b)

5. The drug given during hypertension is
(a) streptomycin (b) chloroxylenol
(c) equanil (d) aspirin

6. A broad spectrum antibiotic is
(a) paracetamol (b) penicillin
(c) aspirin (d) chloramphenicol

7. Which of the following is not true ?
(a) Some disinfectants can be used as antiseptics
(b) Sulphadiazine is a synthetic antibacterial
(c) Aspirin is analgesic as well as antipyretic
(d) Polystyrene is used to make non-stick cookware

8. Pheromones are chemicals
(a) formed by fermentation process of fungi
(b) secreted by endocrine glands of man
(c) secreted outside the body of insects
(d) plant growth hormones

9. One of the oxidants used with liquid propellants is
(a) ammonium perchlorate
(b) nitrocellulose
(c) sulphuric acid
(d) nitrogen tetraoxide (N_2O_4)

10. Match List I with List II and select the correct answer using the codes gives below the lists :

List I	List II
I. Iodoform	A. Anaesthetic
II. Methyl salicylate	B. Antiseptic
III. Diethyl ether	C. Insecticide
IV. Hexachlorocyclohexane	D. Detergent
	E. Pain balm

Codes :
(a) I-B, II-E, III-C, IV-D (b) I-D, II-B, III-A, IV-C
(c) I-B, II-E, III-A, IV-C (d) I-C, II-A, III-D, IV-B

11. The common vehicle used in perfumes is
(a) phenol-water mixture
(b) ethanol-water mixture
(c) acetone-water mixture
(d) methanol-water mixture

12. Which of the following substances cannot be used as a fixative in perfumes?
(a) Benzoin (b) Sandalwood
(c) Glyceryl dinitrate (d) Glyceryl diacetate

13. Which of the following substances is not present in essential oils?
(a) Camphor (b) Linalool
(c) Geraniol (d) Amygdalin

14. Which of the followings forms the base of talcum powder?
(a) Zine stearate
(b) Sodium aluminium silicate
(c) Magnesium hydrosilicate
(d) Chalk

15. Most of the deodorants contain aluminium salts because they
(a) act as antiperspirants
(b) act as anti-bacterial agents
(c) mask body odour
(d) All the these

16. Zinc salts used in deodorants act as
(a) antiperspirants and astringents
(b) antringents as well as antiseptics
(c) antibacterials as well as antiperspirants
(d) antiperspirants and antiseptics

17. Phenolic antibacterial used in body deodrants is
(a) 2, 4-Dichlorophenol (b) p-Chloro-m-xylenol
(c) p-Chlorophenol (d) p-Nitro-m-xylenol

18. The important antioxidant used in food is
(a) BHT (b) BHC
(c) BTX (d) All the three

19. The substance which is not an artificial sweetener
(a) sucralose (b) alitame
(c) saccharin (d) sucrose

20. Which preservative is ultimately excreted in urine as hippuric acid?
(a) Sodium sorbate (b) Sodium benzoate
(c) Sodium metabisulphite (d) Sodium propionate

21. Which of the following is an artificial edible colour?
(a) Melamine (b) Saffron
(c) Carotene (d) Tetrazine

22. Which one of the following is not a characteristic of clay?
(a) Presence of iron oxide, lime, alkali oxides etc. in clay raises its fusion point
(b) It is plastic and mouldable
(c) Its plasticity may be enhanced by aging
(d) None of these

23. Drainage pipes are usually made of
(a) chinawares (b) porcelain
(c) stonewares (d) white wares

24. Which of the following ceramics possesses good strength, translucency and very low porosity
(a) whiteware (b) earthenware
(c) stoneware (d) bricks and tiles

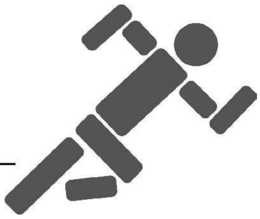
25. Ceramic obtained from chinaclay, feldspar and flint
(a) whiteware (b) brick
(c) tiles (d) stoneware

26. Clay contains mainly
(a) alumina (b) silica
(c) lime (c) Both (a) and (b)

27. Chemical substances used by insects for communication are called
(a) pheromones (b) hormones
(c) enzymes (d) nucleoproteins

28. The environmental friendly method of killing harmful insects is through the use of
(a) insecticides (b) sex attractants
(c) sex hormones (d) pesticides

Hints & Solutions



EXERCISE 1

1. Chloramphenicol.
2. Phenacetin. It is an antipyretic whereas other three are tranquilizers.
3. Antacids.
4. Aspirin (2-acetoxybenzoic acid).
5. Chloroxylenol and terpeneol.
6. Because they are not obtained from micro-organisms like antibiotics.
8. IUPAC name of aspirin is 2-acetoxy benzoic acid.
9. Analgesics: Ibuprofen and diclofenac.
   Tranquilizer: Valium, luminal and chlorodiazepoxide.
   Antiseptic: Hydrogen peroxide.
12. Non-biodegradable detergents are degraded slowly by micro-organisms. Therefore they accumulate in rivers and waterways causing severe water pollution.
19. (*a*) Phenacitin (p-ethoxy acetanalide)
    (*b*) Paetanalide)
    (*c*) Aspirin (2-acetoxy benzoic acid)

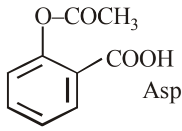
22. **(a)** **23.** **(a)** **24.** **(b)** **25.** **(c)**
26. **(c)** **27.** **(c)** **28.** **(a)** **29.** **(b)**

EXERCISE 2

1. **(b)** Sodium lauryl sulphate is a detergent
2. **(a)** **3.** **(a)** **4.** **(c)** **5.** **(c)** **6.** **(a)**
7. **(b)** **8.** **(a)** **9.** **(a)** **10.** **(d)** **11.** **(b)**
12. **(c)** **13.** **(b)**
14. **(b)** Aspirin or acetylsalicyclic acid, or 2-acetoxybenzoic acid is an analgesic as well as antipyretic; actually all antiseptic compounds have some analgesic action and vice versa
15. **(a)** **16.** **(b)** **17.** **(d)** **18.** **(b)** **19.** **(d)** **20.** **(c)**
21. **(a)** **22.** **(c)** **23.** **(c)** **24.** **(a)** **25.** **(d)** **26.** **(b)**
27. **(c)** **28.** **(a)** **29.** **(a)**

EXERCISE 3

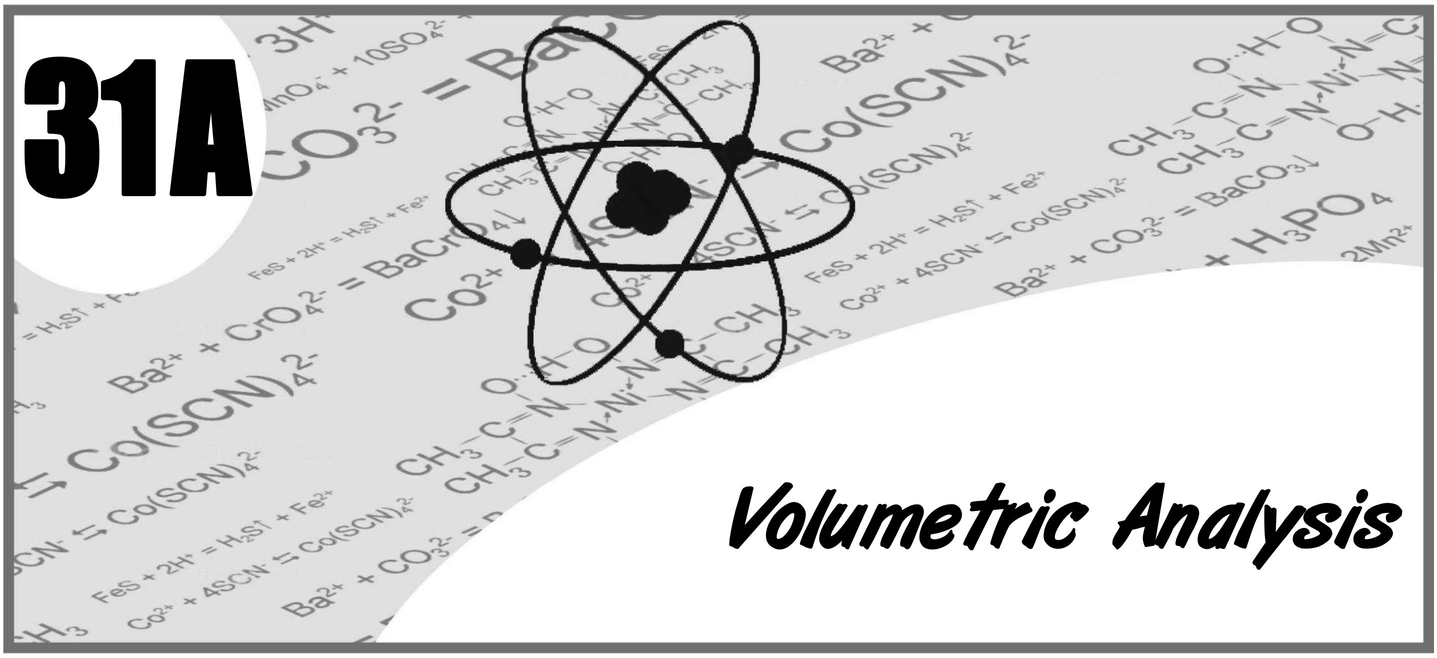
1. **(d)** The mixture of chloroxylenol and terpenol is dettol which is used as antiseptic.
2. **(c)** We know that N-acetyl-para-aminophenol (or paracetamol) is an antipyretic which can also be used as an analgesic to relieve pain.
3. **(d)** Equanil is an important medicine used in depression and hypertension.
4. **(b)**
5. **(b)** Diphenyl hydramine also known as (Banadry) is an antihistamine.
6. **(d)** Chloroamphenicol is a broad spectrum antibiotic.
7. **(b)** Dilute solutions of boric acid and hydrogen peroxide are weak antiseptics.
8. **(b)** Liquid hydrogen and liquid oxygen are used as excellent fuel for rockets. $H_2(\ell)$ has low mass and high enthalpy of combustion whereas oxygen is a strong supporter of combustion.
9. **(c)** An antipyretic is a drug which is responsible for lowering the temperature of the feverish organism to normal but has no effect on normal temperature states.
10. **(a)**



Aspirin (Acetyl salicylic acid)

EXERCISE 4

1. **(c)** Linear alkylbenzenesulphonates (LAB) carrying phenyl chains at secondary positions are biodegradable
2. **(b)** Indigo is not an azo dye, it is a vat dye
3. **(c)** Aspirin or acetylsalicyclic acid, or 2-acetoxybenzoic acid is an analgesic as well as antipyretic; actually all antiseptic compounds have some analgesic action and vice versa
4. **(c)** **5.** **(c)** **6.** **(d)** **7.** **(d)** **8.** **(c)** **9.** **(d)** **10.** **(c)**
11. **(b)** Ethanol-water mixture is the common vehicle used in perfumes.
12. **(c)** Glyceryl dinitrate is not used as fixative in perfumes.
13. **(d)** Amygdalin is not present in essential oils.
14. **(c)** Magnesium hydrosilicate forms base of Talcum powder.
15. **(b)** Aluminium salts present in deodorants act as antibacterial agents.
16. **(b)** Zinc salts in deodorants act as astringents and antiseptics.
17. **(b)** p-chloro-m-xylenol is phenolic antibacterial deodorants.
18. **(a)** BHT is the important antioxidant used in food.
19. **(d)** Sucrose is natural sweetner.
20. **(b)** Hippuric acid is excreted in urine of sodium benzoate is used as preservative.
21. **(b)** Saffron is an artificial edible colour.
22. **(a)** Statement (a) is not characteristics of clay
23. **(c)** Drainage pipes are made of stonewares
24. **(a)** Whiteware possesses good strength, translucency, and low porosity.
25. **(a)** Whiteware is obtained from chinaclay, feldspar and flint
26. **(d)** Clay contains alumina and silica.
27. **(a)** Pheromones are the chemical substances used by insects for communication.
28. **(b)** Sex attractants.



31A

Volumetric Analysis

VOLUMETRIC METHODS :

Volumetric or titrimetric analysis are quantitative analytical techniques which employ a titration in comparing an unknown with a standard. In a titration, a volume of a standardized solution containing a known concentration of reactant 'A' is added incrementally to a sample containing an unknown concentration of reactant 'B' till reactant 'B' is just consumed (stoichiometric completion). This is known as the equivalence point.

At this point we have $N_1V_1 = N_2V_2$.

INDICATOR :

A compound added to the reacting solutions that undergo an abrupt change in a physical property usually a colour .

TYPES OF INDICATORS :

They may be

(i) **Internal -** They are added to the reacting solutions.

(ii) **External -** Electrochemical devices such as pH meters.

END POINT :

The point at which a titration is stopped i.e. equivalence point.

STANDARD SOLUTION :

The solution of known concentration of an acid, base or salt.

EXAMPLES OF VOLUMETRIC METHODS :

(i) **Acidimetry and alkalimetry :**

Sodium Carbonate - Hydrochloric acid Titration

Reaction : $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2 \uparrow$

Indicator : Methyl orange

End Point : Appearance of light pink colour

Note : In presence of phenolphthalein the reaction between Na_2CO_3 and HCl is half complete

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

(ii) **Precipitation titrations :**

(a) $AgNO_3 - NH_4CNS$ or KCNS titration

(Volhard's method)

Reaction :

$$AgNO_3 + KCNS \rightarrow AgCNS \downarrow + KNO_3$$

$$AgNO_3 + NH_4CNS \rightarrow AgCNS \downarrow + NH_4NO_3$$

Slight excess of KCNS or NH_4CNS gives blood red tinge with ferric salt.

$$Fe_2(SO_4)_3 + 6KCNS \rightarrow \underset{(red)}{2\,Fe(CNS)_2} + 3K_2SO_4$$

Indicator : Ferric alum solution

End Point : Appearance of blood red tinge

(b) $AgNO_3$ - NaCl titration **(Mohr's method)**

Reaction : $AgNO_3 + NaCl \rightarrow AgCl \downarrow + NaNO_3$

Slight excess of $AgNO_3$ gives a brick red ppt. with K_2CrO_4

$$2AgNO_3 + K_2CrO_4 \rightarrow \underset{(red)}{Ag_2CrO_4 \downarrow} + 2KNO_3$$

Indicator: Potassium Chromate solution

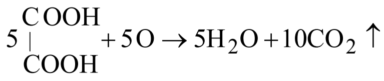
End Point: Appearance of brick red precipitate

(iii) **Redox titrations :**

(a) **Oxalic acid - Potassium permanganate titration**

Reaction :

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$



$$5\begin{array}{c}COOH\\|\\COOH\end{array} + 5O \rightarrow 5H_2O + 10CO_2 \uparrow$$

Indicator : $KMnO_4$ is self indicator

End Point : Appearance of light pink colour

(b) **Ferrous Amm. Sulphate - $KMnO_4$ titration :**

Reaction :

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

$$\underline{\left(2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O\right) \times 5}$$

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4$$

$$\rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

Indicator : $KMnO_4$ is self indicator

End Point : Appearance of light pink colour

(c) **Ferrous Amm. Sulphate - $K_2Cr_2O_7$ titration**

Reaction : $K_2Cr_2O_7 + 4H_2SO_4 \rightarrow$

$$K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$$\underline{\left(2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O\right) \times 3}$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \rightarrow$$

$$K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

Potassium ferricyanide gives blue coloured ppt. with ferrous ions

$$\underset{\text{Pot. ferricyanide}}{2K_3[Fe(CN)_6]} + 3FeSO_4 \rightarrow \underset{\substack{\text{Ferric ferricyanide}\\ \textbf{(Turnbull's blue)}}}{Fe_3[Fe(CN)_6]_2} + 3K_2SO_4$$

Indicator : Potassium ferricyanide (External) or Diphenylamine (internal).

End point : No green colour when $K_3[Fe(CN)_6]$ is used. Bluish violet or purple colour.

When  is used.

(d) **I_2-$Na_2S_2O_3.5H_2O$ Titration :** This is **Iodometry titration**. Since standard solution of iodine is used.

Reaction : $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

Indicator : Freshly prepared starch solution.

End Point : Disappearance of blue colour.

Note : Iodine is dissolved in KI solution and forms soluble KI_3

$$KI + I_2 \rightleftharpoons KI_3$$

Equilibrium shifts to left hand side when iodine is required.

(e) **As_2O_3-I_2 Titration (Iodometry titration) :**

Reaction :

$$As_2O_3 + 2I_2 + 2H_2O \rightarrow As_2O_5 + 4HI$$

Solution of arsenious oxide is prepared in NaOH.

$$6NaOH + As_2O_3 \rightleftharpoons 2Na_3AsO_3 + 3H_2O \ ;$$

$$Na_3AsO_3 + I_2 + H_2O \rightleftharpoons Na_3AsO_4 + 2HI$$

HI is removed by adding $NaHCO_3$ to make reaction irreversible.

$$NaHCO_3 + HI \rightarrow NaI + H_2O + CO_2 \uparrow$$

Indicator : Freshly prepared starch solution.

End point : Disappearance of blue colour.

(f) **Iodometry :** Iodine is liberated during chemical reactions.

$CuSO_4 - Na_2S_2O_3.5H_2O$ titration

Reaction :

$$CuSO_4 + 2KI \rightarrow CuI_2 + K_2SO_4$$

$$2CuI_2 \rightarrow \underset{\text{white ppt.}}{Cu_2I_2} + I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

Indicator : Freshly prepared starch solution

End point : Disappearance of blue colour.

(g) **$K_2Cr_2O_7$-$Na_2S_2O_3.5H_2O$ Titration (Iodometry)**

Reaction :

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$$\left(2KI + H_2O + O \rightarrow 2KOH + I_2\right) \times 3$$

$$\underline{\left(2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O\right) \times 3}$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \rightarrow 4K_2SO_4 + Cr_2(SO_4)_3$$

$$+ 7H_2O + 3I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

Indicator : Freshly prepared starch solution.

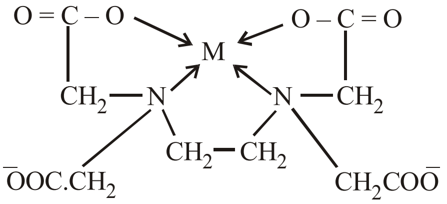
End point : Disappearance of blue colour.

(iv) **Complexation reactions :**

(a) **Hardwater-EDTA Titration**

Reaction : $(Ca^{++}, Mg^{++}) + EDTA \rightarrow \left(^{Ca}_{Mg}EDTA\right)$

stable complex



Indicator : Eriochrome black-T (Alcoholic solution)

End point : Ca^{++}, Mg^{++} of water + Eriochrome black-T

$$\rightarrow \underset{\text{Unstable complex (wine–red)}}{\left[^{Ca}_{Mg}\text{Eriochrome black} - T\right]}$$

$$\xrightarrow{EDTA} \underset{\text{Stable Complex}}{\left[^{Ca}_{Mg}EDTA\right]} + \text{Eriochrome black} - T(\text{blue})$$

Thus wine red colour changes to blue at end point

(i) *Acid base* titration involves proton (H^+) transfer reaction between analyte and titrant.

(ii) *Precipitation* reactions, ions in solution combine to form an insoluble precipitate.

(iii) *Complexation* reactions, analyte and titrant combine to form a very stable complex ion (held together by coordinate bonds)

(iv) *Redox* reaction, electrons transfer between analyte and titrant.

PRIMARY STANDARD :

It is a reagent that is pure enough to be weighed out and used directly to provide a known number of moles eg. Na_2CO_3, $FeSO_4$ $(NH_4)_2SO_4.6H_2O$, etc.

STANDARD SOLUTION :

A solution whose concentration is known. The concentration is generally expressed in terms of normality.

EQUIVALENT MASS :

It is the mass in gram which is chemically equivalent to 1.008 g of hydrogen, 8g of oxygen or 35.46 g of chlorine.

Equivalent mass of an acid

$$= \frac{\text{Mol. mass of an acid}}{\text{No. of replaceable hydrogen atoms present in one molecule}}$$

$$\textit{Equivalent mass of a base} = \frac{\text{Molecular mass of base}}{\text{acidity (replaceable OH groups)}}$$

Equivalent weights of oxidising and reducing agents. On the basis of the change in O.N. of an element in the oxidising or reducing agent.

$$\textit{Eq. wt.} = \frac{\text{Formula weight of oxidising / Reducing agent}}{\begin{array}{c}\text{Total change in O.N. of an element that}\\ \text{undergoes oxidation / reduction}\end{array}}$$

Thus in acidified $KMnO_4$, Mn in MnO_4^- ion is reduced to Mn^{2+}, the change in O.N. is 5. Hence equivalent weight of $KMnO_4$ in acidified solution

$$\textit{Eq. wt.} = \frac{\text{Formula weight of } KMnO_4}{5} = \frac{158}{5} = 31.6$$

In alkaline medium Mn in MnO_4^- ion is reduced to MnO_2, the change in O.N. is 3. Hence equivalent weight of $KMnO_4$ in alkaline medium.

$$\textit{Eq. wt.} = \frac{158}{3} = 52.67$$

Fe in $FeSO_4$ is oxidised to $Fe_2(SO_4)_3$, a change in O.N. is 1. Hence equivalent weight of $FeSO_4$ is

$$\textit{Eq. Wt.} = \frac{\text{Formula weight of } FeSO_4}{1} = \frac{151.8}{1} = 151.8$$

In acidified solution Cr in $K_2Cr_2O_7$, is reduced to Cr^{3+}, the total change in O.N. is 6. Hence equivalent weight of $K_2Cr_2O_7$ is

$$\textit{Eq. wt.} = \frac{\text{Formula weight of } K_2Cr_2O_7}{6} = \frac{294}{6} = 49$$

Equivalent mass of a salt

$$= \frac{\text{Formula weight of salt}}{\text{Total number of positive or negative valencies of the radicals}}$$

Strength of the solution : It is expressed in grams per litre and related to normality and equivalent weight as,

Strength = Normality × equivalent weight.

Relation between normality and molarity :

Normality = n × Molarity

where n = number of equivalents in 1 mole

Miscellaneous Solved Examples

1. Consider a reaction of H_2SO_4 and NaOH. How many ml. of a 0.250 M solution of NaOH must be added to neutralise 35.0 ml of a 0.175 M solution of H_2SO_4?

Sol. Starting with balanced chemical equation

$H_2SO_4\,(aq) + 2\,NaOH\,(aq) \rightarrow 2H_2O\,(l) + Na_2SO_4\,(aq)$

1 Mole $H_2SO_4 \equiv 2$ Mole NaOH

Moles of H_2SO_4 to be neutralised

$$= \frac{35.0 \times 0.175}{1000} = 0.006125$$

Hence Moles of NaOH needed = 2 × 0.006125

Let V ml be the volume of 0.25 M NaOH solution, then

$$\frac{V \times 0.25}{1000} = 2 \times 0.006125$$

$\therefore V = 49$ ml

2. Using a pipette 25.00 mL of HCl (concentration unknown) is placed in a flask. The acid is titrated with a 0.1528 M solution of NaOH. The endpoint is reached when 19.35 mL of NaOH is added. What is concentration of the unknown acid ?

Sol. $HCl + NaOH \longrightarrow NaCl + H_2O$

1 Mole of HCl $\equiv$ 1 Mole of NaOH

Let M be the concentration of HCl then,

$M \times 25.0 = 0.1528 \times 19.35$

$M = 0.1183.$

3. 25 ml of a solution containing ferrous and ferric sulphates acidified with sulphuric acid is reduced by 3g of metallic zinc. The solution required 34.25 ml of 0.1 N solution of potassium dichromate for oxidation. Before reduction with zinc, 25 ml of the same solution required 22.45 ml of the same $K_2Cr_2O_7$ solution. Calculate the weights of $FeSO_4$ and $Fe_2(SO_4)_3$ per litre of the solution.

Sol. Before reduction, the meq of $K_2Cr_2O_7$ required are for ferrous sulphate and meq. of $K_2Cr_2O_7$ after reduction are for both i.e. ferrous sulphate and ferric sulphate.

Volume of solution is 25 ml

After reduction meq. of $K_2Cr_2O_7 = 34.25 \times 0.1 = 3.425$

Before reduction meq. of $K_2Cr_2O_7 = 22.45 \times 0.1 = 2.245$

Meq. of ferric sulphate = 3.425 – 2.245 = 1.18

Weight of $FeSO_4$ per litre = 2.245 × 40 × 0.152 = 13.65 g

Weight of $Fe_2(SO_4)_3$ per litre = 1.18 × 40 × 0.2 = 9.44 g

4. In the analysis of an iron oxide of unknown composition, a sample weighing 0.1 g is dissolved and all the iron is reduced to the divalent state and then titrated with 0.0993 N solution of $K_2Cr_2O_7$ 13.05 ml of which is used up for the titration. What is the formula of iron oxide analysed ?

Sol. Meq. of iron present in solution = 0.0993 × 13.05 = 1.296

Meq. of iron oxide in 0.1 g of oxide = 1.296

Wt. of iron = 1.296 × 0.056 = 0.07257 g

Wt. of oxygen = 0.1 – 0.07257 = 0.02743 g

$$\text{Ratio of atoms of Fe to O} = \frac{0.07257}{0.056} : \frac{0.02743}{0.016} = 0.75 : 1$$

Therefore formula of iron oxide is Fe_3O_4.

5. 25 ml of a solution containing 6.1 g litre^{-1} of an oxalate of formula $K_xH_y(C_2O_4)_z nH_2O$ required for titration 18ml of 0.1 N NaOH and 24 ml of 0.1 N $KMnO_4$ for oxidation. Calculate x, y, z and n.

Sol. $$\text{Normality of oxalate as an acid} = \frac{18 \times 0.1}{25}$$

$$= 0.072 \text{ or } 0.072 \text{ eq litre}^{-1}.$$

$$\text{Normality as reducing agent} = \frac{24 \times 0.1}{25} = 0.096$$

$$\text{Equivalent weight as an acid} = \frac{6.1}{0.072} = 84.72$$

$$\text{Equivalent weight as a reducing agent} = \frac{6.1}{0.096} = 63.54$$

$$\frac{\text{Molecular weight}}{y} = 84.72$$

$$\frac{\text{Molecular weight}}{2z} = 63.54$$

$$\Rightarrow y = 1.5z \text{ but } \frac{x}{y} = 2z \ \therefore x = 0.5z$$

$\therefore$ x, y, z are in the ratio of 1: 3: 2 or x = 1, y = 3 and z = 2

$\therefore$ Molecular weight = 84.72 × 3 = 254

$39x + y + 88z + 18n = 254$

$\therefore 18n = 36 \Rightarrow n = 2$

Hence the formula is $KH_3(C_2O_4)_2.2H_2O$

6. If 3.05 g of the $NaHCO_3$ were added to 0.500 L of 0.450 M H_2SO_4, what would be the final concentration of the reaction mixture ?

Sol. Molar mass of $NaHCO_3 = 84 \text{ g mol}^{-1}$

$$3.05 \text{ g } NaHCO_3 \left(\frac{3.05}{84} \text{mol}\right) = 0.0363 \text{ mol } NaHCO_3$$

$$\left(\frac{1 \text{mol } H_2SO_4}{2 \text{mol } NaHCO_3}\right) = 0.0182 \text{ mol } H_2SO_4$$

total moles of H_2SO_4 – mole of 0.450 M H_2SO_4 used = moles of H_2SO_4 left

or 0.500 L × 0.450 mol/L

= 0.225 moles H_2SO_4 – 0.0182 moles = 0.207 moles

$$\text{so } M = \frac{\text{mole}}{L} = \frac{0.207 \text{mole}}{0.500 L} = 0.414 M$$

7. In basic solution CrO_4^{2-} oxidise $S_2O_3^{2-}$ to form $Cr(OH)_4^-$ and SO_4^{2-}. How many millilitres of 0.154 M Na_2CrO_4 are required to react with 40.0 ml of 0.246 M $Na_2S_2O_3$?

Sol. $$\overset{+6}{Cr}O_4^{2-} \to \overset{+3}{Cr}(OH)_4^-$$

Change in oxidation number of Cr is 3

$\therefore N_1 = 3 \times$ Molarity $= 3 \times 0.154 = 0.462$

$$^{+2}S_2O_3^{2-} \to {}^{+6}SO_4^{2-}$$

Change in oxidation number for 2 atoms of S = 8

$\therefore N_2 = 8 \times 0.246 = 1.968$

$N_1V_1 = N_2V_2$

$0.462 \times V_1 = 1.968 \times 40$

$$V_1 = \frac{1.968 \times 40}{0.462} = 170.4 \text{ ml}$$

8. A solution of potassium permanganate containing 3g per litre is used to titrate a solution of hydrogen peroxide containing 2g per litre. What volume of the permanganate solution will be required to react with 20 ml of the hydrogen peroxide solution? What is the strength of the hydrogen peroxide solution in terms of available oxygen ?

Sol. $$\text{Eq weight of } KMnO_4 = \frac{\text{mol. wt.}}{5} = \frac{158}{5} = 31.6$$

(in acidic media)

$$\text{Eq. weight of } H_2O_2 = \frac{\text{mol. wt.}}{2} = \frac{34}{2} = 17$$

$N_1V_1 = N_2V_2$

$$\frac{\text{weight in g per litre}}{\text{equivalent weight}} \times V_1 = \frac{\text{weight in g per litre}}{\text{equivalent weight}} \times V_2$$

$$\frac{3}{31.6} \times V_1 = \frac{2}{17} \times 20$$

$V_1 = 24.78$ ml

$$\text{Normality of } H_2O_2 \text{ solution} = \frac{2}{17} = 0.1176$$

Normality of H_2O_2 is related to volume strength by the expression, 5.6 V = 1N or Normal = 5.6 V

$\therefore$ 0.1176 N = 5.6 × 0.1176 = 0.66 V

24.78 ml of $KMnO_4$ is required and volume strength of H_2O_2 is 0.66.

$2H_2O_2 \to 2H_2O + O_2$

68g $\equiv$ 22400 ml at NTP $\therefore$ 17 g (eq. wt) $\equiv$ 5600 ml

17g i.e. 1N 1000 ml of H_2O_2 $\equiv$ 5600 ml of O_2

$\therefore$ 1 ml of 1N of H_2O_2 $\equiv$ 5.6 ml of O_2

9. 1.5 gram of a sample of impure potassium dichromate was dissolved in water and made upto 500 cc solution. 25 cc of this solution required iodometrically 24 cc of sodium thiosulphate solution 26 cc. of this sodium thiosulphate solution required 25 cc of N/20 solution of pure potassium dichromate. Find out the percentage purity of the impure smaple of potassium dichromate. Give necessary equations. [K = 39, Cr = 52, O = 16].

Sol. 26 cc of sodium thiosulphate solution required 25 cc of N/20 $K_2Cr_2O_7$ solution. From normality equation,

$$\underset{Na_2S_2O_3}{N_1V_1} = \underset{K_2Cr_2O_7}{N_2V_2}$$

$$N_1 \times 26 = \frac{N}{20} \times 25 \text{ or } N_1 = \frac{5}{104}N$$

Hence normality of $Na_2S_2O_3$ solution is $\frac{5}{104}$

25 c.c. of impure $K_2Cr_2O_7$ solution required 24 cc of $Na_2S_2O_3$ solution of normality $\frac{5}{104}$

$$\underset{K_2Cr_2O_7}{N_1V_1} = \underset{Na_2S_2O_3}{N_2V_2}$$

$$N_1 \times 25 = \frac{5N \times 24}{104} \Rightarrow N_1 = \frac{5N \times 24}{104 \times 25} = \frac{3N}{65}$$

Normality of impure $K_2Cr_2O_7$ solution $= \frac{3}{65}$

Equivalent weight of $K_2Cr_2O_7 = 49$

$\because$ 1000 c.c. N solution contains $K_2Cr_2O_7 = 49g$

$\therefore$ 500 c.c. $\frac{3N}{65}$ solution contains $K_2Cr_2O_7 = \frac{49 \times 500 \times 3}{1000 \times 65}$

$$= 1.13 \text{ g}$$

$\therefore$ 1.50 g of impure sample contains pure $K_2Cr_2O_7 = 1.13$ g

$\therefore$ 100 grams of impure sample contains pure

$$= \frac{1.13}{1.50} \times 100g = 75.33 \text{ g}$$

Hence percentage purity of impure sample of potassium dichromate is 75.33

The equations involved are

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \rightarrow$$

$$4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

10. Find out the percentage of oxalate $C_2O_4^{2-}$ radical in a given sample of an oxalate salt when 0.25 g of which dissolved in 100 ml of the solution required 8 ml of N/20 potassium permanganate solution for 10 ml of oxalate solution.

Sol. 10 ml of impure oxalate salt solution required 8 ml of N/20 $KMnO_4$ solution

$$\underset{\text{oxalate salt}}{N_1V_1} = \underset{KMnO_4}{N_2V_2}$$

$$N_1 \times 10 = \frac{N}{20} \times 8 \Rightarrow N_1 = \frac{N}{20} \times \frac{8}{10} = \frac{N}{25}$$

Equivalent weight of oxalate $C_2O_4^{2-} = \frac{24 + 64}{2} = 44$

$\because$ 1000 c.c. N – solution of oxalate contains = 44 g

$\therefore$ 100 c.c. $\frac{N}{25}$N – solutions of oxalate contains

$$\frac{44 \times 100}{1000 \times 25} = \frac{22}{125} \text{ g}$$

$\because$ 0.25 g of impure sample contains $= \frac{22}{125}$ g oxalate

$\therefore$ 100 g of impure sample contains $= \frac{22 \times 100}{125 \times 0.25} = 70.4\%$

11. 5.39 g of a mixture of $FeSO_4.7H_2O$ and anhydrous ferric sulphate requires 80 c.c. of 0.125 N potassium permanganate for complete oxidation calculate the amount of each component in the mixture.

Sol. Out of the mixture of ferrous and ferric sulphates, only ferrous sulphate is oxidisized by $KMnO_4$ solution.

Therefore, 80 c.c. of 0.125 N $KMnO_4$ solution $\equiv$ 80 c.c. of 0.125N

$FeSO_4.7H_2O$ solution

Equivalent weight of $FeSO_4.7H_2O = 278$

$\because$ 1000 c.c. N - solution contains ferrous sulphate = 278 g

$\therefore$ 80 c.c. of 0.125 N solution contains ferrous sulphate

$$= \frac{278 \times 80 \times 0.125}{1000} = 2.78 \text{ g}$$

Hence the amount of $FeSO_4.7H_2O = 2.78$ g

The amount of $Fe_2(SO_4)_3$ is therefore

= 5.39 – 2.78 = 2.61 gm

12. 1.575 g of $\begin{array}{c}COOH\\ |\\ COOH\end{array}.xH_2O$ are dissolved in water and the solution made upto 250 c.c. 16.67 c.c. of this solution requires 25 cc of N/15 $KMnO_4$ solution for complete oxidation calculate the value of x.

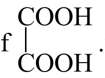
Sol. 250 c.c. of oxalic acid solution contains = 1.575 g acid

$\therefore$ 1000 c.c. of oxalic acid solution contains

$$= \frac{1.575 \times 1000}{250} = 6.3 \text{ g}$$

Hence, strength of oxalic acid = 6.3 gm/litre.

$$\text{Eq. wt. of an acid} = \frac{\text{Molecular weight}}{\text{Number of replaceble H atoms}}$$



Molecular weight of $\begin{array}{l}\text{COOH}\\ | \\ \text{COOH}\end{array}.xH_2O = 24 + 64 + 2 + 18x$

$= 90 + 18\,x$

Eq. wt. of oxalic acid $= \dfrac{90 + 18x}{2} = 45 + 9x$

Strength = Normality × Eq. wt.

$6.3 = N \times (45 + 9\,x)$ or $N = \dfrac{6.3}{45 + 9x}$

16.67 c.c. oxalic acid solution of normality $\dfrac{6.3}{45 + 9x}$ requires 25 c.c. of N/15 $KMnO_4$ solution.

$N_1V_1 = N_2V_2$

$$\therefore \frac{6.3}{45 + 9x}N \times 16.67 = \frac{N}{15} \times 25 \Rightarrow x = 2$$

13. Calculate the volume in c.c. of potassium dichromate solution containing 4.9 g per litre of the salt, required to oxidise 0.5 g of iron dissolved in dilute sulphuric acid. (K = 39, Cr = 52, O = 16, Fe = 56)

Sol. $K_2Cr_2O_7$ reacts with dilute H_2SO_4 as

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

Mol weight of $K_2Cr_2O_7 = 294$

Mol weight of $3O = 3 \times 16 = 48$

$\because$ 48 parts by weight of oxygen is produced from 294 parts by weight of $K_2Cr_2O_7$

Hence eq. wt. of $K_2Cr_2O_7 = 49$

Strength of $K_2Cr_2O_7$ solution = 4.9 g/litre

$\because$ strength = normality × eq. wt.

$4.9 = N \times 49$ or $N = 4.9/49 = 1/10$.

Hence, normality of $K_2Cr_2O_7$ solution = 1/10.

$\because$ 56 g of iron is oxidized by 1000 c.c. N – $K_2Cr_2O_7$ solution.

$\therefore$ 0.5 g of iron is oxidised by

$= \dfrac{1000 \times 0.5}{56}$ c.c. N. $K_2Cr_2O_7$ solution

Hence, volume of N/10 $K_2Cr_2O_7$ solution

$$= \frac{1000 \times 0.5}{56} \times 10 = 89.28 \text{ c.c.}$$

14. 20 c.c. of a copper solution, after necessary treatment, were added with 2g of KI and the liberated iodine required 11.2 c.c. of decinormal hypo solution for titration. Calculate the strength of copper per litre in the solution [Cu = 63.54].

Sol. The reactions for the titration are

$$2Cu^{2+} + 4KI \rightarrow Cu_2I_2 + 4K^+ + I_2$$

$$2\,Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\,NaI$$

The liberated iodine required 11.2 c.c. of N/10 hypo solution.

Therefore, 11.2 c.c. of $\dfrac{N}{10}$ hypo = 11.2 c.c. of $\dfrac{N}{10}\,I_2$

Suppose the normality of copper salt solution, is N_1, then

$$N_1 \times 20 = \frac{N}{10} \times 11.2$$

$$N_1 = \frac{N \times 11.2}{10 \times 20} = \frac{11.2}{200} = 0.056\,N$$

Strength = Normality × Eq. wt. = 0.056 × 63.54

= 3.558 g/litre

15. 30 ml Na_2CO_3 solution is mixed with 20 ml 0.8 N H_2SO_4. The resulting solution required 20 ml 0.7 N HCl for neutralisation. Calculate the strength of Na_2CO_3 solution in $\dfrac{g}{\ell}$. Considering Na_2CO_3 as anhydrous.

Sol. meq of $H_2SO_4 = 20 \times 0.8 = 16$

meq of HCl = 20 × 0.7 = 14

Total meq of acid required of neutralisation = 16 + 14 = 30

$\therefore$ 30 × N meq of Na_2CO_3 = 30 meq of HCl

Hence N = 1 normality of Na_2CO_3

Strength = Eq Wt. × normality = 53 × 1 = 53 g/ ℓ.

16. What volume (NTP) of NH_3 should be passed in 30 ml N H_2SO_4 to reduce the normality of the acid to 0.2 N.

Sol. $N = \dfrac{\text{Wt.} \times 1000}{\text{E.wt.} \times \text{volume}}$

$$\therefore \quad \text{Wt} = \frac{N \times \text{E.wt.} \times V}{1000}$$

Original wt. of $H_2SO_4 = \dfrac{1 \times 49 \times 30}{1000} = 1.47$ g

Wt. of residual $H_2SO_4 = \dfrac{0.2 \times 49 \times 30}{1000} = 0.294$ g

Hence wt. of H_2SO_4 to be neutralised by NH_3

$= (1.47 - 0.2941)\text{g} = 1.176$ g

$$2\,NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

2 mole 1 mole

$\dfrac{2 \times 1.176}{98}$ $\dfrac{1.176}{98}$ mole

0.024 0.012

1 mole of NH_3 = 22400 ml at NTP

0.024 Mole of NH_3 = 22400 × .024 = 537.6 ml

17. 1 g sample of H_2O_2 solution containing x % of H_2O_2 by weight requires x ml of $KMnO_4$ solution for complete oxidation under acidic conditions. Calculate the normality of $KMnO_4$ solution.

Sol. 100 g H_2O_2 contains x g H_2O_2

1 g H_2O_2 contains $\frac{x}{100}$ H_2O_2

geq of $H_2O_2 = \frac{x}{100\times17}$ (17 is E. wt. of H_2O_2

Let N be the normality of $KMnO_4$

geq. of $KMnO_4 = \frac{x\times N}{1000} = \frac{x}{100\times17}$

$\therefore$ $N = 0.588$

18. What volumes of 2.5 N acid and 0.625 N acid should be mixed together to obtain one litre of normal solution.

Sol. $N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$

$$1 = \frac{2.5\times x\,\text{ml} + 0.625\times(1000 - x)\text{ml}}{1000}$$

On solving $x = 200$

$\therefore$ vol of 2.5 N acid $= x = 200$ ml

vol of 0.625 N acid $= (1000 - 200) = 800$ ml

19. How much amount of 95% pure Na_2CO_3 is required to neutralise 45.6 ml 0.235 N H_2SO_4?

Sol. geq of $H_2SO_4 = \frac{45.6\times0.235}{1000} = 0.0107$

geq of Na_2CO_3 required $= 0.0107 = 0.0107\times53$

$= 0.567$g

Since purity of $Na_2CO_3 = 95\%$

For 95 g of pure Na_2CO_3 100 g Na_2CO_3 sample is required

For 0.567 g $= \frac{100}{95}\times0.567 = 0.598$ g required

20. 0.18 g of a metal was dissolved in 50 ml N H_2SO_4 and the solution made up to 500 ml. 20 ml of this solution required 14 ml $\frac{N}{10}$ NaOH for neutralisation. Calculate the equivalent wt. of the metal.

Sol. Let the Eq. wt. of metal be E

geq of $H_2SO_4 = \frac{50\times1}{1000} = 0.05$

geq of NaOH required for neutralisation of total acid.

Left after reaction with metal $= 25\times\frac{14}{10\times1000} = 0.035$

geq of acid reacted with metal $= (0.05 - 0.035) = 0.015$

$\therefore$ $\frac{0.18}{E} = 0.015$

$E = 12$

21. 6.9 g of metallic carbonate was mixed with 60 ml 2N HCl. Excess of acid was neutralised by 20 ml N NaOH. Calculate Eq. wt. of metal.

Sol. Let equivalent weight of metal carbonate be E

geq of metal carbonate $= \frac{6.9}{E}$

geq of acid taken $= \frac{60\times2}{1000}$

geq of NaOH $= \frac{20\times1}{1000}$

$\therefore$ $\frac{6.9}{E} + \frac{20}{1000} = \frac{60\times2}{1000}$

$E = 69$

Eq. wt. of metal carbonate

$= $ Eq. wt. of metal $+$ Eq. wt. of CO_3^{--}

Eq. wt of metal $= 69 - 30 = 39$ (E. w. of $CO_3^{--} = 30$)

22. 3.15 g of a mixture of $CaCO_3$ and silica was dissolved in 100 ml of 1 N HCl. After completion of the reaction it was filtered and the solution was made upto 200 ml by adding water to it. 20 ml of this solution required 25 ml of 0.2N NaOH for complete neutralisation. Find that the percentage of $CaCO_3$ in the mixture.

Sol. In the mixture of $CaCO_3$ and silica only $CaCO_3$ will react with HCl. Let the amount of silica by x g, then amounts of $CaCO_3$ will be $(3.15 - x)$ g

geq of $CaCO_3 = \frac{(3.15 - x)}{50}$

geq of acid taken $= \frac{100\times1}{1000}$

geq of NaOH for neutralisation of HCl left $= \frac{25\times0.2\times10}{1000}$

$\therefore$ $\frac{3.15 - x}{50} + \frac{25\times0.2\times10}{1000} = \frac{100\times1}{1000}$

On solving $x = 0.65$

$\therefore$ $CaCO_3 = (3.15 - 0.65) = 2.5$ g

$\therefore$ % of $CaCO_3 = \frac{2.5\times100}{3.15} = 79.36$

23. 25 ml of H_2O_2 solution were added to excess of acidified solution of KI. The I_2 liberated required 20 ml of 0.1 N $Na_2S_2O_3$ for titration. Calculate the strength of H_2O_2 in terms of normality, percentage and volume

Sol. $N_1V_1 = N_2V_2$

$25 \times N = 20 \times 0.1$

$$\therefore \quad N = \frac{20 \times 0.1}{25} = 0.08\,N$$

$$\text{Strength} = N \times E = 0.08 \times 17\ g/l = 1.36\ \frac{g}{\ell}$$

$$= 0.136\ \frac{g\ ml^{-1}}{100} = \frac{0.136}{100} \times 100 = 0.136\%$$

$$\text{Volume strength} = \frac{68 \times V}{22.4} = N \times E$$

$$\therefore \quad V = \frac{0.08 \times 17 \times 22.4}{68} = 0.448$$

24. 0.5 g mixture of $K_2Cr_2O_7$ and $KMnO_4$ was treated with excess of KI in acidic medium. I_2 liberated required 100 cm^3 of 0.15 N $Na_2S_2O_3$ solution for titration. Find the % amount of each of the mixture.

Sol. Let the amount of $KMnO_4$ in the mixture be x g

then amount of $K_2Cr_2O_7$ in the mixture = $(0.5 - x)$ g

$$\text{geq of } K_2Cr_2O_7 = \frac{0.5 - x}{49}$$

$$\text{geq of } KMnO_4 = \frac{x}{31.6}$$

$$\text{geq of } Na_2S_2O_3 = \frac{100 \times 0.15}{1000}$$

$$\therefore \quad \frac{0.5 - x}{49} + \frac{x}{31.6} = \frac{100 \times 0.15}{1000}$$

$31.6 \times 0.5 - 31.6x + 49x = 0.015 \times 49 \times 31.6$

$x = 0.426$ g which is $KMnO_4$

and $(0.5 - 0.426) = 0.074$ g which is $K_2Cr_2O_7$

$$\%\text{ of } KMnO_4 = \frac{0.426}{0.5} \times 100 = 85.2\%$$

$$\%\text{ of } K_2Cr_2O_7 = \frac{0.074}{0.5} \times 100 = 14.8\%$$

25. 100 ml of Ozonized oxygen at NTP were passed through a solution of KI. The liberated iodine required 10 ml of decinormal solution of sodium thiosulphate. What is the volume of Ozone at NTP in the mixture of Ozone and oxygen.

Sol. $O_3 + 2KI + H_2O \longrightarrow 2KOH + I_2 + O_2$

$2\,Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

$$\text{geq of } Na_2S_2O_3 = \frac{10 \times 0.1}{1000} = \text{geq of Ozone}$$

$$\text{Wt. of Ozone} = \frac{10 \times 0.1 \times 24}{1000} = 0.024\ g$$

(Eq. wt. of Ozone is 24)

$$\text{Volume of ozone at NTP} = \frac{22400 \times 0.024}{48} = 11.2\ ml$$

Exercise-1 | CONCEPTUAL MCQs

1. Equivalent weight of crystalline oxalic acid is:
(a) 45
(b) 90
(c) 126
(d) 63

2. The equivalent weight of $KMnO_4$ in acidic and neutral medium respectively are:
(a) M/5 and M/3
(b) M/3 and M/5
(c) M/5 and M/2
(d) M/2 and M/3

3. If 5 mL N/5 NaOH is titrated against 15 mL of oxalic acid, the normality of oxalic acid is:
(a) 0.4
(b) 0.066
(c) 0.2
(d) 1.0

4. One litre of a sodium hydroxide solution contains 4.0 g of NaOH. The concentration of the solution is:
(a) 0.4 N
(b) 4.0 N
(c) 0.1 N
(d) 1.0 N

5. The normality of 400 mL NaOH is N/10. What will be the normality of 500 mL oxalic acid which neutralize this alkali:
(a) 0.2
(b) 0.08
(c) 0.3
(d) 0.5

6. The amount of zinc required to produce 224 mL of H_2 at STP on treatment with dilute H_2SO_4 will be:
(a) 6.5 g
(b) 0.65 g
(c) 0.065 g
(d) 65 g

7. The volume of CO_2 liberated at STP when 10 g of 90% pure limestone is heated completely is:
(a) 2.016 L
(b) 20.16 L
(c) 2.24 L
(d) 22.4 L

8. $KMnO_4$ reacts with oxalic acid according to the equation:

$$2MnO_4^- + 5C_2O_4^- + 16H^+ \rightarrow 2Mn^{++} + 10CO_2 + 8H_2O$$

Here 20 mL of 0.1 M $KMnO_4$ is equivalent to:
(a) 20 mL of 0.5 M $H_2C_2O_4$
(b) 50 mL of 0.5 M $H_2C_2O_4$
(c) 50 mL of 0.1 M $H_2C_2O_4$
(d) 20 mL of 0.1 M $H_2C_2O_4$

9. A sample of $Na_2CO_3.H_2O$ weighing 0.62 g is added to 100 mL of 0.1 N – H_2SO_4 solution. The resulting solution would be:
(a) acidic
(b) neutral
(c) alkaline
(d) None of the above

10. The strength of an aqueous solution of I_2 can be determined by titrating the solution with standard solution of:
(a) oxalic acid
(b) sodium thiosulphate
(c) sodium hydroxide
(d) Mohr's salt

11. Which of the following cannot undergo iodometric titration?
(a) Ag^+
(b) Cu^{++}
(c) Pb^{2+}
(d) Fe^{3+}

12. How many moles of ferrous sulphate will be consumed by one mole of potassium dichromate in acidic medium:
(a) 1
(b) 3
(c) 6
(d) 5

13. 10 mL of 1 M NaOH solution is neutralized by .... mL of 1 M H_2SO_4 solution:
(a) 2.5
(b) 2.0
(c) 10
(d) 5

14. A solution of 10 mL $\frac{M}{10}$ $FeSO_4$ is titrated with $KMnO_4$ solution in acidic medium the amount of $KMnO_4$ used will be :
(a) 5 mL of 0.1 M
(b) 10 mL of 0.1 M
(c) 10 mL of 0.5 M
(d) 10 mL of 0.02 M

15. The indicator used in the titration of acetic acid with sodium hydroxide for quantitative estimation is:
(a) phenolphthalein
(b) methyl orange
(c) methyl red
(d) a mixture of methyl red and methyl orange

16. What mass of sodium hydroxide is required to neutralize 100 mL of 0.1 N HCl
(a) 4.0 g
(b) 0.40 g
(c) 0.04 g
(d) 2.0 g

17. 0.1 N solution of dibasic acid is made by dissolving 0.45 g acid in water. The volume of the solution is 100 mL. The molecular weight of acid will be:
(a) 45
(b) 90
(c) 135
(d) 180

18. 6 mL 0.5 M HCl is mixed with 15 mL 0.3 M H_2SO_4 and 15 mL 0.2 M HNO_3. The normality of the acid mixture will be:
(a) 0.42
(b) 0.32
(c) 0.25
(d) 0.10

19. Which one of the following solutions of sulphuric acid will exactly neutralize 25 mL of 0.2 M sodium hydroxide solution?
(a) 12.5 mL of 0.1 M solution
(b) 25 mL of 0.1 M solution
(c) 25 mL of 0.2 M solution
(d) 50 mL of 0.2 M solution

20. Equal volumes of 0.1 M HCl and 0.1 M NaOH are mixed. The concentration of the NaCl will be:
(a) 0.1 M
(b) 0.02 M
(c) 0.2 M
(d) 0.05 M

21. In the reaction,

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$$

when 1 mole of ammonia and 1 mole of oxygen are made to react to completion
(a) 1.0 mole of H_2O is produced
(b) 1.0 mole of NO will be produced
(c) all the ammonia will be consumed
(d) all the oxygen will be consumed

22. 20 mL of HCl solution requires 19.85 mL of 0.01 M NaOH solution for complete neutralization. The molarity of HCl solution is:
(a) 0.0099 (b) 0.09
(c) 0.99 (d) 9.9

23. How many gram of NaOH will be required to neutralize 12.2 g of benzoic acid:
(a) 40 g (b) 4 g
(c) 16 g (d) 122 g

24. Formation of polythene from CaC_2 takes place as follows:

$$CaC_2 + H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

$$C_2H_2 + H_2 \rightarrow C_2H_4$$

$$n(C_2H_4) \rightarrow (-CH_2 - CH_2-)_n$$

the amount of polythene obtained from 64.1 kg CaC_2 is:
(a) 7 (b) 14 kg
(c) 21 kg (d) 28 kg

25. How much quicklime can be obtained from 25 g of $CaCO_3$:
(a) 18 g (b) 14 g
(c) 28 g (d) 34 g

26. How many mL of 1 M H_2SO_4 is required to neutralize 10 mL of 1.0 M NaOH solution:
(a) 20mL (b) 25mL
(c) 5mL (d) 10mL

27. The number of moles of $KMnO_4$ needed to react completely with one mole of ferrous oxalate in acidic solution are :
(a) $\frac{3}{5}$ (b) $\frac{2}{5}$
(c) $\frac{4}{5}$ (d) 1

28. The number of moles of $KMnO_4$ needed to react with one mole of sulphite ion in acidic solution are :
(a) $\frac{2}{5}$ (b) $\frac{3}{5}$
(c) $\frac{4}{5}$ (d) 1

29. The normality of 0.3 M phosphorus acid (H_3PO_3) is:
(a) 0.1 (b) 0.3
(c) 0.6 (d) 0.9

30. What will be the molarity of a solution containing 5 g of sodium hydroxide in 250 mL solution:
(a) 0.5 (b) 1.0
(c) 2.0 (d) 0.1

31. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralize 10 mL of this solution is:
(a) 40mL (b) 20mL
(c) 10mL (d) 4mL

Exercise-2 | PAST COMPETITION MCQs

1. 25ml of a solution of barium hydroxide on titration with a 0.1 molar solution of hydrochloric acid gave a litre value of 35ml. The molarity of barium hydroxide solution was
(a) 0.14 **[AIEEE 2003]**
(b) 0.28
(c) 0.35
(d) 0.07

2. Excess of KI reacts with $CuSO_4$ solution and then $Na_2S_2O_3$ solution is added to it. Which of the statements is **incorrect** for this reaction ? **[AIEEE 2004]**
(a) $Na_2S_2O_3$ is oxidised
(b) CuI_2 is formed
(c) Cu_2I_2 is formed
(d) Evolved I_2 is reduced

3. The density (in g mL^{-1}) of a 3.60 M sulphuric acid solution that is 29% H_2SO_4 (molar mass = 98 g mol^{-1}) by mass will be
(a) 1.45 **[AIEEE 2007]**
(b) 1.64
(c) 1.88
(d) 1.22

4. Amount of oxalic acid present in a solution can be determined by its titration with $KMnO_4$ solution in the presence of H_2SO_4. The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl
(a) gets oxidised by oxalic acid to chlorine **[AIEEE 2008]**
(b) furnishes H^+ ions in addition to those from oxalic acid
(c) Oxidises oxalic acid to carbon dioxide and water
(d) reduces permanganate to Mn^{2+}

5. The mass of potassium dichromate crystals required to oxidise 750 cm^3 of 0.6 M Mohr's salt solution is :
(Given molar mass potassium dichromate = 294, Mohr's salt = 392) **[AIEEE -2011]**
(a) 0.45 g (b) 22.05 g
(c) 2.2 g (d) 0.49 g

6. In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is
(a) (Molecular weight)/2 **[IIT JEE-2001S]**
(b) (Molecular weight)/6
(c) (Molecular weight)/3
(d) Same as molecular weight

Exercise-3 | Applied MCQs

1. Normality of phosphoric acid solution (sp.gr. 1.426) and contains 60% by weight of pure acid (P=31)
(a) 26.19 (b) 16.19
(c) 8.73 (d) 20.01

2. How many ml. of 33% HCl (specific gravity 1.17) will be required to prepare 250 ml of 0.1 N HCl
(a) 12.36 (b) 2.36
(c) 6.15 (d) 10.20

3. What volume of water must be added to a litre of 1.123 N acid solution to make it exactly a normal solution
(a) 103 ml (b) 123 ml
(c) 110 ml (d) 65 ml

4. 20 ml of 10 N HCl are mixed with 10 ml of 36 N H_2SO_4 and mixture made upto one litre. The normality of mixture is
(a) 0.56 N (b) 0.46 N
(c) 0.16 N (d) 0.2 N

5. The equivalent weight of $KClO_3$ in the following equation

$$ClO_3^- + Fe^{++} + H^+ \rightarrow Cl^- + Fe^{+++} + H_2O$$

(a) 20.416 (b) 17.52
(c) 15.10 (d) 22.16

6. What quantity of limestone on heating will give 56 g of CaO ?
(a) 1000 g (b) 100 g
(c) 560 g (d) 44 g

7. What is the normality of 1 M solution of H_3PO_4 ?
(a) 0.5 N (b) 1 N
(c) 2 N (d) 3 N

8. The weight of oxalic acid required to neutralise 100 ml of normal NaOH
(a) 6.3 g (b) 126 g
(c) 530 g (d) 63 g

9. 0.45 g of acid molecular weight 90 is neutralised by 20 ml of 0.5N caustic potash. The basicity of acid is
(a) 1 (b) 2
(c) 3 (d) 4

10. 0.62 g of $Na_2CO_3.H_2O$ is added to 100 ml of 0.1 N sulphuric acid. The resulting solution will be
(a) acidic (b) basic
(c) neutral (d) amphoteric

11. Normality of $FeSO_4.7H_2O$ solution containing 6g/250 ml in presence of sulphuric acid.
(a) 1.08 N (b) 0.08
(c) 0.8 (d) 2.1

12. 20 ml of 0.1 N NaOH neutralises 25 ml of a dibasic acid solution containing 6.0 g of acid per litre. The molecular weight of acid is :
(a) 150 (b) 75
(c) 175 (d) 50

13. Volume of 3% solution of sodium carbonate necessary to neutralise a litre of 0.1 N sulphuric acid
(a) 176.66 (b) 156.6
(c) 116.0 (d) 196.1

14. Equivalent weight of As_2O_3 in the following equation

$$As_2O_3 + 2I_2 + 2H_2O \rightarrow As_2O_5 + 4HI$$

(a) 49.5 (b) 198
(c) 94 (d) None of these

15. Six grams of Mg atoms (atomic weight 24) reacts with excess of an acid. The amount of hydrogen produced:
(a) 0.5 g (b) 1.0 g
(c) 2 g (d) 4 g

16. The minimum quantity in g of H_2S needed to precipitate 63.5 g of Cu^{++} ions would be
(a) 63.5 g (b) 31.75 g
(c) 34 g (d) 20 g

17. The weight of sulphuric acid required to completely dissolve 10g $CaCO_3$ is
(a) 98 g (b) 49 g
(c) 9.8 g (d) 0.98 g

18. 3.92 g of ferrous ammonium sulphate react completely with 50 ml $\frac{N}{10}$ $KMnO_4$ solution. The percentage purity of the sample is
(a) 50 (b) 78.4
(c) 80 (d) 39.2

19. The milliequivalent of 4 M H_2SO_4 in 60 ml solution is
(a) 240 (b) 480
(c) 24 (d) 28

20. The normality of 26% (wt/vol) solution of ammonia (density = 0.855) is approximately :
(a) 1.5 (b) 0.4
(c) 15.3 (d) 4

21. Phosphoric acid (H_3PO_4) is a tribasic acid and one of its salt is sodium dihydrogen phosphate (NaH_2PO_4). What volume of 1M NaOH solution should be added to 12 gm of sodium dihydrogen phosphate, (Mol. wt = 120) to exactly convert it into trisodium phosphate Na_3PO_4 ?
(a) 100 cc (b) 200 cc
(c) 80 cc (d) 300 cc

22. The strength of a 10 cc of 20 vol. solution of H_2O_2 in gm/ litre is
(a) 60.7 (b) 6.07
(c) 58.5 (d) 44

23. 0.7 gm of $Na_2CO_3.xH_2O$ were dissolved in 100 ml, 20 ml of this solution required 19.8 ml of N/10 HCl for complete neutralisation, the value of x is
(a) 1 (b) 2
(c) 3 (d) 4

24. 0.5 gm of fuming H_2SO_4 is diluted with water. This solution is completely neutralised by 26.7 ml of 0.4 N NaOH. The percentage of free SO_3 in the same solution is

(a) 20.6% (b) 41.2%
(c) 10.3% (d) 2.06%

25. 1.25 g of a sample of Na_2CO_3 and Na_2SO_4 is dissolved in 250 ml solution. 25 ml of this solution neutralises 20 ml of 0.1N H_2SO_4. The % of Na_2CO_3 in this sample is

(a) 84.8% (b) 8.48%
(c) 15.2% (d) 42.4%

26. What quantity of ammonium sulphate is necessary for the production of ammonia gas sufficient to neutralize a solution containing 292 gm of HCl ?
(HCl = 36.5, $(NH_4)_2SO_4$ = 132 ; NH_3 = 17)

(a) 272 gm (b) 408 gm
(c) 528 gm (d) 1056 gm

27. A solution containing Na_2CO_3 and NaOH requires 300 ml of 0.1N HCl using phenolphthalein as an indicator. Methyl orange is then added to above titrated solution when a further 25 ml of 0.2N HCl is required. The amount of NaOH present in solution is (NaOH = 40 , Na_2CO_3 = 106)

(a) 0.8 gm (b) 1.0 gm
(c) 1.5 gm (d) 2 gm

28. 50 ml of an aqueous solution of H_2O_2 was treated with an excess of KI solution and dil H_2SO_4. The liberated iodine required 20 ml of 0.1 $Na_2S_2O_3$ solution for complete neutralisation. The concentration of H_2O_2 in g/ℓ is

(a) 0.98 g/ℓ (b) 0.68 g/ℓ
(c) 1.68 g/ℓ (d) 1.98 g/ℓ

29. In the reaction

$$Ca(OH)_2 + H_3PO_4 \longrightarrow CaHPO_4 + 2H_2O$$

The equivalent weight of H_3PO_4 is (H = 1, O = 16, P = 31, Ca = 40)

(a) 69 (b) 49
(c) 79 (d) 29

30. 1 g of a metal carbonate was dissolved in 25 ml N HCl. The resulting solution required 50 ml N/10 NaOH for neutralisation. The equivalent weight and atomic weight of metal is, if the metal is bivalent in nature.

(a) 20, 40 (b) 40, 80
(c) 25, 50 (d) 30, 60

31. Normality of a mixed solution of sulphuric acid and hydrochloric acid is 0.6 N 20 ml of this solution gives 0.4305 g of AgCl on reacting with $AgNO_3$ solution. The strength of H_2SO_4 in g/ℓ in the mixed solution is

(a) 42.05 g/ℓ (b) 22.05 g/ℓ
(c) 28.56 g/ℓ (d) 37.05 g/ℓ

32. 1.5 g of a sample of ammonium sulphate was boiled with excess of NaOH solution. Evolved NH_3 was passed in 100 ml. N H_2SO_4. The partially neutralised acid required 160 ml, N/2 NaOH for complete neutralisation. The percentage purity of ammonium sulphate in the sample is

(a) 80.0% (b) 100.0%
(c) 75.0% (d) 50.0%

33. One gram atom of Ca was burnt in excess of oxygen and the oxide was dissolved in water to make up 1 litre solution. The normality of the resulting solution is

(a) 2 N (b) 3 N
(c) 4 N (d) 6 N

34. A mixture of aluminium and zinc weighing 1.67 g was completely dissolved in acid and evolved 1.69 litre of H_2 at NTP. The weight of aluminium in the original mixture is

(a) 2.24 g (b) 1.24 g
(c) 6.8 g (d) 4.2 g

35. The volume in ml of 0.1 N HCl solution required to react completely with 1.0 g of a mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of the two compounds

(a) 119 ml (b) 158 ml
(c) 122 ml (d) 58 ml

36. 1.245 g of $CuSO_4 . xH_2O$ was dissolved in water and H_2S was passed till CuS was completely precipitated. The H_2SO_4 produced in the filtrate required 10 ml of N NaOH. The value of x is

(a) 7 (b) 5
(c) 8 (d) 6

37. 1.25 g of a sample of bleaching powder was dissolved in 100 ml of water and 25 ml of which are litrated with KI solution. The iodine so liberated required 12.5 ml of N/25 hypo solution in titration. The percentage of chlorine in the sample of bleaching powder

(a) 5.68% (b) 7.68%
(c) 9.68% (d) 10.12%

38. To a 25 ml H_2O_2 solution excess of acidified solution of KI was added. The iodine liberated required 20 ml of 0.3 N $Na_2S_2O_3$ solution. The volume strength of H_2O_2 solution is

(a) 4.314 V (b) 1.344 V
(c) 3.11 V (d) 2.446 V

39. A sample of 1.0 g solid Fe_2O_3 of 80 % purity is dissolved in a moderately conc. HCl solution which is reduced by Zn dust. The resulting solution required 16.7 ml of a 0.1 M solution of oxidant. Calculate the number of electrons taken up by the oxidant. (Fe = 56, O = 16)

(a) 5 (b) 2
(c) 4 (d) 6

Hints & Solutions

EXERCISE 1

1. **(d)** Crystalline oxalic acid is a dibasic acid $(COOH)_2.2H_2O$

$$\therefore \text{Eq wt.} = \frac{\text{Mol. wt.}}{2} = \frac{126}{2} = 63$$

2. **(a)** In acidic medium $\overset{+7}{MnO_4^-}$ changes to Mn^{2+}.

$$\therefore \text{Eq wt.} = \frac{\text{Mol. wt.}}{5} = \frac{M}{5}$$

In neutral medium $\overset{+7}{MnO_4^-}$ changes to MnO_2

$$\therefore \text{Eq wt.} = \frac{M}{3}$$

3. **(b)** $N_1V_1 = N_2V_2 \therefore 5 \times \frac{1}{5} = 15 N_2 \therefore N_2 = 0.066$

4. **(c)** $N = \frac{\text{wt.} \times 1000}{\text{Eq. Wt} \times V} = \frac{4 \times 1000}{40 \times 1000} = 0.1N$

5. **(b)** $N_1V_1 = N_2V_2 \therefore 400 \times \frac{1}{10} = 500 \times N$

$\therefore N = 0.08\,N$

6. **(b)** $\underset{1\,\text{Mole}}{Zn} + H_2SO_4 = ZnSO_4 + \underset{1\text{Mole}}{H_2}$

Moles of H_2 produced $\frac{224}{22400} = 0.01$;

Moles of Zn required = 0.01

$\therefore$ Amount of Zn = 65.39 × 0.01 = 0.65 g

7. **(a)** Actual weight of $CaCO_3$ in 10 g of $CaCO_3 = \frac{90}{100} \times 10 = 9\,g$

$\therefore \text{moles} = \frac{9}{100}$ $\quad \underset{\substack{1\,\text{Mole}\\0.09}}{CaCO_3} = CaO + \underset{\substack{1\,\text{Mole}\\0.09}}{CO_2}$

$\therefore$ Volume of CO_2 produced = 22.4 × 0.09 = 2.016 L

8. **(c)** Meq of A = Meq of B. Meq of $KMnO_4$ = 20 × 0.5 = 10

Meq of 50 ml of 0.1 M $H_2C_2O_4$ = 50 × 0.2 = 10

(0.1 M $H_2C_2O_4$ = 0.2 N $H_2C_2O_4$)

9. **(b)** geq of $Na_2CO_3.H_2O = \frac{0.62}{62} = 0.01$

geq of $H_2SO_4 = \frac{100 \times 0.1}{1000} = 0.01$

Hence solution will be neutral

10. **(b)** $I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$

11. **(d)** Fe^{3+}

12. **(c)** $K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$

$2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O$

For 3O, $FeSO_4$ required will be 6 moles.

13. **(d)** $N_1V_1 = N_2V_2 \therefore 10 \times 1 = V \times 2 \therefore V = 5\,ml$

14. **(d)** Meq of $FeSO_4 = 10 \times \frac{1}{10} = 1$

Meq. of $KMnO_4$ needed = 1

$\therefore$ Meq of 10 ml of 0.02 M = 10 × 0.1 = 1

(1 M $KMnO_4$ = 5 N $KMnO_4$ in acid medium)

15. **(a)** NaOH is strong base hence indicator used is phenolphthalein.

16. **(b)** geq. of an acid = geq. of base $\Rightarrow \frac{100 \times 0.1}{1000} = \frac{x}{40}$

$\therefore x = 0.40\,g$

17. **(b)** $N = \frac{\text{wt.} \times 1000}{\text{Eq. Wt.} \times V}$

$\therefore 0.1 = \frac{0.45 \times 1000}{\text{Eq.Wt.} \times 100} \Rightarrow \text{Eq. Wt.} = 45$

Molecular weight = 2 × 45 = 90. Since the acid is dibasic

18. **(a)** $N = \frac{N_1V_1 + N_2V_2 + N_3V_3}{V_1 + V_2 + V_3} = \frac{6 \times 0.5 + 15 \times 0.6 + 15 \times 0.2}{6 + 15 + 15}$

= 0.42 (0.3 M H_2SO_4 = 0.6 N H_2SO_4)

19. **(b)** Meq of NaOH = 25 × 0.2 = 5

Meq. of 25 mol of 0.1 M H_2SO_4 = 25 × 0.2 = 5

20. **(d)** $HCl + NaOH = NaCl + H_2O$. Since the volume doubles on mixing concentration of NaCl = 0.05

21. **(d)** $\underset{\substack{4\\0.8}}{4NH_3} + \underset{\substack{5\\1}}{5O_2} \rightarrow \underset{\substack{4\\0.8}}{4NO} + \underset{\substack{6\\1.2}}{6H_2O}$

All oxygen will be consumed.

22. **(a)** $N_1V_1 = N_2V_2$; 20 × N_1 = 19.85 × 0.01 $\therefore$ N = 0.0099

(for HCl normality and molarity is the same)

23. **(b)** geq. of NaOH = geq. of benzoic acid

$$\therefore \frac{W}{40} = \frac{12.2}{122} = 4\,g$$

24. **(d)** $CaC_2 + H_2O \rightarrow Ca(OH)_2 + C_2H_2$;

$C_2H_2 + H_2 \rightarrow C_2H_4$; $nC_2H_4 \rightarrow -\!\!(CH_2 - CH_2)\!\!-_n$

64.0 g CaC_2 will give 28 g C_2H_4

$\therefore$ 64.1 kg will give 28 kg of C_2H_4

25. **(b)** $\underset{\substack{100g\\25g}}{CaCO_3} \rightarrow \underset{\substack{56g\\14g}}{CaO} + \underset{44g}{CO_2}$

26. (c) $N_1V_1 = N_2V_2 \Rightarrow V \times 2 = 10 \times 1.0 \therefore V = 5\ ml$

27. (a) $\overset{2+}{Fe}\overset{3+}{C}_2O_4 \rightarrow Fe^{3+} + 2\overset{4+}{C}O_2 + 3e^-$; In acid medium

MnO_4^- changes to Mn^{2+} and consumes 5e

$\therefore$ 3e will be consumed by 3/5 moles of $KMnO_4$.

28. (a) $SO_3^- + O \rightarrow SO_4^-$;

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

5 [O] from 2 moles of $KMnO_4$,

$\therefore$ 1 [O] from 2/5 moles of $KMnO_4$

29. (c) Phosphorous acid is a dibasic acid

$\therefore$ 0.3 M H_3PO_3 will be 0.6 N H_3PO_3

30. (a) $M = \dfrac{Wt \times 1000}{M.Wt \times V} = \dfrac{5 \times 1000}{40 \times 250} = 0.5$

31. (a) Normality of oxalic acid $= \dfrac{6.3 \times 1000}{63 \times 250} = 0.4$;

$N_1V_1 = N_2V_2$

$V_1 \times 0.1 = 10 \times 0.4$

$\therefore V_1 = 40\ mL$

EXERCISE 2

1. (d) $25 \times N = 0.1 \times 35$; $N = 0.14 \therefore M = 0.07\ M$

$Ba(OH)_2$ is diacidic base

2. (b) $4KI + 2CuSO_4 \rightarrow I_2^0 + Cu_2I_2 + 2K_2SO_4$

$\overset{0}{I_2} + 2Na_2\overset{2+}{S_2}O_3 \rightarrow Na_2\overset{+2.5}{S_4}O_6 + 2Na\overset{-1}{I}$

In these reactions, CuI_2 is not formed.

3. (d) Since molarity of solution is 3.60 M. It means 3.6 moles of H_2SO_4 is present in its 1 litre solution. Mass of 3.6 moles of H_2SO_4

= Moles × Molecular mass $= 3.6 \times 98\ g = 352.8\ g$

$\therefore$ 1000 ml solution has 352.8 g of H_2SO_4

Given that 29 g of H_2SO_4 is present in = 100 g of solution

$\therefore$ 352.8 g of H_2SO_4 is present in

$= \dfrac{100}{29} \times 352.8$ g of solution $= 1216$ g of solution

$\text{Density} = \dfrac{\text{Mass}}{\text{Volume}} = \dfrac{1216}{1000} = 1.216\ g/ml = 1.22\ g/ml$

4. (d) The titration of oxalic acid with $KMnO_4$ in presence of HCl gives unsatisfactory result because of the fact that $KMnO_4$ can also oxidise HCl along with oxalic acid. HCl on oxidation gives Cl_2 and HCl reduces $KMnO_4$ to Mn^{2+} thus the correct answer is (d)

5. (b) Potassium dichromate oxidise Fe^{++} to Fe^{+++} as

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

i.e., change in O.S. of Cr per atom = 6

Therefore the eq.wt. of $K_2Cr_2O_7 = \dfrac{294}{6}$

Now, since

Normality = Gram Eq. / volume of solution in litre

or $N \times V = \dfrac{W}{E}$

$0.6 \times 0.75 \times 1 = \dfrac{W}{294} \times 6$

$W = 22.05\ g$

6. (b) Hypo solution are used as the reducing agent with potassium dicromate solution

$K_2\overset{+6}{Cr_2}O_7 = \dfrac{\text{Molecular weight}}{6}$

EXERCISE 3

1. (a) Normality $= \dfrac{Wt \times sp.gr \times 10}{Eq.Wt} = \dfrac{60 \times 1.426 \times 10}{32.6} = 26.19$

2. (b) First find normality of 33% HCl. $N = \dfrac{33 \times 1000}{36.5 \times 100} = 9.04$

Now apply $N_1V_1 = N_2V_2$.

$9.04 \times V = 250 \times 0.1$

$\therefore V = 2.76\ ml$

3. (b) Apply $N_1V_1 = N_2V_2$;

$1000 \times 1.123 = 1 \times V$; $\therefore V = 1123\ ml$

Thus water to be added $= (1123 - 1000) = 123\ ml$

4. (a) Normality on mixing the two solutions (N)

$= \dfrac{N_1V_1 + N_2V_2 + \ldots\ldots\ldots\ldots}{V_1 + V_2 + \ldots\ldots\ldots\ldots\ldots\ldots}$

$N = \dfrac{20 \times 10 + 10 \times 36}{1000} = 0.56$

5. (a) In $ClO_3^- + Fe^{++} + H^+ \rightarrow Fe^{+++} + H_2O + Cl^-$

The change in O.N of Cl is 6 (from + 5 to – 1). Hence equivalent wt. of $KClO_3$

$= M.wt / 6 = 122.5/6 = 20.416$

6. (b) $\underset{100g}{CaCO_3} \overset{heat}{\rightleftharpoons} \underset{56g}{CaO} + \underset{44g}{CO_2}$

7. (d) Phosphoric acid is a tribasic acid. Normality = n × Molarity.

Where n = Number of equivalents in 1 mole

$\therefore N = 3 \times 1 = 3$

8. (a) Number of Eq. of NaOH = Number of Eq. of oxalic acid

Then $\dfrac{100 \times 1}{1000} = \dfrac{\text{wt.of oxalic acid}}{63} \therefore W = 6.3\ g$

9. (b) Eq. of acid = Eq of base $\therefore \dfrac{0.45}{E.wt} = \dfrac{20 \times 0.5}{1000}, E.wt = 45$

$\text{Basicity} = \dfrac{M.wt}{E.wt} = \dfrac{90}{45} = 2$

10. (c) Eq. of $Na_2CO_3.H_2O = \dfrac{0.62}{62} = 0.01$, Eq of acid

$= \dfrac{100 \times 0.1}{1000} = 0.01$. Since Eq of both are same, solution will be neutral

11. (a) $N = \frac{\text{wt} \times 1000}{\text{E.wt.} \times V} = \frac{6 \times 1000}{275 \times 250} = 0.08$

12. (a) $20 \times 0.1 = 25 \times N$; $\therefore N = 0.08$ (Where N is normality of acid)
$\therefore$ Eq. Wt of acid, $S = E \times N$; $6.0 = E \times 0.08$; $E = 75$
$\therefore$ M.wt = 150 (strength = E.wt × normality)

13. (a) Normality of 3% $Na_2CO_3 = \frac{3 \times 1000}{53 \times 100} = 0.567$

Apply $N_1V_1 = N_2V_2$

or $0.567\ V = 0.1 \times 1000$

$\therefore V = \frac{0.1 \times 1000}{0.567} = 176.66$ ml

14. (a) The equation is

$$As_2^{+6}O_3 + 2I_2 + 2H_2O \rightarrow As_2^{+10}O_5 + 4HI$$

The change in O. N of two As atoms is 4.

$\text{Eq.wt.} = \frac{\text{Mol.wt}}{4} = \frac{198}{4} = 49.5$

15. (a) The reaction of acid with Mg is

$$\underset{24g}{Mg} + 2HCl \rightarrow MgCl_2 + \underset{2g}{H_2}$$

Hence 6 g Mg will give 0.5 g H_2

16. (c) The desired equation is $\underset{63.5g}{Cu^{++}} + \underset{34g}{H_2S} \rightarrow CuS + 2H^+$

$\therefore H_2S$ needed is 34 g

17. (c) The desired equation is

$$\underset{100g}{CaCO_3} + \underset{98g}{H_2SO_4} \rightarrow CaSO_4 + H_2O + CO_2 \uparrow$$

Hence H_2SO_4 needed for 10 g of $CaCO_3$ is 9.8 g

18. (a) Eq of $KMnO_4$ used $= \frac{50 \times 1}{1000 \times 10} = 0.005$

$\therefore$ Eq of FAS reacted = 0.005
$\therefore$ weight of FAS needed = 0.005 × 392 = 1.96 g
Thus percentage purity of FAS is 50%

19. (b) Meq = normality × volume in ml
$\therefore$ Meq = 8.0 × 60 = 480

20. (c) Wt. of $NH_3 = 26\text{ g} = \frac{26}{17}\text{ g eq} = 1.53\text{ g eq}$

Vol. of soln. = 100 mc = 0.1 L

$\therefore \text{Normality} = \frac{1.53}{0.1} = 15.3\ N$

21. (b) Eq. wt of NaH_2PO_4 is $= \frac{120}{2} = 60.$

Eq of NaH_2PO_4 in 12 g = 12/60
Eq. of NaOH to convert it into Na_3PO_4 = 12/60

$\therefore \frac{V \times 1}{1000}$ (Eq. of NaOH) = 12/60 $\therefore$ V = 200 ml

22. (a) The strength of H_2O_2 in g/litre =

$\frac{68 \times \text{Volume}}{22.4} = \frac{68 \times 20}{22.4} = 60.7\ \text{g/l}$

23. (b) Eq. of $Na_2CO_3.xH_2O_2$ in 0.7 g $= \frac{0.7}{53 + 9x}$. This amount is present in 100 ml

Eq. of acid used to neutralize their amount $= \frac{19.8 \times 5}{10 \times 1000}$

Equate Eq of acid and base $\frac{0.7}{53 + 9x} = \frac{19.8 \times 5}{10 \times 1000} \therefore x = 2$

24. (a) Fuming sulfuric acid is ($H_2SO_4 + SO_3$) and NaOH reacts with H_2SO_4 and SO_3.
Let the weight of SO_3 be x g, then wt of H_2SO_4 $= (0.5 - x)$ g
Eq of SO_3 + Eq of H_2SO_4 = Eq of NaOH

$\frac{x}{40} + \frac{0.5 - x}{49} = \frac{26.7 \times 0.4}{1000} \therefore x = 0.105$

$\therefore$ Percentage of $SO_3 = \frac{0.105}{0.5} \times 100 = 21\%$

25. (a) Let the amount of Na_2CO_3 present in the mixture be xg . Na_2SO_4 will not react with H_2SO_4. Then

$\frac{x}{53} = \frac{20 \times 0.1 \times 10}{1000} \therefore x = 1.06g$

$\therefore$ Percentage of $Na_2CO_3 = \frac{1.06 \times 100}{1.25} = 84.8\%$

26. (c) Eq of $(NH_4)_2SO_4$ = Eq of HCl
Let the amount of $(NH_4)_2SO_4$ needed x g. Then

$\frac{x}{132/2} = \frac{292}{36.5}$. Hence $x = 528$ g

27. (b) Let x Eq of Na_2CO_3 and y Eq of NaOH be present in the solution. In presence of phenolphthalein the reaction are

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

$$NaOH + HCl \rightarrow NaCl + H_2O$$

$\therefore \frac{x}{2} + x = \frac{300 \times 0.1}{1000} = 0.03$

In presence of methyl orange rest of Na_2CO_3 reacts

$\frac{x}{2} = \frac{25 \times 0.2}{1000} = 0.005$

$\therefore x = 0.01$ Then weight of $Na_2CO_3 = 0.01 \times 53 = 0.53$ g and $y = 0.03 - 0.005 = 0.025$ thus weight of NaOH $= 0.025 \times 40 = 1$g

28. (b) Let the normality of H_2O_2 be N then $\frac{50 \times N}{1000} = \frac{20 \times 0.1}{1000}$;

N = 0.04
Strength = 0.04 × 17 = 0.68 g/l (S = E × N)

29. (b) $Ca(OH)_2 + H_3PO_4 \longrightarrow CaHPO_4 + 2H_2O$

2H atoms are replaced in a molecule of H_3PO_4.

$\therefore$ Basicity of $H_3PO_4 = 2$

$\therefore$ Eq. wt. of $H_3PO_4 = \frac{\text{Mol. wt.}}{\text{Basicity}} = \frac{98}{2} = 49$

30. (a) The acid neutralised by metal carbonate

$$=\left(\frac{25\times N}{1000}-\frac{50\ N}{10\times 1000}\right)=(0.025-0.005)=0.02$$

0.02 geq ≡ 1 g

$$1\text{ geq}\equiv\frac{1}{0.02}=50$$

Eq. wt. of metal carbonate is 50. Since the Eq. wt. of CO_3^{--} is $\frac{60}{2}=30$. The Eq. wt. of metal = 20. The metal is bivalent, hence its atomic weight = 40.

21. (b) ∵ 143.5 g of AgCl = 36.5 HCl

$$0.4305\text{ g AgCl}=\frac{36.5\times 0.4305}{143.5}\text{ g HCl}$$

$$\text{geq of HCl}=\frac{36.5\times 0.4305}{143.5\times 36.5}=\frac{0.4305}{143.5}$$

$$\text{Normality of HCl}=\frac{0.4305}{143.5}\times\frac{1000}{20}=0.15$$

Normality of $H_2SO_4=0.6-0.15=0.45$

Strength of $H_2SO_4=49\times 0.45=22.05\text{ g}/\ell$

32. (b) $(NH_4)_2SO_4+2NaOH\rightarrow Na_2SO_4+2NH_3+2H_2O$

150 g 34 g

1.50 g 0.34 g

$$\text{geq of }H_2SO_4\text{ taken }\frac{100\times 1}{1000}=0.1$$

geq of NaOH required to neutralise acid

$$=\frac{160}{2\times 1000}=0.08$$

geq of acid neutralised by $NH_3=0.1-0.08=0.02$

or geq of $NH_3=0.02$

Hence amount of NH_3 evolved $0.02\times 17=0.34$ g

33. (a) $Ca+\frac{1}{2}O_2\longrightarrow CaO\xrightarrow{H_2O}Ca(OH)_2$

74 g

N = geq/litre = 2 (geq of $Ca(OH)_2=74/37=2$)

34. (b) Aluminium and zinc both evolve H_2 with acid. Let x gm be the weight of Al in the mixture.
Then wt. of Zn = $(1.67-x)$ g

$$\left(\frac{x}{\text{Eq.wt.of Al}}+\frac{(1.67-x)}{\text{Eq.wt.of Zn}}\right)=\text{geq of }H_2$$

$$\frac{x}{9}+\frac{1.67-x}{32.7}=\frac{1.69}{11.2}\qquad\therefore\ x=1.24\text{ g}$$

(Eq. wt. of Al = 27/9 and Zn = 65.4/2)

35. (b) Let the amount of Na_2CO_3 be x g, then

$NaHCO_3=(1-x)$ g

Since the mixture is equimolar $\frac{x}{106}=\frac{1-x}{84}$

∴ $x=0.558$ g

Molecular wt. of $Na_2CO_3=106$ and

Mol. wt. of $NaHCO_3=84$

Again geq of Na_2CO_3 + geq of $NaHCO_3$ = geq of acid

$$\frac{0.558}{53}+\frac{0.442}{84}=\frac{V\times .01}{1000}\qquad\therefore\ V=157.9\text{ ml}$$

36. (b) $CuSO_4.xH_2O+H_2S\longrightarrow CuS+H_2SO_4+xH_2O$

geq of $CuSO_4.xH_2O$ ≡ geq of H_2SO_4 ≡ geq of NaOH

$$=\frac{10\times 1}{1000}=0.01\text{ or }0.01=\frac{159.5+18x}{2}$$

$$\therefore\ \frac{1.245}{(159.5+18x)/2}=0.01\qquad\text{Hence }x=5$$

37. (a) geq of hypo = 12.5/25 × 1000 = 0.0005

≡ geq of I_2 ≡ geq of Cl_2

geq of chlorine from 100 ml = 0.0005 × 4 = 0.002

weight of chlorine liberated = 0.002 × 35.5 = 0.071

$$\text{Percentage of available chlorine}=\frac{0.071}{1.25}\times 100=5.68\%$$

38. (b) geq of 25 ml H_2O_2 = geq of I_2 = geq of hypo

$$=\frac{20\times 0.3}{1000}=0.006$$

$$\text{Normality of }H_2O_2=\text{geq/litre}=\frac{0.006}{25}\times 1000=0.24$$

Use the formula,

$$\frac{68\times\text{Volume strength}}{22.4}=\text{Normality}\times\text{Eq. wt.}$$

$$\therefore\quad V=\frac{0.24\times 17\times 224}{68}=1.344$$

39. (d) Weight of pure $Fe_2O_3=\frac{1\times 80}{100}=0.8$ g

$$Fe_2O_3+6HCl\longrightarrow 2FeCl_3+3H_2O$$

$$FeCl_3+H_2\xrightarrow{\text{Zn dust}}FeCl_2+HCl$$

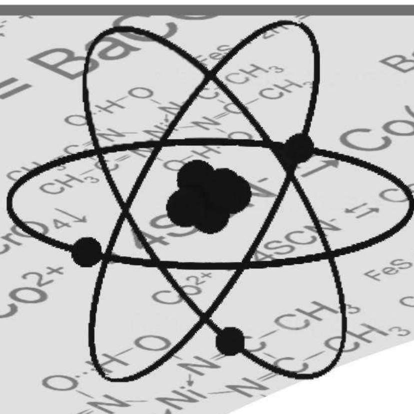
$$Fe^{++}+\text{Oxidant}\longrightarrow Fe^{+++}+\text{Reductant}$$

$$\text{Eq. wt. of }Fe_2O_3=\frac{\text{Mol.wt.}}{2}=\frac{160}{2}=80\text{ g}$$

Meq of Fe_2O_3 = Meq of oxidant

$$\frac{0.8}{80}\times 10^3=16.7\times 0.1\ (x)$$

∴ x = 6



31B

Principles related to Practical Chemistry

1. DETECTION OF NITROGEN, SULPHUR AND HALOGENS IN ORGANIC COMPOUNDS :-

Detection of nitrogen:

(i) ***Soda-lime test:***

organic compound + NaOH → smell of $NH_3\uparrow$

(Not reliable since $-NH_2$, $-NO_2$ and $-N=N$-groups do not respond).

(ii) ***Lassaigne's test:*** Common for N, S and X (halogens)

Lassaigne's filtrate or sodium extract is prepared by fusing the organic compound with Na in ignition tube. Fused mass is dissolved in water, boiled and filtered. The filtrate is sodium extract which contains

$Na + C + N \rightarrow$ NaCN sodium cyanide

$2Na + S \rightarrow$ Na_2S Sodium sulphide

$Na + X \rightarrow$ NaX (Sodium halide)

$Na + C + N + S \rightarrow$ NaCNS (Sodium Sulphocyanide)

Test for nitrogen : Sod. extract + freshly prepared $FeSO_4$ solution + $FeCl_3$ solution + dil. H_2SO_4 → green or blue colouration or sometimes blood red colour

$2NaCN + FeSO_4 \rightarrow Fe(CN)_2 + Na_2SO_4$

$4NaCN + Fe(CN)_2 \rightarrow Na_4[Fe(CN)_6]$

$3Na_4[Fe(CN)_6] + 4FeCl_3 \rightarrow \underset{\text{(prussian blue)}}{\underset{\text{ferric ferocyanide}}{Fe_4[Fe(CN)_6]_3}} + 12NaCl$

$FeCl_3 + 3NaCNS \rightarrow \underset{\text{(Blood red)}}{\underset{\text{Ferric sulphocyanide}}{Fe(CNS)_3}} + 3NaCl$

($NH_2.NH_2$ and diazo compounds do not give this test, diazo compounds are decomposed to give N_2 and $NH_2.NH_2$ does not contain C)

Test for sulphur :

$Na_2S + \underset{\text{Sodium nitropruside}}{Na_2[Fe(CN)_5NO]} \rightarrow \underset{\text{Purple coloured complex}}{Na_4[Fe(CN)_5NOS]}$

$Na_2S + (CH_3COO)_2Pb \rightarrow \underset{\text{black ppt.}}{PbS} + 2CH_3COONa$

Test for halogens:

Sod. extract + Conc. HNO_3 + $AgNO_3$ Solution

(i) If white precipitate soluble in NH_4OH → Cl^- present

$NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$

$AgCl + 2NH_4OH \rightarrow \underset{\text{Soluble Complex}}{[Ag(NH_3)_2]Cl} + 2H_2O$

(ii) If light yellow precipitate sparingly soluble in NH_4OH → Br^- present

$NaBr + AgNO_3 \rightarrow AgBr\downarrow + NaNO_3$

$AgBr + 2NH_4OH \rightarrow \underset{\text{Complex}}{\underset{\text{Sparingly Soluble}}{[Ag(NH_3)_2]Br}} + 2H_2O$

(iii) If yellow precipitate insoluble in NH_4OH → I^- present

$NaI + AgNO_3 \rightarrow AgI\downarrow + NaNO_3$

$AgI + NH_4OH \rightarrow$ No Complex

(a) ***Function of Conc. HNO_3*** : It decomposes NaCN and Na_2S to avoid their interference

$NaCN + HNO_3 \rightarrow NaNO_3 + HCN\uparrow$

$Na_2S + 2HNO_3 \rightarrow 2NaNO_3 + H_2S\uparrow$

$NaCN + AgNO_3 \rightarrow \underset{\text{white ppt.}}{AgCN\downarrow} + NaNO_3$

$Na_2S + 2AgNO_3 \rightarrow \underset{\text{Black ppt.}}{Ag_2S} + 2NaNO_3$

(b) ***Layer test for bromine and iodine:***

Sod. extract + dil. $HNO_3 + CHCl_3$ or CCl_4 or CS_2

$+ Cl_2$ water $\xrightarrow{\text{Shake}}$ Brown layer Br

$\rightarrow$ Violet layer I

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$$

$$Br_2 + \text{Solvent} - \text{Brown layer}$$

$$2NaI + Cl_2 \rightarrow 2NaCl + I_2$$

$$I_2 + \text{Solvent} - \text{Violet layer}$$

(c) ***Beilstein's test:***

Organic compounds containing halogens when heated over Cu wire loop, give blue or green colour flame due to formation of volatile copper halides.

(Not reliable since thiourea, urea, pyridine and organic acids also give this test)

2. DETECTION OF THE FUNCTIONAL GROUPS :-

Alcoholic group (–OH)

(i) ***Ceric ammonium nitrate lest***

Treat 2 drops of the organic substance with 0.5 c.c. of ceric ammonium nitrate solution and dilute with 2 c.c. of water. A red colour indicates alcoholic group

$$2ROH + (NH_4)_2Ce(NO_3)_6 \rightarrow$$

$$Ce(NO_3)_4R(OH)_2 + 2\ NH_4NO_3$$

(ii) ***Sodium test***

2 cc of organic substance +a piece of anhydrous $CaCl_2$ to absorb water if present. Transfer the organic substance to another test tube and add a dry piece of sodium. Effervescence indicate the presence of an alcohol

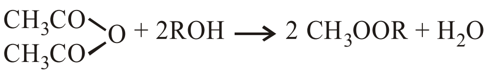
$$2ROH + Na \rightarrow 2RONa + H_2 \uparrow$$

(iii) ***Evolution of HCl***

Take 0.5 cc or 0.3 g of the original substance in a dry test tube and add to it about 6 drops of acetyl chloride or PCl_5. Vigrous reaction takes place with the evolution of HCl fumes

$$ROH + CH_3COCl \rightarrow CH_3COOR + HCl \text{ gas}$$

The same test could be repeated with acetic anhydride when a characteristic. Fruity odour is obtained

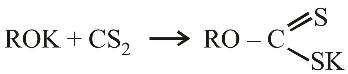


$$\begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>O + 2ROH \longrightarrow 2\ CH_3OOR + H_2O$$

(iv) ***Xanthate test***

To 1 c.c. of the conc. aq solution of the original substance add 2 pallets of KOH. Heat and cool. Add 1 c.c. of the ether and 2-3 drops of CS_2. Formation of yellow ppt. indicate the presence of alcoholic group

$$ROH + KOH \longrightarrow ROK + H_2O$$



$$ROK + CS_2 \longrightarrow RO-C\begin{matrix} \nearrow\!\!\!\!\nearrow S \\ \searrow SK \end{matrix}$$

yellow ppt.

Distinction between 1°, 2° and 3° alcohol :

2 ml of organic compound + 8 ml of Lucas reagent and shake.

Separation of an insoluble layer at once –3° alcohol Appearance of cloudiness within 4-5 minutes –2° alcohol solution remains clear –1° alcohol.

Phenolic group (–OH)

(i) ***Ferric Chloride Test***

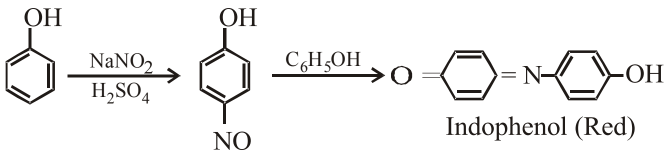
2 c.c. of aqs. or alcoholic solution + 2 drops of ferric chloride $\rightarrow$ deep colour change shows the presence of phenols.

(ii) ***Leibermann's Reaction***

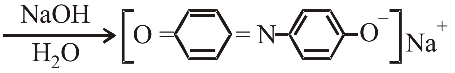
1 c.c. of conc. H_2SO_4 + small amount of O.S. + few crystals of $NaNO_2 \xrightarrow{\text{Shake}}$ pour the contents of the test tube to a beaker half full of water

$\rightarrow$ a deep red colour, then add NaOH solution

$\rightarrow$ red colour changes to blue green



Indophenol (Red)



Sodium salt deep blue

(iii) Phthalein Test

0.5g O.S. + 1.0 g phthalic anhydride + drop of conc. $H_2SO_4 \xrightarrow[\text{1 minute}]{\text{heat}} \xrightarrow{\text{Cool}}$ add dil. NaOH solution $\xrightarrow[\text{20 c.c. } H_2O]{\text{pour in}}$ characteristic colour

Aldehydic group (–CHO)

(i) ***Schiff's reagent***

5-6 drops or 0.1 g of O.S. + 2c.c. Schiff's reagent

$\rightarrow$ Shake and wait for 1-2 minutes $\rightarrow$ Deep red or violet colour

(ii) ***Tollen's reagent.***

5-6 drops or 0.1 g of O.S. + 2 c.c. Tollen's reagent

$\rightarrow$ warm and allow to stand the contents for 2-3 minutes

$\rightarrow$ Formation of silver mirror or grey ppt.

$$2Ag(NH_3)_2\,OH + RCHO \rightarrow$$

$$2Ag + RCOONH_4 + 3NH_3 + H_2O$$

(iii) ***Fehling solution :***

5-6 drops or 0.1 g of O.S. + 5 c.c. Fehling solution

$\rightarrow$ boil $\rightarrow$ Red ppt.

$$2CuO + RCHO \rightarrow Cu_2O + RCOOH \text{ Red ppt}$$

Note : Aromatic aldehydes do not respond to this test.

(iv) ***Benedict's solution :***

0.1 g of O.S. + 2-3 c.c. of Benedict's solution → Boil → Appearance of red yellow ppt.

Ketonic group $\left(\begin{smallmatrix}R\\R\end{smallmatrix}>C{=}O\right)$ **:**

(i) ***2, 4–Dinitro phenyl hydrazine test :***

1–2 drops or 0.1g of O.S. + 2c.c. of reagent

— Shake vigrously and heat if necessary– A yellow or orange ppt.

(ii) ***Sodium bisulphite test :***

5-6 drops or 0.2 g of O.S. + 1 c.c. of saturated solution of sodium bisulphite-shake vigrously

—A crystalline white ppt.

(iii) Sodium Nitroprusside Test :

5-6 drops or 0.1 g of O.S. + 2 c.c. of 0.5 % aqs sodium nitroprusside solution + 2–3 drops of NaOH–A red or purple colour

Note-Benzophenone does not give this test

-First two tests are also given by aldehydes

Carboxylic group (–COOH) :

(i) ***Sodium bicarbonate test***

Small amount of O.S. + 3 c.c. of saturated solution of sodium bicarbonate-Brisk effervescence

$$RCOOH + NaHCO_3 \rightarrow RCOONa + H_2O + CO_2 \uparrow$$

(ii) ***Litmus test***

Place O.S. on moist blue litmus paper. If it changes to red the O.S. may be an acid

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

Note- Phenols also give this test

(iii) ***Ester test***

Small quantity of O.S. + 4-5 drops of $C_2H_5OH + 2-3$ drops of conc. $H_2SO_4 \xrightarrow{\text{warm}}$ fruity smell

$$RCOOH + C_2H_5OH \xrightarrow{H_2SO_4} \underset{\substack{\text{Ester}\\\text{(Fruity smell)}}}{RCOOC_2H_5} + H_2O$$

Amino group (–NH$_2$, primary)

(i) ***Carbylamine test :***

2 drops of O.S. + 2 drops of $CHCl_3$ + 2c.c. of alcoholic caustic potash → Intolerable offensive odour

$$RNH_2 + CHCl_3 + 3KOH \rightarrow \underset{\text{Carbylamine}}{RNC} \uparrow + 3KCl + 3H_2O$$

Aromatic or aliphatic 1° amines give this test

(ii) ***Nitrous acid test***

0.2 g of O.S. + 10 c.c. of $HCl \xrightarrow[\text{(ii) Cool}]{\text{(i) Heat}}$ Add 10% aqs $NaNO_2$ → Brisk effervescence (aliphatic 1° amine)

$$RNH_2 + HNO_2 \rightarrow ROH + H_2O + N_2 \uparrow$$

A yellow oily layer is formed (2° amine)

$$R_2NH + HONO \rightarrow \underset{\substack{\text{Nitrosamine}\\\text{(yellow oil)}}}{R_2N} \rightarrow NO + H_2O$$

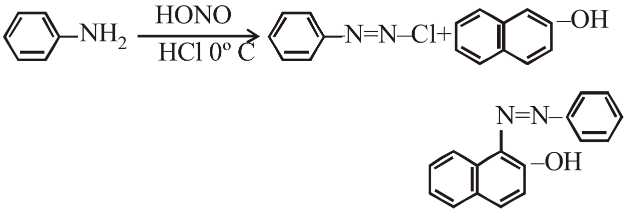
No visible change (3° amine)

$$R_3N + HONO \rightarrow \underset{\text{Trialkyl ammonium nitrate}}{R_3N^+HONO^-}$$

(iii) ***Azo-Dye test :***

This test is given by 1° aromatic amines.

(0.2 g or 0.2 ml of O.S. + 2 ml conc. HCl (Cool) + 10% aqs $NaNO_2$ (cold)) pour into a beaker containing 10% alkaline β – naphthol → Bright Orange/red dye



Orange/red ppt.

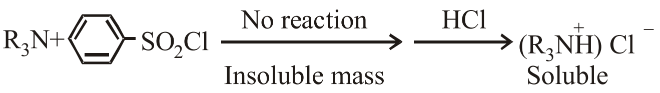
(iv) ***Distinguishing test for*** 1°, 2° and 3° ***amines***

Hinsberg's Test :

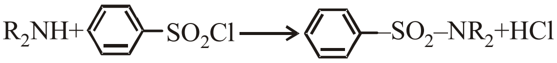
0.5 ml of O.S. + 2 ml of 25% NaOH + 1 ml of benzene sulphonyl chloride. Shake and Cool.

→ If ppt is obtained add 2 ml of conc HCl

(i) Precipitate dissolves in conc HCl → 3° amine

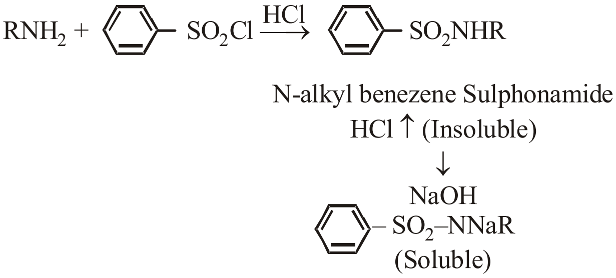


(ii) Precipitals does not dissolve in conc. HCl → 2° amine



N, N-dialkylbenzene sulphonamide
(Insoluble in NaOH)

(v) ***Clear solution.*** On addition of conc HCl, insoluble mass is formed → 1° amine



(vi) ***Solubility Test***

Small amoums of O.S. + 2-3ml dil HCl

→ shake - If soluble, it may be an amine

$$RNH_2 + HCl \rightarrow (R\overset{+}{N}H_3)Cl^-$$

Amines are basic in nature

(vi) ***Litmus Test***

Place O.S. on moist red limus paper. If it is changes to blue the O.S. may be an amine.

$$RNH_2 + H_2O \rightleftharpoons RN^+H_3 + OH^-$$

3. CHEMISTRY INVOLVED IN PREPARATION OF INORGANIC COMPOUNDS :-

Ferrous Ammonium Sulphate (Mohr's salt)

Reagents: Iron fillings, ammonium sulphate and conc. sulphuric acid.

Procedure : Take 60 c.c. of distilled water in a conical flask and add to 8 c.c. of conc. sulphuric acid. Gradually add 10 gm of iron filling's and heat to boiling. Now add 20 gm of ammonium sulphate and evaporate to one third of its volume. Cool the flask slowly and set aside to crystallise.

Formula - $FeSO_4.(NH_4)_2SO_4.6H_2O$

Potash alum reagents: Potassium sulphate, Aluminium sulphate crystals

Procedure : 2.9 gm of potassium sulphate is dissolved in 30 c.c. of distilled water. 11.2 gm of aluminium sulphate is dissolved in 30 c.c. of distilled water. Mix the two solutions and leave overnight. Choose the well formed crystal and allow it to grow in the solution. Recrystallise by dissolving in minimum quantity of water.

Formula : $K_2SO_4.\,Al_2(SO_4)_3.\,24H_2O$

4. CHEMISTRY INVOLVED IN PREPARATION OF ORGANIC COMPOUNDS:-

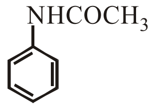
Acetanilide :

Reagents :	Aniline	10 ml
	Acetic anhydride	10 ml
	Acetic acid	10 ml
	Zinc dust	0.05 gm

Procedure : Take 10 ml of aniline in 150 ml of conical flask and add a mixture of 10 ml of acetic anhydride and 10 ml of acetic acid. Add 0.05 gm of Zinc dust. Reflux using water condenser for 15 minutes. Pour the hot mixture in 200 ml of ice cold water with constant stirring. Filter the crystals of acetanilide formed and wash with cold water.

→ Recrystallise from dil. acetic acid (20 ml glacial acetic acid + 40 ml water)

Formula :



White shining flakes mpt 113°C

Iodoform :

Reagents : Alcohol (5 gm); Sodium Carbonate (10 gm); Iodine (10 gm).

Procedure : 5 gm of ethyl alcohol and 10 gm of sodium carbonate in 50 ml of water are taken in round bottom flask. 10 gm of iodine is added in small fractions and the solution is stirred well and heated on water bath until the iodine has disappeared. Then cool, crystals of iodoform will separate. Wash them with distilled water

Formula : CHI_3

Bright yellow

Aniline yellow :

Reagents:	Aniline	7ml
	Conc. HCl	10ml
	Sodium nitrite	2.5g
	Sodium accetate	10.5g

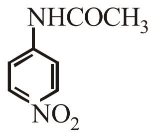
Procedure: Take 7ml of aniline in 250ml of conical flask and add 10ml of Conc. HCl followed by 40ml of water and shake. Flask is placed on a water bath containing crushed ice. 2.5g of sodium nitrite dissolved in 10ml of water added gradually and stirred. When sodium nitrite solution has been completely added, keep the solution for 5 minutes in the water bath. Dissolve 10.5g of sodium acetate in 20ml of water and slowly added to the contents in the flask. Keep the flask in water bath for 20min and stirred. A yellow ppt. of aniline yellow is obtained. This yellow solid is washed with water and then dry between folds of filter paper. The crude dye is recrystallise busing light petroleum.

p-nitro acetanilide :

Reagents :	Acetanilide	5 g
	Glacial acetic acid	5 ml
	Fuming HNO_3	2 ml
	Conc. H_2SO_4	10 ml
	Methylated spirit 20 ml	

Procedure : Take 5 g of powdered acetanilide in 100 ml conical flask. Add 5 ml of glacial acetic acid and shake. Take 2 ml of fuming nitric acid in a test tube and cool it in a freezing mixture. Add to it 2 ml of conc. sulphuric acid drop by drop with constant shaking and cooling. Add 8 ml of conc. H_2SO_4 drop by drop to the conical flask containing acetanilide and glacial acetic acid and place the flask in a freezing mixture. Add nitrating mixture to this flask drop by drop with constant stirring. Remove the conical flask from the freezing mixture and keep at room temperature for 15-20 minutes. Pour the contents of the flask on crushed ice in a beaker. Stir and filter the crude product. Crystallise the p-nitro acetanilide by dissolving it in methylated spirit and washing with cold water.

Formula :



Colourless crystalline solid mpt $214^\circ C$

5. CHEMISTRY INVOLVED IN THE TITRIMETRIC EXERCISES :-

Volumetric or titrimetric analyses are quantitative analytical techniques which employ a titration in comparing an unknown with a standard. In a titration, a volume of a standarized solution containing a known concentration of reactant 'A' is added incrementally to a sample containing an unknown concentration of reactant 'B' till reactant 'B' is just consumed (stoichiometric completion). This is known as the equivalence point.

At this point we have $N_1V_1 = N_2V_2$.

Indicator :

A compound added to the reacting solutions that undergo an abrupt change in a physical property usually a colour .

Types of indicators :

They may be

(i) ***Internal*** **-** They are added to the reacting solutions.

(ii) ***External*** **-** Electrochemical devices such as pH meters.

End point :

The point at which a titration is stopped i.e. equivalence point.

Standard solution :

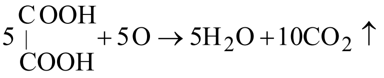
The solution of known concentration of an acid, base or salt.

Examples of volumetric titrations :

(i) **Prepare a standard solution M/100 of oxalic acid. Using this solution. determine the molarity of the given solution of $KMnO_4$.**

Theory - **The reactions involed are :**

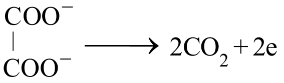
$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$



$$5\begin{array}{l}COOH\\ |\\ COOH\end{array} + 5O \rightarrow 5H_2O + 10CO_2\uparrow$$

In this reaction oxalate ion is behaving as reducing agent and MnO_4^- ion as oxidising agent.

Oxidation half reaction



$$\begin{array}{l}COO^-\\ |\\ COO^-\end{array} \longrightarrow 2CO_2 + 2e$$

Reduction half reaction

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{++} + 4H_2O$$

by using molarity equation we can calculate the molarity of solution.

$$n_1 \times M_1 \times V_1 = n_2 \times M_2 \times V_2$$

($KMnO_4$ solution) (oxalic acid)

where $n_1 = 5$ and $n_2 = 2$

Indicator : $KMnO_4$ is self indicator

End Point : Appearance of light pink colour

Observation

Molarity of oxalic acid solution = M/100

Volume of oxalic acid solution = 25 ml.

S.No	Initial burette reading (R_1)	Final burette reading (R_2)	Volume of $KMnO_4$ used($R_2 - R_1$)
1			

Calculation - $n_1 \times M_1 \times V_1 = n_2 \times M_2 \times V_2$

(KMnO) (oxalic acid)

$$\text{Molarity of } KMnO_4\ (M_1) = \frac{n_2 \times M_2 \times V_2}{n_1 \times V_1}$$

(ii) Prepare a standard solution of M/100 ferrous ammonium sulphate. Using this solution determine the molarity of the given solution of $KMnO_4$.

Theory - The reactions involved are

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

$$\left(2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O\right) \times 5$$

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4$$

$$\rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

The reaction shown above is a redox reaction and hence the titration between ferrous ammonium sulphate and $KMnO_4$ is a redox titration.

In this reaction ferrous sulphate from Mohr's salt is behaving as reducing agent and $KMnO_4$ is acting as oxidising agent.

Oxidation half reaction -

$$Fe^{++} \longrightarrow Fe^{+++} + e$$

Reduction half reaction

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{++} + 4H_2O$$

by using molarity equation we can calculate the molarity of solution.

$$n_1 \times M_1 \times V_1 = n_2 \times M_2 \times V_2$$

($KMnO_4$) ($FeSO_4$)

Indicator : $KMnO_4$ is self indicator

End Point : Appearance of light pink colour

Observation -

Molarity of ferrous ammonium sulphate = M/100

Volume of ferrous ammonium sulphate = 25 ml

S.No	Initial burette reading (R_1)	Final burette reading (R_2)	Volume of $KMnO_4$ used($R_2 - R_1$)
1			

Calculation :

$$\text{Molarity of } KMnO_4\ (M_1) = \frac{n_2 \times M_2 \times V_2}{n_1 \times V_1}$$

6. CHEMICAL PRINCIPLES INVOLVED IN THE QUALITATIVE SALT ANALYSIS :-

A **salt** is a substance which is formed by the combination of an acid and base e.g

$$Cu(OH)_2 + H_2SO_4 \rightarrow CuSO_4 + 2H_2O$$

A salt thus consists of cation known as basic radical and anion known as acid radical. The identification of salts is known as inorganic alnalysis. The tests employed are (i) **Dry tests** (ii) **Wet tests**

1. Dry tests - It includes

(a) ***Physical appearance -*** It gives valuable information about certain salts eg

Salts	PbO_2, Bi_2S_3	are dark brown
Salts of	Mn^{2+}	are light pink
	Co^{2+}	are pink
Salts of	Fe^{2+}, Ni^{2+} and Cr^{3+}	are green
Salts of	Fe^{3+}	are Yellow
Salt	Fe_2O_3	Redish brown
Salts	HgO, HgI_2, Pb_3O_4	are Red
Salt	CuO	Black

(b) ***Action of heat -*** Some salts change their colour when heated

Substance	***Colour in Cold***	***Colour in Hot***
HgO	Red	Black
HgS	Scarlet	Black
SnO_2	Straw	Yellowish brown
PbO	Light burff	Red
Pb_3O_4	Red	Chocolate
$CuCl_2$	Blue	Brown
$CuSO_4$	Blue	White
Bi_2O_3	Yellow	Brown
HgI_2	Crimson	Yellow

NaCl, KI, $Pb(NO_3)_2$ and $Ba(NO_3)_2$ ***Decrepitate (Cracking sound)***

Alums, bortates and phosphate ***Swell up on heating***

$HgCl_2$, Hg_2Cl_2, Sb_2O_3, AS_2O_3, $AlCl_3$ and NH_4X – **are *white and sublime on heating***

AS_2O_3, HgI_2 ***Yellow and sublime***

(c) ***Gas evolved on heating***

Gas evolved	***Possible compound***
CO burns with blue flame	Oxalate $(COO)_2Ca \rightarrow CaO + CO + CO_2$
CO_2 turns lime water milky	Carbonate (except carbonate of alkali metals)
NH_3 white fumes with HCl	Ammonium salts $(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + NH_3$
SO_2 smell of burning sulpher turns $K_2Cr_2O_7$ Soln green	Sulphites $CaSO_3 \rightarrow CaO + SO_2$
H_2S Smell of rotten eggs	Sulphides $Na_2S + 2H_2O \rightarrow 2NaOH + H_2S$
Br_2 Reddish brown	Bromide $2CdBr_2 + O_2 \rightarrow 2CdO + 2Br_2$
I_2 Violet vapours	Iodide $2ZnI_2 + O_2 \rightarrow 2ZnO + I_2$
NO_2 reddish brown	Nitrate (except Ba and alkali metals)

(d) ***Flame tests -*** Salt + 1–2 drops of Conc HCl →Heat in a non luminous (oxidising) Bunsen flame using platinum wire.

Element	***Colour (to naked eye)***	***Colour (through cobalt glass)***
Sodium	Golden yellow	Nil
Potassium	Lilac	Crimson
Calcium	Brick red	Light green
Strontium	Crimson	crimson
Barium	Apple green	green
Copper	Bluish green	–
Tin	Greyish blue	–
Antimony	Greyish green	–
Manganese	Green	–
Boron	Bright green	–
AS, Bi, Hg, Pb	Bluish white	–
Li	Caramine red	–

(e) ***Borax bead test -*** Borax is heated on a loop of Pt. wire when colourless glassy bead of sodium metaborate and boric anhydride is formed

$Na_2B_4O_7 . 10H_2O \rightarrow Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_3$

Coloured salts are then heated on the glassy bead when coloured metaborate is formed in the oxidising flame

$CuSO_4 + B_2O_3 \longrightarrow Cu(BO_2)_2 + SO_3$

Copper metaborate (blue)

In reducing flame we have $2Cu(BO_2)_2 + C \longrightarrow 2CuBO_2 + B_2O_3 + CO$

$2Cu(BO_2)_2 + 2C \longrightarrow 2Cu + 2B_2O_3 + 2CO$

Hence different clolour appear in differnt flames

Metal			***Colour of heat in***	
	Oxidising flame		***Reducing - flame***	
	Hot	***Cold***	***Hot***	***Cold***
Copper	Green	Blue	Colourles	Brown red
Iron	Brown yellow	Pale yellow	Bottle green	Bottle green
Chromium	Green	Green	Green	Green
Cobalt	Blue	Blue	Blue	Blue
Manganese	Violet	Amethyst Red	Grey	Grey
Nickel	Violet	Brown	Grey	Grey

Note - Metals undergoing change in oxidation state eg Fe^{2+} and Fe^{3+} and Cu^{+} and Cu^{2+} form two metaborates

$Fe_2(SO_4)_3 + 2B_2O_3 \longrightarrow 2Fe(BO_2)_3 + 3SO_3$

Yellow (oxidising flame)

$2Fe(BO_2)_3 + C \longrightarrow 2Fe(BO_2)_2 + B_2O_3 + CO$

Green

(reducing flame)

(f) ***Charcoal cavity test -*** Inorganic substance +(K_2CO_3& Na_2CO_3) fusion mixture in a charcoal cavity + Reducing flame with blow pipe. Observe the colour of bead formed or metal

$CuSO_4 + Na_2CO_3 \longrightarrow CuCO_3 + Na_2SO_4$

$CuCO_3 \longrightarrow CuO + CO_2$

$CuO + C \longrightarrow Cu + CO$

$Pb(NO_3)_2 + Na_2CO_3 \longrightarrow PbCO_3 + 2NaNO_3$

$PbCO_3 \longrightarrow PbO + CO_2$

$PbO + C \longrightarrow Pb + CO$

S. No.	***Bead***	***Incrustation or Residue***	***Cation indicated***
1.	Lustrous, white, malleable	None	Ag
2.	White, malleable, does not mark paper	White when cold, yellowish when hot	Sn
3.	White malleable which marks paper	Yellowish when cold, reddish brown hot	Pb
4.	White brittle, when hot gives white fumes	White	Sb
5.	White brittle with reddish tinge yellow when cold	Orange yellow when hot ,	Bi
6.	Red or scales	None	Cu

S. No.	*Bead*	*Incrustation or Residue*	*Cation indicated*
7.	None	White, white fumes with gralic odour	As
8.	None	Reddish brown	Cd
9.	None	White when cold, yellow when hot	Zn
10.	Grey magnetic powder obtained by washing with water	None	Mn,Fe,Cu,Ni
11.	White infusible mass which glows on heating	None	Al,Ba,Sr,Ca,Mg

(g) ***Cobalt nitrate test -*** It is an extension of charcoal cavity test. If the residue left in charcoal cavity is white add one drop of cobalt nitrate solution and heat again in the oxidising flame and observe the Colour

Colour of residue	*Compounds formed*	*Inferance*
Blue $CoO.\ Al_2O_3$	Al, PO_4,BO_3 silicate	
Green CoO. ZnO	Zn	
Light pink	CoO. MgO	Mg
Dirty bluish green	CoO. SnO	Sn

Reactions

$$ZnSO_4+Na_2CO_3 \longrightarrow ZnCO_3+Na_2SO_4$$

$$ZnCO_3 \longrightarrow ZnO+CO_2$$

$$ZnO+CoO \longrightarrow CoO.ZnO \qquad \text{Cobalt zincate}$$

$$MgO+CoO \longrightarrow CoO.MgO$$

$$Al_2O_3+CoO \longrightarrow CoO.Al_2O_3$$

$$2Co(NO_3)_2 \longrightarrow 2CoO+4NO_2+O_2$$

(h) ***Microcosmic bead test -*** It is similer to borax bead test. Here microcosmic salt $Na(NH_4)HPO_4$ is used in place of borax which forms a colourless, transparent bead on a loop of Pt. wire of sodium meta phosphate on heating

$$[Na(NH_4)HPO_4 \longrightarrow NaPO_3+NH_3+H_2O]$$

The metallic oxides then combine with sodium metaphosphate to form coloured ortho phosphates eg

$$NaPO_3+CoO \longrightarrow NaCo.PO_4$$

Cobalt orthophosphate blue

Metal	*Colour of the bead in*			
	oxidising flame		*Reducing flame*	
	Hot	*Cold*	*Hot*	*Cold*
Copper Cu	Green	Blue	Colourless	Red
Iron Fe	Yellow or reddish brown	Yellow	Yellow	Yellow
Chromium Cr	Green	Green	Green	Green
Manganese Mn	Violet	Violet	Colourless	Colourless
Cobalt Co	Blue	Blue	Blue	Blue
Nickel Ni	Brown	Brown	Grey	Grey

Wet tests **Identification of acid radicals**

Type I The radicals decomposed by dil . H_2SO_4 or dil HCl

$$\left.\begin{array}{l} CO_3^{2-} \to CO_2 \\ SO_3^{2-} \to SO_2 \\ S^{2-} \to H_2S \\ NO_2^- \to NO_2 + NO \\ CH_3COO^- \to CH_3COOH \end{array}\right\} \text{gas evolved}$$

Type II The radicals decomposed by Conc H_2SO_4

$$\left.\begin{array}{l} Cl^- \to HCl \\ Br^- \to HBr + Br_2 \\ I^- \to HI + I_2 \\ NO_3^- \to NO_2 \\ C_2O_4^{-\,-} \to CO+CO_2 \end{array}\right\} \text{gas liberated}$$

$$F^- \to HF$$

Detection of acid radicals - Type I

(i) ***Carbonate and bicarbonate*** (CO_3^{2-}, HCO_3^-)

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O \text{ (white ppt)}$$

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2 \text{ soluble}$$

SO_2 from sulphite also turns lime water milky but it has smell of burning sulpher.

$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3\downarrow + H_2O \text{ (white ppt)}$$

(ii) ***Sulphite*** (SO_3^{2-})

$$CaSO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + SO_2$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow$$

$$K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

green

SO_2 gives white precipitate of $BaSO_3$ with $BaCl_2$ which is soluble in dil. HCl

(iii) ***Sulphide*** **(S^{2-})**

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$

$$H_2S + (CH_3COO)_2Pb \longrightarrow 2CH_3COOH + PbS \text{ black}$$

$$CdCO_3 + H_2S \longrightarrow H_2O + CO_2 + CdS \text{ yellow}$$

Sodium carbonate extract of inorganic mixture containing S^{--} give violet colour with sodium nitroprusside

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$$

Sod thionitro prusside

Sulphides of **Pb, Ca, Ni, Co, Sb and Sn** (iv) are not decomposed by dil acid. Conc. HCl is used for them.

(iv) ***Nitrite*** (NO_2^-)

$$Ba(NO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HNO_2$$

$$2\,HNO_2 \longrightarrow H_2O + NO + NO_2$$

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

$$2\,KI + 2NO_2 \longrightarrow 2\,KNO_2 + I_2$$

$$\text{Starch} + I_2 \longrightarrow \text{starch iodide blue}$$

- $FeSO_4.7H_2O + NO \longrightarrow [Fe(H_2O)_5NO]\,SO_4 + 2\,H_2O$
  Brown colour complex

(v) ***Acetate*** (CH_3COO^-)

$$(CH_3COO)_2Ca + H_2SO_4 \longrightarrow CaSO_4 + 2CH_3COOH$$

$$2CH_3COONa + H_2C_2O_4 \longrightarrow 2CH_3COOH + Na_2C_2O_4$$

All acetates dissolve in water. Their aqueous solution with neutral $FeCl_3$ give blood red colour.

$$3CH_3COONa + FeCl_3 \longrightarrow 3NaCl + (CH_3COO)_3Fe$$

blood red ferric acetate

Detection of acid radicals Type-II

(i) ***Chloride*** **(Cl^-)**

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl\uparrow$$

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$

(white fumes)

$$AgNO_3 + HCl \longrightarrow AgCl\downarrow + HNO_3 \text{ (white ppt)}$$

$$AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl$$

Soluble complex $+2H_2O$

Chromyl chloride test -

$$4\,NaCl + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2\,Na_2SO_4 + 2\,CrO_2Cl_2 + 3H_2O \text{ (Orange red)}$$

$$4\,NaOH + CrO_2Cl_2 \longrightarrow 2\,NaCl + Na_2CrO_4 + 2H_2O$$

(Yellow solution)

$$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow 2\,CH_3COONa + PbCrO_4$$

(yellow precipitate)

(The test not is given by chlorides of **Hg(ic), Sn, Ag, Pb**, and **Sb**) and not by Br^- and I^-

(ii) ***Bromide*** **(Br^-)**

$$2\,KBr + H_2SO_4 \longrightarrow K_2SO_4 + 2\,HBr$$

$$2\,HBr + H_2SO_4 \longrightarrow 2\,H_2O + SO_2 + Br_2$$

More brown fumes when MnO_2 is added

- $2NaBr + MnO_2 + 3H_2SO_4 \longrightarrow 2\,NaHSO_4 + MnSO_4 + 2H_2O + Br_2$
- $NaBr + AgNO_3 \longrightarrow AgBr\downarrow + NaNO_3$ (yellow ppt)
- $AgBr + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Br + 2\,H_2O$
- $2NaBr + Cl_2 \longrightarrow 2\,NaCl + Br_2$
  Soluble complex

$$Br_2 + CHCl_3 \longrightarrow \text{brown layer}$$

Excess of chlorine water should be avoided since layer becomes colourless due to conversion of Br_2 into HBrO

$$Br_2 + 2H_2O + Cl_2 \longrightarrow 2\,HBrO + 2\,HCl$$

(iii) ***Iodiode*** **(I^-)**

$$KI + H_2SO_4 \longrightarrow KHSO_4 + HI$$

$$H_2SO_4 + 2HI \longrightarrow H_2O + I_2 + SO_2$$

- $I_2 + \text{starch} \longrightarrow \text{blue colour}$
- $2\,KI + MnO_2 + 3\,H_2SO_4 \longrightarrow 2\,KHSO_4 + MnSO_4 + 2H_2O + I_2$

(more fumes)

- $NaI + AgNO_3 \longrightarrow AgI + NaNO_3$ (yellow ppt)
  AgI insoluble in NH_4OH as it does not form any complex
- $2NaI + Cl_2 \longrightarrow 2NaCl + I_2$

  $I_2 + CHCl_3 \longrightarrow$ Violet

  $I_2 + 5Cl_2$(exces)$+ 6H_2O \longrightarrow 2HIO_3 + 10\,HCl$
  violet colour disappear

(iv) ***Nitrate*** $(\overline{NO_3})$

$Mg(NO_3)_2 + H_2SO_4 \longrightarrow MgSO_4 + 2HNO_3$

$4HNO_3 \longrightarrow 2H_2O + 4NO_2 + O_2$ (brown)

On adding copper turnings the brown fumes intensify

$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

Ring test - $2FeSO_4 + NO \longrightarrow FeSO_4NO$ brown ring or

$[Fe(H_2O)_6]^{2+} + NO \longrightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$

(v) ***Fluoride*** $(\overline{F})$ Sodium carbonate extract after neutralisation with acetic acid is treated with $CaCl_2$, a white precepitate insoluble in dil H_2SO_4 indicates the presence of F^-

$2NaF + CaCl_2 \longrightarrow 2NaCl + CaF_2$ (White ppt)

$CaF_2 + \text{Conc}\ H_2SO_4 \longrightarrow CaSO_4 + 2HF$

$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$

$3\,SiF_4 + 3\,H_2O \longrightarrow H_2SiO_3 + 2H_2SiF_6$
Silicic acid Hydrofluorosilisic acid
(Waxy white deposit)

(vi) ***Oxatate*** $(C_2O_4^{\ 2-})$

$Na_2C_2O_4 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO + CO_2$

$2CO + O_2 \longrightarrow 2CO_2$

CO burns with blue flame

(b) Na_2CO_3 extract + excess $CH_3\,COOH$ (neutralise) + $CaCl_2$ $\longrightarrow$ White ppt

Soluble in dil H_2SO_4

$Na_2C_2O_4 + CaCl_2 \longrightarrow 2\,NaCl + CaC_2O_4$ (white ppt)

$CaC_2O_4 + \text{dil}\ H_2SO_4 \longrightarrow CaSO_4 + H_2C_2O_4$

acidified solution of white ppt. decolorises $KMnO_4$ solution

$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

(vii) ***Sulphate*** $(SO_4^{\ 2-})$

$Na_2SO_4 + BaCl_2 \longrightarrow 2NaCl + BaSO_4$ (white ppt.)

All sulphates except **Ba, Sr, Ca** and **Pb** are soluble in water

(viii) ***Borate*** (BO_3^{3-})

$2Na_3BO_3 + 3H_2SO_4 \longrightarrow 3\,Na_2SO_4 + 2H_3BO_3$

$H_3BO_3 + 3C_2H_5OH \longrightarrow (C_2H_5)_3BO_3 + 3\,H_2O$
ethyl borate
(burns with green flame)

(ix) ***Phosphate*** (PO_4^{3-}) Phosphates give canary yellow precipitate with ammonium molybdate

$Ca_3(PO_4)_2 + 6HNO_3 \longrightarrow 3Ca(NO_3)_2 + 2H_3PO_4$

$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow (NH_4)_3PO_4.12MoO_3 + 21\,NH_4NO_3 + 12\,H_2O$

ammonium phospho molybdate canary yellow ppt.

(x) ***Sodium carbonate extract*** **-** One part inorganic compound or mixture + three parts of Na_2CO_3+25–30ml H_2O. Boil the solution for 10–15 minutes and filter. The filterate is known as sodium cabonate extract. By double decomposition insoluble carbonates of cations are formed and soluble sodium salts of anions

$PbSO_4 + Na_2CO_3 \longrightarrow PbCO_3\downarrow + Na_2SO_4$

$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2\,NaCl$

$BaCl_2 + Na_2CO_3 \longrightarrow BaCO_3\downarrow + 2NaCl$

Sodium Carbonate extract is basic in nature and before the test of anions it is neutralised with suitable acid.

Now basic radicals can be tested from I to IV groups without removing interferring radicals like phosphate, oxalate, fluoride and borate.

Analysis of basic radicals :

Preparation of the original solution - The solution must be prepared in solvent following the order.

1. Water 2 dil HCl 3. Conc. HCl 4. dil HNO_3 5. Conc. HNO_3 6. Aqua regia

Conc HNO_3 and Conc H_2SO_4 must be avoided for preparing the solution. Conc HNO_3 precipitates and converts sulphides of Ba, Sr, Pb to insoluble sulphates.

- $2HNO_3 + H_2S \longrightarrow 2H_2O + 2\,NO_2 + S$
  Sulphuric acid also forms insoluble sulphates of Ba, Sr and Pb
- If mixture is completely soluble in cold dil. HCl Ag^+, Pb^{2+}, Hg_2^{2+} are absent
- Hot Conc HCl solution on cooling or dilution give needle like crystals, Pb^{2+} is present and if turbidity appears Bi^{3+} or Sb^{3+} may be present

  $BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$

  $SbCl_3 + H_2O \rightarrow \underset{\text{White ppt.}}{SbOCl} + 2HCl$

  The precipitate disappears if little HCl is added

- A white crystalline precipitate of NaCl and $BaCl_2$ is formed by adding Conc HCl due to common ion effect

Separation of metallic ions into groups

Group	Group reagent	Ions	Composition and colour of the precipitate	
1.	Dilute HCl	Ag^+	AgCl white	Insoluble in cold dil HCl
		Pb^{2+}	$PbCl_2$ white	
		Hg_2^{2+}	Hg_2Cl_2 white	
2A.	H_2S in presence of dil HCl	Hg^{2+}	HgS Black	Soluble in yellow ammonium sulphide
		Pb^{2+}	PbS Black	
		Bi^{3+}	Bi_2S_3 Black	
		Cu^{2+}	CuS Black	
		Cd^{2+}	CdS yellow	
2B		AS^{3+}	AS_2S_3 yellow	
		Sb^{3+}	Sb_2S_3 orange	
		Sn^{2+}	SnS brown	
		SnS^{4+}	SnS_2 yellow	
3.	NH_4OH in presence of NH_4Cl	Fe^{3+}	$Fe(OH)_3$ reddish brown	
		Al^{3+}	$Al(OH)_3$ white	
		Cr^{3+}	$Cr(OH)_3$ green	
4.	H_2S in presence of NH_4OH	Ni^{2+}	NiS Black	
		Co^{2+}	CoS Black	
		Zn^{2+}	ZnS Greyish white	
		Mn^{2+}	MnS Buff	
5.	$(NH_4)_2CO_3$ in presence of NH_4OH	Ba^{2+}	$BaCO_3$ white	
		Sr^{2+}	$SrCO_3$ white	
		Ca^{2+}	$CaCO_3$ white	
6.	Na_2HPO_4	Mg^{2+}	$Mg(NH_4)PO_4$ white	
	NaOH	NH_4^+	NH_3 gas is given out	
		Na^+ K^+	Flame and other tests	

Tests (Chemical reactions) involved in detection of basic radicals

Group I

1 – Lead Pb⁺⁺

$Pb(NO_3)_2 + 2HCl \rightarrow PbCl_2 + 2HNO_3$ white ppt. soluble in hot H_2O

$PbCl_2 + HCl\ (\text{excess}) \rightarrow H[PbCl_3]$ soluble complex

(i) ***KI :*** $PbCl_2 + 2KI \longrightarrow \mathbf{PbI_2} + 2KCl$
yellow ppt.

$PbI_2 + 2KI \longrightarrow K_2[PbI_4]$
soluble complex
decomposes on dilution

(ii) ***dil H₂SO₄*** **:** $PbCl_2 + H_2SO_4 \longrightarrow \mathbf{PbSO_4} + 2HCl$
white ppt

$PbSO_4 + 2CH_3COONH_4$

$\longrightarrow (CH_3COO)_2Pb + (NH_4)_2SO_4$
Soluble

(iii) ***K₂CrO₄*** **:** $PbCl_2 + K_2CrO_4 \longrightarrow \mathbf{PbCrO_4} + 2KCl$
yellow ppt

$PbCrO_4 + 4NaOH \longrightarrow \mathbf{Na_2PbO_2} + Na_2CrO_4 + 2H_2O$
soluble

(iv) ***H₂S :*** $2PbCl_2 + H_2S$

$\xrightarrow{\text{Conc HCl}} \mathbf{Pb_2SCl_2} + 2HCl$
Red ppt. Lead sulphochloride

$Pb_2SCl_2 + H_2S \longrightarrow \mathbf{2PbS} + 2HCl$ **Black**

$3PbS + 8HNO_3 \longrightarrow \mathbf{3Pb(NO_3)_2} + 2NO + 3S + 4H_2O$

2 – Ag⁺

(i) **dil HCl :** $AgNO_3 + HCl \longrightarrow AgCl \downarrow + HNO_3$
(white ppt)

$AgCl + 2NH_4OH \longrightarrow Ag[(NH_3)_2]Cl + 2H_2O$
Soluble complex

(ii) **Dil HNO₃ :** $Ag(NH_3)_2Cl + 2HNO_3$

$\longrightarrow \mathbf{AgCl} \downarrow + 2NH_4NO_3$

(iii) **KI :** $Ag(NH_3)_2Cl + KI \longrightarrow \mathbf{AgI} + 2NH_3 + KCl$
yellow ppt

(iv) **K₂CrO₄ Solution :** $2Ag(NH_3)_2Cl + K_2CrO_4$

$\xrightarrow{\text{acetic acid}} \mathbf{Ag_2CrO_4} + 2KCl + 2NH_3$
Brick red ppt.

3 – Mercury (Hg_2^{++}) **ous**

(i) ***dil HCl*** : $Hg_2(NO_3)_2 + 2HCl \longrightarrow \mathbf{Hg_2Cl_2} + 2HNO_3$
white ppt.

$Hg_2Cl_2 + 2NH_4OH$

$\longrightarrow \mathbf{[Hg + Hg(NH_2)Cl]} + NH_4Cl + 2H_2O$
Black ppt soluble in aqua regia

$HNO_3 + 3HCl \longrightarrow NOCl + 2Cl + 2H_2O$

$Hg + 2Cl \longrightarrow HgCl_2$

(ii) ***SnCl₂ solution :***

$2HgCl_2 + SnCl_2 \longrightarrow \mathbf{Hg_2Cl_2} + SnCl_4$
white ppt

$Hg_2Cl_2 + SnCl_2 \longrightarrow \mathbf{2Hg} + SnCl_4$
Grey

(iii) ***KI solution :***

$Hg_2(NO_3)_2 + KI \longrightarrow \mathbf{Hg_2I_2} + 2KNO_3$
green ppt

$Hg_2I_2 + 2KI \longrightarrow K_2[HgI_4] + Hg$
soluble Black ppt

(iv) ***K₂CrO₄ soln. :***

$Hg_2(NO_3) + K_2CrO_4 \longrightarrow \mathbf{Hg_2CrO_4} + 2KNO_3$
Brown ppt.

Group IIA

1 – Mercury (Hg^{++})

(i) ***H_2S*:** $3HgCl_2 + 2H_2S \longrightarrow \underset{\text{white}}{\mathbf{HgCl_2.2HgS}} + 4HCl$

$$HgCl_2.2HgS + H_2S \longrightarrow \underset{\text{Black}}{\mathbf{3HgS}} + 2\,HCl$$

$$3HgS + \underbrace{6HCl + 2HNO_3}_{\text{Aqua regia}} \longrightarrow 3HgCl_2 + 3S + 2\,NO + 4\,H_2O$$

(ii) ***$SnCl_2$* soln.:** $2HgCl_2 + SnCl_2 \longrightarrow \underset{\textbf{white ppt}}{Hg_2Cl_2} + SnCl_4$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{\textbf{grey}}{2Hg} + SnCl_4$$

(iii) ***KI Soln*:** $HgCl_2 + 2KI \longrightarrow \underset{\textbf{Red ppt}}{\mathbf{HgI_2}} + 2KCl$

$$HgI_2 + 2KI \longrightarrow \underset{\textbf{Soluble}}{K_2[HgI_4]}$$

(iv) ***Copper turnings*:**

$$HgCl_2 + Cu \longrightarrow CuCl_2 + \underset{\text{grey film}}{Hg}$$

2 – *Bismuth* (Bi^{+++})

(i) ***H_2S*:** $2\,BiCl_3 + 3H_2S \longrightarrow \underset{\text{Black ppt}}{Bi_2S_3} + 6\,HCl$

$$Bi_2S_3 + 8HNO_3 \longrightarrow \underset{\text{soluble}}{2\,Bi(NO_3)_3} + 2NO + 3S + 4\,H_2O$$

(ii) ***NH_4OH*:** $Bi(NO_3)_3 + 3NH_4OH \longrightarrow \underset{\text{white ppt}}{\mathbf{Bi(OH)_3}} + 3NH_4NO_3$

$$Bi(OH)_3 \xrightarrow{\text{Boil}} \underset{\textbf{yellow}}{BiO.OH} + H_2O$$

$$Bi(OH)_3 + 3\,HCl \longrightarrow \underset{\text{(soluble)}}{\mathbf{BiCl_3}} + 2HCl$$

(iii) ***H_2O*:** $BiCl_3 + H_2O \longrightarrow \underset{\substack{\textbf{white ppt}\\ \text{Bismuth oxychloride}}}{BiOCl} + 2HCl$

$$Bi(NO_3)_3 + H_2O \longrightarrow BiO(NO_3) + 2HNO_3$$

$$2Bi(NO_3)_3 + \underset{\text{excess}}{3H_2O} \longrightarrow \underset{\text{Basic salt}}{\mathbf{(BiO)_2(OH)(NO_3)}} + 5HNO_3$$

(iv) ***Sodium stannite soln*:**

$$SnCl_2 + 2NaOH \longrightarrow \underset{\text{white ppt}}{Sn(OH)_2} + 2NaCl$$

$$Sn(OH)_2 + 2NaOH \longrightarrow \underset{\substack{\text{sod. stannite}\\ \text{soluble}}}{Na_2SnO_2} + 2H_2O$$

$$2BiCl_3 + 3Na_2SnO_2 + 6NaOH \longrightarrow 3H_2O + 3Na_2SnO_3 + 6NaCl + \underset{\substack{\text{Black metallic}\\ \text{Bi}}}{\mathbf{2Bi}}$$

(v) **KI:** $BiCl_3 + 3KI \longrightarrow \underset{\textbf{Brown ppt}}{\mathbf{BiI_3}} + 3KCl$

$$BiI_3 + KI \longrightarrow \underset{\text{soluble}}{\mathbf{K[BiI_4]}}$$

$$BiI_3 + H_2O \xrightarrow{\text{dilution}} \underset{\textbf{Orange ppt}}{\mathbf{BiOI}} + 2HI$$

3 – Cu^{++}

(i) ***H_2S*:** $CuCl_2 + H_2S \longrightarrow \underset{\text{Black}}{\mathbf{CuS}} + 2HCl$

$$3CuS + 8NHO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$$

(ii) ***NH_4OH*:** $2CuSO_4 + NH_4OH$

$$\longrightarrow \underset{\text{Blue ppt basic salt}}{\mathbf{Cu(OH)_2.CuSO_4}} + (NH_4)_2SO_4$$

$$CuSO_4.Cu(OH)_2 + (NH_4)_2SO_4 + 6NH_4OH \longrightarrow \underset{\text{Blue soluble complex}}{\mathbf{2[Cu(NH_3)_4]SO_4}} + 8H_2O$$

(iii) ***$K_4[Fe(CN)_6]$*:** $[Cu(NH_3)_4]SO_4 + 4CH_3COOH$

$$\longrightarrow CuSO_4 + 4CH_3COONH_4$$

$$2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow \underset{\textbf{Brown red ppt}}{\mathbf{Cu_2[Fe(CN)_6]}} + 2K_2SO_4$$

(iv) ***KCN*:** $[Cu(NH_3)_4]\,SO_4 + 2KCN + 4\,H_2O$

$$\longrightarrow \mathbf{Cu(CN)_2} + K_2SO_4 + 4NH_4OH$$

$$2Cu(CN)_2 \longrightarrow \mathbf{Cu_2(CN)_2} + (CN)_2\uparrow$$

$$Cu(CN)_2 + 6KCN \longrightarrow \mathbf{2K_3[Cu(CN)_4]}$$

(v) ***Fe*:** $CuSO_4 + Fe \longrightarrow Cu\downarrow + FeSO_4$

(The copper complex is very slightly dissociated in soln and the concentration of Cu^{++} ions is so small that the solubility product of CuS is never reached on passing H_2S into the soln)

4 – Cadmium Cd^{++}

(i) ***H_2S*:** $CdCl_2 + H_2S \longrightarrow \underset{\text{yellow ppt}}{\mathbf{CdS}\downarrow} + 2HCl$

$$3CdS + 8HNO_3 \longrightarrow 3Cd(NO_3)_2 + 2NO + 3S + 4H_2O$$

(ii) ***NH_4OH*:** $CdSO_4 + 2NH_4OH$

$$\longrightarrow \underset{\text{White}}{\mathbf{Cd(OH)_2}\downarrow} + (NH_4)SO_4$$

$$Cd(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH$$

$$\longrightarrow \underset{\text{complex}}{\mathbf{[Cd(NH_3)_4]SO_4}} + 4H_2O$$

(iii) ***KCN*:** $[Cd(NH_3)_4]SO_4 + 2KCN$

$$\longrightarrow \underset{\text{white}}{Cd(CN)_2\downarrow} + K_2SO_4 + 4NH_3$$

$$Cd(CN)_2 + 2KCN \longrightarrow \mathbf{K_2[Cd(CN)_4]}$$

$$K_2[Cd(CN)_4 \rightleftharpoons 2K^+ + [Cd(CN)_4]^{--}$$

$$[Cd\,(CN)_4{}^-]^- \rightleftharpoons Cd^{++} + 4CN^-$$

A sufficient high concentration of Cd^{++} ions is produced by the dissociation of the complex ion to give ppt of CdS with H_2S

$$K_2[Cd(CN)_4] + H_2S \longrightarrow \mathbf{CdS}\downarrow + 2KCN + 2HCN$$

Group IIB

As_2S_3- yellow ; SnS_2 yellow; SnS dark brown $Sb_2S_3^-$ orange

On treatment with hot $(NH_4)_2S_2$, the arsenious, antemonious and stannous sulphides are oxidised to higher sulphides and then dissolve to form thio salts

$$As_2S_3 + 2(NH_4)_2S_2 \longrightarrow 2(NH_4)_2S + As_2S_5$$

$$Sb_2S_3 + 2(NH_4)_2S_2 \longrightarrow 2(NH_4)_2S + Sb_2S_5$$

$$SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2S + SnS_2$$

$$As_2S_5 + 3(NH_4)_2S \longrightarrow \underset{\text{Amm thio arsenate}}{2(NH_4)_3AsS_4}$$

$$Sb_2S_5 + 3(NH_4)_2S \longrightarrow \underset{\text{Ammthioantimonate}}{2(NH_4)_3SbS_4}$$

$$SnS_2 + (NH_4)_2S \longrightarrow \underset{\text{Ammthiostannate}}{(NH_4)_2SnS_3}$$

$$Sn_2S + (NH_4)_2S_2 \longrightarrow \underset{\text{Ammthiostannate}}{(NH_4)_2SnS_3}$$

dil HCl decomposes thio salts precipitating sulphides of As, Sb, and Sn. Excess of $(NH_4)_2S$ is decomposed precipitating sulphur

$$2(NH_4)_3As\,S_4 + 6HCl \longrightarrow AS_2S_5 + 6NH_4Cl + 3H_2S$$

$$2(NH_4)_3SbS_4 + 6HCl \longrightarrow Sb_2S_5 + 6NH_4Cl + 3H_2S$$

$$(NH_4)_2SnS_3 + 2HCl \longrightarrow SnS_2 + 2NH_4Cl + H_2S$$

$$(NH_4)_2S + 2HCl \longrightarrow 2NH_4Cl + H_2S + S$$

Separation : As_2S_5 is insoluble in conc HCl while SnS_2 and Sb_2S_5 are soluble

$$Sb_2S_5 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S + 2S$$

$$SbCl_3 + HCl \longrightarrow H[SbCl_4]$$

$$SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2H_2S$$

$$SnCl_4 + 2HCl \longrightarrow H_2[SnCl_6]$$

To the filtrate iron fillings or granulated zinc is added which reduces $SnCl_4$ to $SnCl_2$

$$SnCl_4 + Zn \longrightarrow SnCl_2 + ZnCl_2$$

$$SnCl_4 + Fe \longrightarrow SnCl_2 + FeCl_2$$

As : (i) Arsenic sulphide dissolves in conc HNO_3 to arsenic acid

$$As_2S_3 + 10HNO_3 \longrightarrow 2H_3AsO_4 + 10NO_2 + 2H_2O + 3S$$

$$As_2S_5 + 10HNO_3 \longrightarrow \underset{\text{arsenic acid}}{2H_3AsO_4} + 10NO_2 + 2H_2O + 5S$$

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3$$

$$\longrightarrow \underset{\substack{\text{Amm. arseno Molybedate}\\ \text{Yellow ppt}}}{(NH_4)_3AsO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

(ii) $As_2S_3 + 3(NH_4)_2CO_3$

$$\longrightarrow \underset{\text{Ammarsenite}}{(NH_4)_3AsO_3} + \underset{\text{Ammthioarsenite}}{(NH_4)_3AsS_3} + 3CO_2$$

$$As_2S_5 + 3(NH_4)_2CO_3$$

$$\longrightarrow \underset{\text{Ammoxythioarsenate}}{(NH_4)_3AsSO_3} + \underset{\text{Ammthioarsenate}}{(NH_4)_3\,AsS_4} + 3CO_2$$

dil HCl decomposes these giving yellow ppt. of As_2S_3 and As_2S_5

$$2(NH_4)_3\,AsS_4 + 6HCl \longrightarrow As_2S_5 + 6NH_4Cl + 3H_2S$$

$$2(NH_4)_3\,AsS_3 + 6HCl \longrightarrow As_2S_3 + 6NH_4Cl + 3H_2S$$

Amm arsenite and amm. oxy thio arsenate are like wise decomposed

$$2(NH_4)_3\,AsO_3 + 12HCl \longrightarrow 2AsCl_3 + 6NH_4Cl + 6H_2O$$

$$2(NH_4)_3\,AsSO_3 + 12HCl$$

$$\longrightarrow 2AsCl_3 + 6NH_4Cl + 6H_2O + S$$

When H_2S is passed $AsCl_3$ is converted in yellow As_2S_3

$$2AsCl_3 + 3H_2S \longrightarrow As_2S_3 + 6HCl$$

Tin (Sn) It forms two types of compounds, stannous and stannic in which it is bivalent and tetravalent.

(i) **H_2S :** $SnCl_2 + H_2S \longrightarrow \underset{\text{Brown ppt}}{SnS} + 2HCl$

$$SnCl_4 + 2H_2S \longrightarrow \underset{\text{Yellow ppt}}{SnS_2} + 4HCl$$

SnS does not dissolve in ordinary amm. sulphide and KOH or NaOH while SnS_2 dissolves.

$SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2SnS_3$

$SnS_2 + (NH_4)_2S \longrightarrow (NH_4)_2SnS_3$

$3SnS_2 + 6KOH \longrightarrow \mathbf{K_2SnO_3} + 2K_2SnS_3 + 3H_2O$

On acidification SnS_2 is precipitated

$$(NH_4)_2.\ SnS_3 + 2HCl \longrightarrow 2NH_4Cl + H_2S + SnS_2\downarrow$$

$$K_2SnO_3 + 2K_2SnS_3 + 6HCl \longrightarrow 6KCl + 3H_2O + 3SnS_2\downarrow$$

$$SnS_2 + 4HCl \xrightarrow{\text{Conc.}} SnCl_2 + 2H_2S$$

$$SnCl_4 + 2HCl \longrightarrow \mathbf{H_2[SnCl_6]}$$

(ii) **Oxalic acid :** $SnCl_4 + 4(NH_4)_2C_2O_4$

$$\longrightarrow \underset{\text{Complex ion not decomposed by } H_2S}{\mathbf{(NH_4)[Sn(C_2O_4)_4(H_2O)_2]}} + 4\,NH_4Cl$$

(iii) **Metals :** $SnCl_4 + Fe \longrightarrow SnCl_2 + FeCl_2$

$$SnCl_2 + 2HgCl_2 \longrightarrow SnCl_4 + \underset{\text{White}}{Hg_2Cl_2}\downarrow$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow SnCl_4 + \underset{\text{grey}}{2Hg}\downarrow$$

Antimony (Sb^{+++})

(i) **H_2S :** $2\,SbCl_3 + 3H_2S \longrightarrow \underset{\text{orange ppt}}{\mathbf{Sb_2S_3}} + 6\,HCl$

$$2\,SbCl_5 + 5H_2S \longrightarrow \mathbf{Sb_2S_5} + 10\,HCl\downarrow$$

$$Sb_2S_3 + 3(NH_4)_2S_2 \longrightarrow \mathbf{2(NH_4)_3\,SbS_4} + S$$

$$Sb_2S_5 + 3(NH_4)_2S \longrightarrow \mathbf{2(NH_4)_3\,SbS_4}$$

$2\,Sb_2S_3 + 4KOH \longrightarrow \mathbf{KSbO_2} + 3\,KSbS_2 + 2\,H_2O$

$Sb_2S_5 + 6KOH \longrightarrow K_3SbO_3 + K_3SbS_4 + 3\,H_2O$

On acidifcation of the above soln with dil HCl $\mathbf{Sb_2S_5}$ is precipitated.

$$2\,(NH_4)_3\,SbS_4 + 6HCl \longrightarrow Sb_2S_5 + 6\,NH_4Cl + 3H_2S$$

$$K_3SbO_3 + K_3SbS_4 + 6HCl \longrightarrow Sb_2S_5 + 6\,KCl + 3H_2O$$

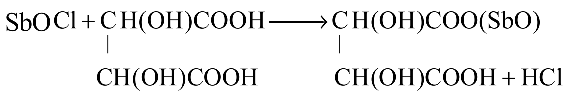
$$K\,SbO_2 + 3K\,SbS_2 + 4HCl \longrightarrow 2Sb_2S_3 + 4\,KCl + 2H_2O$$

These sulphides dissolve in Conc HCl to form chlorides

$$Sb_2S_3 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S$$

$$Sb_2S_5 + 6HCl \longrightarrow 2SbCl_3 + 2S + 3H_2S$$

(ii) **Water :** $SbCl_3 + H_2O \longrightarrow \underset{\text{White ppt antimony oxychloride}}{SbOCl} + 2HCl$



$$SbOCl + \begin{array}{l} CH(OH)COOH \\ | \\ CH(OH)COOH \end{array} \longrightarrow \begin{array}{l} CH(OH)COO(SbO) \\ | \\ CH(OH)COOH \end{array} + HCl$$

Soluble antimonyl tartrate

(iii) **Metals :** $2\,SbCl_3 + 3Fe \longrightarrow Sb + 3FeCl_2$

Group III

Members : Fe^{+++}, Al^{+++}, Cr^{+++}

Group reagent : NH_4OH in presence of NH_4Cl (excess)

Precautions

1. Before oxidation with HNO_3, H_2S must be completely removed otherwise it will be partly oxidised to H_2SO_4 which will precipitate the sulphates of Ba, Sr, etc.
2. The soln is boiled with conc HNO_3 to oxidise Fe^{++} ions to Fe^{+++} to ensure complete precipitation of iron as $Fe(OH)_3$. $Fe(OH)_2$ is not completely precipitated by NH_4OH in presence of NH_4Cl and will pass in the filtrate of IV gp

   $2FeCl_2 + 8HNO_3$

   $$\longrightarrow \mathbf{2Fe(NO_3)_3} + 4HCl + 2NO_2 + 2H_2O$$
3. Mn is usually precipitaled in gp IV but sometimes due to insufficient quantity of NH_4Cl and presence of air bubbles in soln, it is precipitated with the radicals of III gp. as manganic hydroxide MnO.OH
4. The precipitation should be carried out in hot soln otherwise Cr may be incompletely precipitated due to the formation of violet soluble complex chromamine in presence of excess of NH_4Cl. The complex may be decomposed by boiling.
5. Large excess of NH_4OH should be avoided because $Al(OH)_3$ dissolves giving complex compound.
6. Addition of NH_4Cl is absolutely essential otherwise the basic radicals of subsequent gps ppt out as hydroxides in this gp

   NH_4Cl suppresses the ionisation of NH_4OH and prevents the precipitation of higher gp hydroxides in gp III.

Function of NH_4Cl :

1. The hydoxides of ***Fe, Al*** and ***Cr*** have a strong tendency to pass into **colloidal state.** These are ***congulated by NH_4Cl*** which is a strong electrolyte
2. The hydroxides of ***Al, Cr,* and *Zn*** are amphoteric. They supply negative ions in soln which form insoluble salts with other metallic ions (eg CrO_2, $Co(AlO_2)_3$, $Fe\,(ZnO_2)_3$ etc. This entraping of metallic ions by these hydroxides is known as "carrying down" . ***It is prevented by NH_4Cl***
3. The hydroxides of III gp absorb other metal ions in the form of hydroxides eg $[XFe(OH)_3.\ Y\ Ni(OH)_2]$ such hyroxide formation is prevented by NH_4Cl separation.

Separation : By treating with Na_2O_2 or NaOH and Br_2 water the hydroxides of ***Cr*** and ***Al*** dissolve as sodium chromate and aluminate respectively. While ***$Fe(OH)_3$*** and manganic hydroxide remain uneffected. MnO.OH is oxidised by PbO_2 and HNO_3 to permanganic acid $HMnO_4$ which gives violet or pink colour. $Fe(OH)_3$ dissolves in HCl forming $FeCl_3$

1. **Iron Fe^{+++} :**

Fe^{++} salts are easily oxidised when heated with HNO_3

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

(i) **NH_4OH :** $FeCl_3 + 3NH_4OH$

$$\longrightarrow \underset{\text{Reddish brown}}{Fe(OH)_3\downarrow} + 3NH_4Cl$$

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

(ii) **$K_4[Fe(CN)_6]$:**

$$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\textbf{Prussian Blue}}{Fe_4[Fe(CN)_6]_3\downarrow} + 12KCl$$

$$FeCl_3 + K_4[Fe(CN)_6] \longrightarrow \underset{\textbf{K. ferric ferrocyanide}}{KFe[Fe(CN)_6]} + 3KCl$$

(iii) **NH_4CNS or KCNS**

$$FeCl_3 + KCNS \longrightarrow \underset{\textbf{Blood red colouration}}{Fe(CNS)Cl_2\downarrow} + KCl$$

others believe that complex ferric sulpho cyanate is formed

$$2FeCl_3 + 6NH_4CNS \longrightarrow Fe[Fe(CNS)_6] + 6NH_4Cl$$

(iv) **Sod acetate solution**

$$FeCl_3 + 3CH_3COONa \longrightarrow 3NaCl + \underset{\textbf{reddish brown colouration}}{Fe(CH_3COO)_3\downarrow}$$

2. **Aluminium Al^{+++}**

(i) **NH_4OH :** $Al_2(SO_4)_3 + 6NH_4OH$

$$\longrightarrow \underset{\substack{\textbf{white}\\ \textbf{gelatinous ppt}}}{\mathbf{2Al(OH)_3}\downarrow} + (NH_4)_2SO_4$$

$$Al(OH)_3 + 3HCl \longrightarrow \underset{\text{Soluble}}{\mathbf{AlCl_3}} + 3H_2O$$

$$Al(OH)_3 + NaOH \longrightarrow \underset{\substack{\text{sod. aluminate}\\ \text{(soluble)}}}{\mathbf{NaAlO_2}} + 2H_2O$$

(ii) **NH_4Cl :**

$$NaAlO_2 + NH_4Cl + H_2O \longrightarrow Al(OH)_3 + NH_3 + NaCl$$

$$NaAlO_2 + HCl + H_2O \longrightarrow Al(OH)_3 + H_2O + NaCl$$

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

3. **Chromium (Cr^{+++})**

(i) **NH_4OH :**

$$CrCl_3 + 3NH_4OH \longrightarrow \underset{\substack{\textbf{Bluish green}\\ \textbf{gelatenous ppt}}}{\mathbf{Cr(OH)_3}} + 3NH_4Cl$$

$$Cr(OH)_3 + 6NH_4OH \xrightarrow[\text{excess}]{\text{Cold}} \underset{\substack{\textbf{Voilet pink soln}\\ \textbf{(chrome - ammine)}}}{[Cr(NH_3)_6](OH)_2} + 6H_2O$$

(ii) **NaOH and Br_2 water :**

$$2Na_2O_2 + H_2O \longrightarrow 4NaOH + 2O$$

$$Br_2 + NaOH \longrightarrow NaBr + HBr + O$$

$$2Cr(OH)_3 + 4NaOH + 3O \longrightarrow \underset{\textbf{Sod. chromate (yellow)}}{\mathbf{2Na_2CrO_4}} + 5H_2O$$

(iii) **Lead acetate :**

$$Na_2CrO_4 + (CH_3COO)_2Pb \xrightarrow[\text{acid}]{\text{Acetic}} \underset{\text{Yellow}}{\mathbf{PbCrO_4}\downarrow} + 2CH_3COO\,Na$$

$$PbCrO_4 + 4NaOH \longrightarrow \underset{\textbf{Soluble}}{\mathbf{Na_2PbO_2}} + Na_2CrO_4 + 2H_2O$$

Group IV

The ppt consists NiS, CoS, ZnS and MnS

Separation : ppt + dil HCl $\longrightarrow$ **ZnS** and **MnS** dissolve as $ZnCl_2$ and $MnCl_2$ and **NiS and CoS** remain insloluble

$$ZnS + 2HCl \longrightarrow ZnCl_2 + H_2S$$

$$MnS + 2HCl \longrightarrow MnCl_2 + H_2S$$

The soln is heated with NaOH

$$ZnCl_2 + 2NaOH \longrightarrow \underset{\text{ppt}}{Zn(OH)_2} + 2NaCl$$

$$MnCl_2 + 2NaOH \longrightarrow \underset{\text{ppt}}{Mn(OH)_2} + 2NaCl$$

Excess NaOH :

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sod. Zincate soluble}}{\mathbf{Na_2ZnO_2}} + 2H_2O$$

(i) $Na_2ZnO_2 + H_2S \xrightarrow{\text{acidified}} \underset{\textbf{White ppt}}{\mathbf{ZnS}} + 2NaOH$

(ii) $Na_2ZnO_2 + 2CH_3COOH$

$$\longrightarrow (CH_3COO)_2Zn + 2NaOH$$

$$2(CH_3COO)_2\,Zn + K_4[Fe(CN)_6] \longrightarrow \underset{\textbf{Bluish white}}{\mathbf{Zn_2[Fe(CN)_6]}} + 4CH_3COOK$$

Mn: The residue consists of $Mn(OH)_2$

(i) **Residue + Conc HNO_3 +PbO_2 or Pb_3O_4**

$\longrightarrow$ Pink Coloured permanganic acid

$$Mn(OH)_2 + 2HNO_3 \longrightarrow Mn(NO_3)_2 + 2H_2O$$

$$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

$$5PbO_2 + 2Mn(NO_3)_2 + 6HNO_3 \longrightarrow \underset{\text{permanganic acid (pink)}}{\mathbf{2KMnO_4}} + 5Pb(NO_3)_2$$

(ii) With oxidising fusion mixture green mass of Na_2MnO_4

$$2KNO_3 + 2NaOH + Mn(OH)_2 \longrightarrow 2KNO_2 + \underset{\text{sod. manganate green}}{\mathbf{Na_2MnO_4}} + H_2O$$

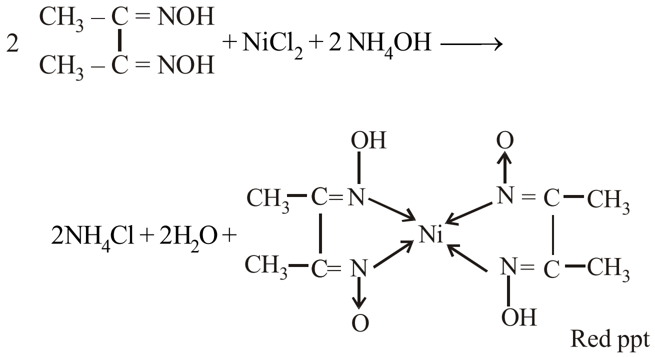
Nickel and Cobalt :

NiS and CoS soluble in aqua regia

$$3NiS + 3HNO_3 + 6HCl \longrightarrow \mathbf{3NiCl_2} + 2NO + 3S + 4H_2O$$

$$3CoS + 3HNO_3 + 6HCl \longrightarrow \mathbf{3CoCl_2} + 2NO + 3S + 4H_2O$$

1. **Method I :** Nickel salt with **DMG** in **ammonical** medium gives red ppt of NDMG



$$2\begin{array}{l} CH_3 - C = NOH \\ \quad\;\; | \\ CH_3 - C = NOH \end{array} + NiCl_2 + 2\,NH_4OH \longrightarrow$$

Red ppt

Cobaltous (Co^{++}) salt with amm. thio cyanate gives blue colour due to

$$CoCl_2 + 4NH_4CNS \longrightarrow \underset{\text{Amm. Cobalto thiocyanate blue}}{\mathbf{(NH_4)_2\,Co\,(CNS)_4}} + 2NH_4Cl$$

2. **Method II**

(a) Cobaltous salts form **Sod. Cabalto carbonate** with **$NaHCO_3$.** Br_2 oxidises this complex to Sod. **Cobalt carbonate** which is apple green and stable towards heat.

$$CoCl_2 + 2NaHCO_3 \longrightarrow \mathbf{Co(HCO_3)_2} + 2\,NaCl$$

$$Co(HCO_3)_2 \longrightarrow CoCO_3 + CO_2 + H_2O$$

$$CoCO_3 + 2NaHCO_3 \longrightarrow \underset{\text{Sod. cobalto carbonate}}{\mathbf{Na_4[Co(CO_3)_3]}} + 2CO_2 + 2H_2O$$

$$Br_2 + H_2O \longrightarrow 2HBr + O$$

$$2Na_4[Co(CO_3)_3] + 2NaHCO_3 + O \longrightarrow \underset{\text{(apple green Sod. cobalti carbonate)}}{\mathbf{2Na_3[Co(CO_3)_3]}} + 2Na_2CO_3 + 2H_2O$$

(b) **Nickel** : Does not form any complex with $NaHCO_3$ but forms black **Ni_2O_3** in alkaline Soln of Br_2

$$NiCl_2 + 2NaHCO_3 \longrightarrow Ni(HCO_3)_2 + 2NaCl$$

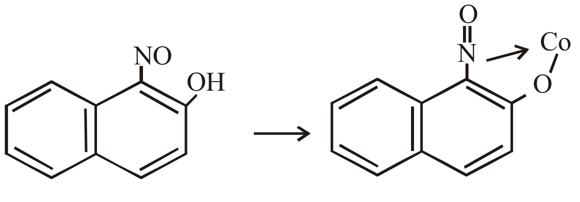
$$Ni(HCO_3)_2 \xrightarrow{\Delta} NiCO_3 + H_2O + CO_2$$

$$2NaHCO_3 + Br_2 \longrightarrow 2NaBr + NaOBr + 2CO_2$$

$$2NiCO_3 + NaOBr + 3H_2O \longrightarrow 2Ni(OH)_3 + NaBr + 2CO_2$$

$$2Ni(OH)_3 \xrightarrow{\Delta} \underset{\text{Black}}{\mathbf{Ni_2O_3}} + 3H_2O$$

3. **Method III :** Cobalt salts with α-nitro β - naphthol form brown complex



cobaltinitroso β - naphthol Reddish brown

4. **Method IV :**

KCN form the following ***Colourless soluble complexes*** with ***Cobalt*** and ***Nickel salts.***

$$CoCl_2 + 6KCN \longrightarrow \underset{\text{K- cobaltocyanide colourless}}{\mathbf{K_4[Co(CN)_6]}} + 2KCl$$

$$NiCl_2 + 4KCN \longrightarrow \underset{\text{Pot. nickelo cyanide colourless}}{\mathbf{K_2[Ni(CN)_4]}} + 2KCl$$

If the soln is treated with sod. hypobromite (Br_2 in presence of NaOH) the Ni cyanide is decomposed and black ppt of Ni_2O_3 is obtained

$$Br_2 + 2NaOH \longrightarrow NaBr + NaOBr + H_2O$$

$$NaOBr \longrightarrow NaBr + O$$

$$2K_2[Ni(CN)_4] + 4NaOH + O \longrightarrow \underset{\text{Black}}{\mathbf{Ni_2O_3}} + 4NaCN + 4KCN + 2H_2O$$

And K. cobalto cyanide is oxidised to K. cobalti cyanide which is still **colourless**

$$4K_4[Co(CN)_6] + 2H_2O + 2O \longrightarrow \underset{\text{K- cobalti cyanide colourless}}{4K_3[Co(CN)_6]} + 4KOH$$

5. **Method V :** When **KNO_2** is added to a cobaltous salt soln in presence of acetic acid a bright yellow ppt of **K-*cobaltinitrite*** is obtained.

$$CoCl_2 + 2KNO_2 \longrightarrow Co(NO_2)_2 + KCl$$

$$KNO_2 + CH_3COOH \longrightarrow CH_3COOK + HNO_2$$

$$Co(NO_2)_2 + 3\,KNO_2 + 2HNO_2 \longrightarrow \mathbf{K_3[Co(NO_2)_6]} + NO + H_2O$$

K- cobalti nitrite yellow ppt

The corresponding sod. salt is soluble in H_2O and hence reagent for K^+ ions. Nickel does not form any ppt in presence of CH_3COOH acid

Some precautions for IV gp analysis.

1. **H_2S** must be passed in **hot** soln otherwise **ZnS** and **MnS** will form colloidal soln.
2. H_2S should not be passed for a long time otherwise **NiS** will turn to colloidal solution
3. The NH_4Cl checks the formation of colloidal soln.
4. KCNS cannot be used in place of NH_4CNS in test of Co(see method I above)
5. After dissolving sulphides in dil **HCl** the H_2S should be completely removed by boiling the soln before adding NaOH soln otherwise **ZnS** will be ppted and may be confused for **$Mn(OH)_2$**
6. When both Co and Ni are present then the soln is first treated with little **NH_4OH** and green **$Co(OH)_2$** is removed by filtration. The test for Ni with DMG should be performed in the filtrate because cobalt interferes in the Ni test reacting with DMG to form brown coloured complex ion.

Group V

Member : Ba^{++}, Sr^{++} Ca^{++} ppted as carbonates

Group reagent : $(NH_4)_2CO_3$ in presence of **NH_4Cl** and **NH_4OH**

1. High concentration of **NH_4Cl** prevents complete precipitation of the carbonates of this group.
2. Before adding $(NH_4)_2CO_3$ the volume of the solution must be reduced to one-third by evaporation because the solution becomes very dilute upto Vth group.
3. **Barium chromate** can not be precipitated in presence of an appreciable hydrogen ion concentration, therefore **acetic acid** is used and that too in minimum possible amount.
4. It is better to use saturated solution of **$(NH_4)_2SO_4$** to detect Sr^{++} radical. After addition of the reagent, wait for few minutes to see if a precipitate of $SrSO_4$ is obtained.
5. The solubility product of $SrSO_4$ is sufficiently large which may result in its incomplete precipitation. Sr^{++} ions may, therefore, co-precipitate as SrC_2O_4 along with CaC_2O_4
6. From concentrated solutions calcium may get co-precipitated as calcium sulphate with strontium sulphate.
7. Sometimes calcium does not get precipitated in its group due to the formation of $Ca(HCO_3)_2$ on addition of $(NH_4)_2CO_3$ to the concentrated filtrate of Vth group as $Ca(HCO_3)_2$ is soluble and so it passes into the filtrate of Vth group. Hence filtrate of Vth group must be tested for calcium before proceeding to VIth group of the analysis.
8. $BaCrO_4$ is not sufficiently volatile to give flame test therefore it should be converted to chloride.
9. The insoluble carbonate of Ba, Sr and Ca are precipitated on the addition of $(NH_4)_2CO_3$ to the filtrate of group IV.
10. Barium chromate is insoluble in acetic acid while the chromates of Sr and Ca are soluble in it.
11. Ammonium sulphate brings about the precipitation of $SrSO_4$ only while calcium is not precipitated by this reagent due to the formation of complex salt $(NH_4)_2\,[Ca(SO_4)_2]$.
12. Calcium oxalate being insoluble in acetic acid, is precipitated by the addition of ammonium oxalate.

1. **Barium (Ba^{++})**

(i) $BaCl_2 + (NH_4)_2CO_3 \longrightarrow \mathbf{BaCO_3}\downarrow + 2NH_4Cl$

white ppt

$$BaCO_3 + 2CH_3COOH \longrightarrow \mathbf{(CH_3COO)_2Ba} + H_2O + CO_2$$

(ii) **Pot. chromate**

$$(CH_3COO)_2Ba + K_2CrO_4 \longrightarrow \mathbf{BaCrO_4}\downarrow + 2CH_3COOK$$

yellow

- **Soluble in mineral** acids but **insoluble in CH_3COOH.** Chromates of **Sr** and **Ca** are soluble in acetic acid

$$(CH_3COO)_2Ba + K_2CrO_4 \longrightarrow \mathbf{BaCrO_4} + 2CH_3COOK$$

(iii) **H_2SO_4 :** $BaCl_2 + H_2SO_4 \longrightarrow \mathbf{BaSO_4}\downarrow + 2HCl$

(iv) **Amm. oxalate :** $BaCl_2 + (NH_4)_2C_2O_4 \longrightarrow \mathbf{BaC_2O_4} + 2\,NH_4Cl$

White ppt readily **soluble** in CH_3COOH

2. **Sr^{++}**

(i) **$(NH_4)_2CO_3$:** $SrCl_2 + (NH_4)_2CO_3 \longrightarrow \mathbf{SrCO_3} + NH_4Cl$

white ppt

$$SrCO_3 + 2CH_3COOH \longrightarrow \mathbf{(CH_3COO)_2Sr} + H_2O + CO_2$$

soluble

On adding K_2CrO_4 for the detection of Ba **$SrCrO_4$** is not ppted in presence of acetic acid.

$$Sr(CH_3COO)_2 + K_2CrO_4 \longrightarrow \mathbf{SrCrO_4} + 2CH_3COOK$$

soluble

(ii) **$(NH_4)_2SO_4$:** $SrCrO_4 + (NH_4)_2SO_4 \longrightarrow SrSO_4 + (NH_4)_2CrO_4$

white ppt

Ca remain in the solution as soluble complex.

(iii) **Amm oxalate Soln :** $SrCrO_4 + (NH_4)_2C_2O_4$

$$\longrightarrow \mathbf{SrC_2O_4} + (NH_4)_2CrO_4$$

white ppt insoluble in acetic acid

3. **Ca^{++}**

(i) **$(NH_4)_2CO_3$:** $CaCl_2 + (NH_4)_2CO_3$

$$\longrightarrow \mathbf{CaCO_3} + 2NH_4Cl$$

white ppt

$CaCO_3 + 2CH_3COOH$

$$\longrightarrow (CH_3COO)_2Ca + CO_2 + H_2O$$

soluble.

On adding K_2CrO_4

Ca chromate : is not ppted but remains in the soln

$Ca(CH_3COO)_2 + K_2CrO_4$

$$\longrightarrow \mathbf{CaCrO_4} + 2CH_3COOK$$

Soluble

On adding $(NH_4)_2SO_4$ to $CaCrO_4$; **$CaSO_4$** is not ppted but soluble complex is formed..

$CaCrO_4 + 2(NH_4)_2SO_4$

$$\longrightarrow \mathbf{(NH_4)_2[Ca(SO_4)_2]} + NH_4CrO_4$$

Soluble complex

(ii) **Amm oxalate :** $(NH_4)_2[Ca(SO_4)_2]$ + **$(NH_4)_2C_2O_4$**

$$\longrightarrow CaC_2O_4 + (NH_4)_2SO_4$$

- White ppt **insoluble** in **acetic acid** but **soluble** in mineral acids.

(iii) **$K_4[Fe(CN)_6]$Soln :** $CaCl_2 + K_4[Fe(CN)_6]$

$$\longrightarrow \mathbf{Ca.K_2[Fe(CN)_6]}\downarrow + 2KCl$$

white ppt

VI group analysis

1. **Mg++**

(i) **Sod. hydrogen phosphate soln :**

$Mg(NO_3)_2 + Na_2HPO_4 + NH_4OH$

$$\longrightarrow \mathbf{Mg(NH_4)PO_4} + 2NaNO_3 + H_2O$$

White ppt.

(ii) **NH_4OH:**

$MgCl_2 + 2NH_4OH \longrightarrow \mathbf{Mg(OH)_2} + 2NH_4Cl$

white ppt. soluble in excess of NH_4Cl

2. **Ammonium :** (NH_4^+)

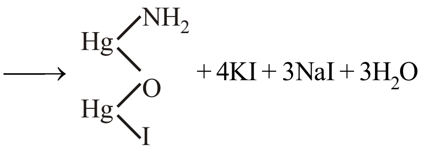
(i) **NaOH :** $NH_4Cl + NaOH \longrightarrow NH_3\uparrow + H_2O + NaCl$

$NH_3 + HCl \longrightarrow NH_4Cl\uparrow$ White fumes

(ii) **Nessler's reagent :** $2KI + HgCl_2 \longrightarrow \mathbf{HgI_2} + 2KCl$

$HgI_2 + 2KI \longrightarrow \mathbf{K_2[HgI_4]}$

$2K_2[HgI_4] + NH_4OH + 3NaOH$



Iodide of millon's base (Brown ppt)

(iii) **Mercurous nitrate :** $Hg_2(NO_3)_2 + 2NH_3$

$$\longrightarrow \underbrace{\mathbf{Hg(NH_2)NO_2 + Hg}}_{\textbf{Black}} + NH_4NO_2$$

(iv) **$CuSO_4$:** $CuSO_4 + 4NH_3 \longrightarrow \mathbf{[Cu(NH_3)_4]SO_4}$

deep blue

3. **Sodium Na^+**

(i) **Pot. dihydrogen antimonate :**

$KH_2SbO_4 + NaCl \longrightarrow \mathbf{NaH_2SbO_4} + KCl$

white ppt

(ii) **Uranyl Mg. acetate solution :**

$NaCl + 3UO_2(CH_3COO)_2 + Mg(CH_3COO)_2$

$+ CH_3COOH \longrightarrow HCl + \mathbf{NaMg(UO_2)_3(CH_3COO)_9}$

yellow ppt

(iii) **Uranyl zinc acetate Reagent :**

yellow crystalline Sod. Zinc acetate **$NaZn(UO_2)_3(CH_3COO)_9\,9H_2O$**

4. **Potassium K^+**

(i) **Chloroplatinic acid :** Golden yellow crystalline ppt. in neutral or acid medium.

(ii) **Sod. Cobaltinitrite :**

$Na_3[Co(NO_2)_6] + 3KCl \longrightarrow \mathbf{K_3[Co(NO_2)_6]} + 3NaCl$

K.cobalti nitrite yellow ppt. (fischer's salt)

(iii) **Sod. hydrogen tartrate :** In conc. solution the reagent in the presence of alcohol gives a white ppt on scratching the sides with a glass rod

$$KCl + \begin{array}{l} CH(OH)COONa \\ | \\ CH(OH)COOH \end{array} \longrightarrow \begin{array}{l} CH(OH)COOK \\ | \\ CH(OH)COOK\downarrow \end{array} + NaCl$$

white ppt

- $2KCl + H_2PtCl_6 \longrightarrow K_2PtCl_6 + 2HCl$

ACTION OF HEAT ON SOME INORGANIC COMPOUNDS

1. <u>Carbonates</u> **:-** Except Li_2CO_3 all alkali metal carbonates are stable.

(i) $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2\uparrow$

(ii) $2(NH_4)_2CO_3 \longrightarrow NH_3 + NH_4HCO_3$

smelling salt

(iii) $2Ag_2CO_3 \longrightarrow 4Ag + 2CO_2 + O_2$

(iv) $2Hg_2CO_3 \longrightarrow 4Hg + 2CO_2 + O_2$

(v) Rest – give metal oxide and CO_2

2. **Nitrates** :- Except $LiNO_3$ all alkali metal nitrates decompose to nitrites and O_2.

$$Na, K, Rb, Cs \longrightarrow MNO_2 + O_2$$

$$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$

$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

$$Hg_2(NO_3)_2 \longrightarrow 2Hg + 2NO_2 + O_2$$

$$NH_4NO_3 \longrightarrow 2H_2O + N_2O \text{ (laughing gas)}$$

$$\text{Rest} \longrightarrow \text{metal oxide} + NO_2 + O_2$$

3. **Sulphates** :- Alkali metal sulphates are stable to heat. On heating they loose water of crystallisation

$$\underset{\text{Glauber's salt}}{Na_2SO_4\cdot10H_2O} \longrightarrow \underset{\text{salt cake}}{Na_2SO_4} + 10H_2O$$

$$\underset{\text{Epsom salt}}{MgSO_4\cdot7H_2O} \xrightarrow{150^\circ C} MgSO_4\cdot H_2O \xrightarrow{200^\circ C} MgSO_4$$

$$\underset{\text{Gypsum}}{CaSO_4\cdot2H_2O} \xrightarrow{125^\circ C} \underset{\text{Plaster of Paris}}{CaSO_4\cdot\frac{1}{2}H_2O} \xrightarrow{200^\circ C}$$

$$\underset{\text{Anhydride}}{CaSO_4} \xrightarrow{500^\circ C} CaO + SO_3$$

$$\underset{\text{Blue vitriol}}{CuSO_4\cdot5H_2O} \xrightarrow{100^\circ C} CuSO_4\cdot H_2O \xrightarrow{230^\circ C}$$

$$\underset{\text{White}}{CuSO_4} \xrightarrow{750^\circ C} CuO + \frac{1}{2}SO_2 + \frac{1}{2}O_2$$

$$\underset{\text{Green vitriol}}{FeSO_4\cdot7H_2O} \longrightarrow \underset{\text{white}}{FeSO_4} + 7H_2O \longrightarrow$$

$$\underset{\text{Red brown}}{Fe_2O_3} + SO_2 + SO_3$$

$$Fe_2(SO_4)_3 \longrightarrow Fe_2O_3 + 3SO_3$$

$$3HgSO_4 \xrightarrow{\Delta} Hg_2SO_4 + Hg + 2SO_2 + 2O_2$$

$$(NH_4)_2SO_4 \longrightarrow NH_4\cdot HSO_4 + NH_3 \xrightarrow[\Delta]{\text{Strong}}$$

$$NH_3 + N_2 + SO_2 + H_2O$$

$$Ag_2SO_4 \longrightarrow 2Ag + SO_2 + O_2$$

$$\underset{\text{White vitriol}}{ZnSO_4\cdot7H_2O} \xrightarrow{100^\circ C} ZnSO_4\cdot H_2O \xrightarrow{280^\circ C}$$

$$ZnSO_4 \xrightarrow{800^\circ C} ZnO + SO_3$$

4. Bicarbonates on heating give $H_2O + CO_2$

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

5. **Chlorides** :-

$$\underset{\text{Ammonium chloride}}{NH_4Cl} \underset{\text{Cool}}{\overset{\Delta}{\rightleftharpoons}} NH_3 + HCl \quad \text{(It sublimes)}$$

$$CuCl_2\cdot2H_2O \longrightarrow CuCl_2 + 2H_2O$$

$$2CuCl_2 \longrightarrow Cu_2Cl_2 + Cl_2$$

$$ZnCl_2\cdot2H_2O \longrightarrow Zn(OH)Cl + HCl + H_2O$$

$$2Zn(OH)Cl \longrightarrow Zn_2OCl_2 + H_2O$$

$$MgCl_2\cdot6H_2O \xrightarrow{200^\circ C} Mg(OH)Cl + HCl + 5H_2O$$

$$Mg(OH)Cl \xrightarrow{600^\circ C} MgO + HCl$$

$$MgCl_2\cdot6H_2O \xrightarrow[\text{HCl gas}]{\text{heat in}} MgCl_2 + 6H_2O$$

$$2FeCl_3 \xrightarrow{\Delta} 2FeCl_2 + Cl_2$$

$$\underset{\text{Calomel}}{Hg_2Cl_2} \longrightarrow \underset{\substack{\text{Corrosive}\\\text{sublimate}}}{HgCl_2} + Hg$$

6. **Iodides** :-

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

7. **Phosphates** :-

$$\underset{\text{Sod. pr. phosphate}}{NaH_2PO_4} \xrightarrow{\Delta} \underset{\text{sod. meta phosphate}}{NaPO_3} + H_2O$$

$$\underset{\substack{\text{disodium hydrogen}\\\text{phosphate}\\\text{(Sod. sec. phosphate)}}}{2Na_2HPO_4} \xrightarrow{\Delta} \underset{\text{sod. pyrophosphate}}{Na_2P_2O_7} + H_2O$$

$$2Mg(NH_4)PO_4 \longrightarrow \underset{\text{Mg. Pyrophosphate}}{Mg_2P_2O_7} + 2NH_3 + H_2O$$

$$\underset{\text{Microcosmic salt}}{Na(NH_4)HPO_4\cdot4H_2O} \longrightarrow Na(NH_4)HPO_4 + 4H_2O$$

$$\longrightarrow \underset{\substack{\text{Sod. meta}\\\text{phosphate (Glassy Bead)}}}{NaPO_3} + H_2O + NH_3$$

$$[CuO + NaPO_3 \longrightarrow \underset{\text{Blue bead}}{CuNaPO_4}]$$

$$\underset{\substack{\text{Orthophosphorous}\\\text{acid}}}{2H_3PO_4} \xrightarrow{250^\circ C} \underset{\substack{\text{Pyrophosphoric}\\\text{acid}}}{H_4P_2O_7} + H_2O$$

$$\xrightarrow{600^\circ C} \underset{\substack{\text{Meta phosphoric}\\\text{acid}}}{2HPO_3} + H_2O$$

$$\underset{\substack{\text{Hypophosphorous}\\\text{acid}}}{2H_3PO_2} \xrightarrow{\Delta} H_3PO_4 + PH_3$$

$$\underset{\text{Orthophosphorous acid}}{4H_3PO_3} \longrightarrow 3H_3PO_4 + PH_3$$

8. **Oxides :-**

$$PbO_2 \longrightarrow 2PbO + O_2$$

$$\underset{\substack{\text{Minimum}\\ \text{Red lead, litharge}}}{2Pb_3O_4} \longrightarrow 6PbO + O_2$$

$$2HgO \longrightarrow 2Hg + O_2$$

$$2BaO_2 \longrightarrow 2BaO + O_2$$

$$\underset{\text{White}}{ZnO} \underset{\text{Cool}}{\overset{\Delta}{\rightleftharpoons}} \underset{\text{Yellow}}{ZnO}$$

9. $$(NH_4)_2Cr_2O_7 \xrightarrow[\text{Volcano}]{\text{Chemical}} N_2 + Cr_2O_3 + 4H_2O$$

10. $$4KClO_3 \xrightarrow[\text{melts}]{\Delta} 2KClO_4 + 2KCl$$

$$KClO_4 \longrightarrow KCl + 2O_2$$

11. $$\underset{\text{Borax}}{Na_2B_4O_7 \,.\, 10H_2O} \xrightarrow[\text{Swell up}]{\Delta} \underset{\text{Swelled borax}}{Na_2B_4O_7 + 10H_2O}$$

$$\xrightarrow[\Delta]{\text{Strong}} \underset{\text{Glassy residue}}{2NaBO_2 + B_2O_3}$$

12. $$\underset{\substack{\text{Orthoboric}\\ \text{acid}}}{H_3BO_3} \xrightarrow{100°C} \underset{\substack{\text{metaboric}\\ \text{acid}}}{HBO_2} \xrightarrow{160°C} \underset{\substack{\text{Tetraboric}\\ \text{acid}}}{H_2B_4O_7}$$

$$\xrightarrow[\text{heat}]{\text{Red}} \underset{\substack{\text{Boric anhydride}\\ \text{glassy residue}}}{2B_2O_3} + H_2O$$

13. $$\underset{\text{Amm. cyanate}}{NH_4CNO} \longrightarrow \underset{\text{Urea}}{NH_2CONH_2}$$

14. $$4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4 + \underset{\text{Green}}{2Cr_2O_3} + 3O_2$$

15. $$\underset{\text{Pot. permanganate}}{2KMnO_4} \longrightarrow \underset{\text{Pot. Manganate}}{K_2MnO_4} + MnO_2 + O_2$$

16. $$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

17. Common alum

$$K_2SO_4.Al_2(SO_4)_3.24H_2O \rightarrow K_2SO_4.Al_2(SO_4)_3 + 24H_2O$$

$$K_2SO_4.Al_2(SO_4)_3 \longrightarrow K_2O + Al_2O_3 + 4SO_3$$

18. Nitric acid

$$4HNO_3 \longrightarrow 4NO_2 + 2H_2O + O_2$$

CHEMICAL PRINCIPLES INVOLVED IN SOME EXPERIMENTS:

To determine the heat of neutralisation of a strong acid with a strong base

Apparatus :

Calorimeter (or a thermos flask), Thermometer, Glass stirrer, 200 c.c. N NaOH and 200 c.c. N HCl

Theory :

The neutralisation reaction of a strong acid with a strong base is essentially the combination of one equivalent of H^+ ions with one equivalent of OH^- ions

$$H^+ + OH^- \rightarrow H_2O + 13.7 \text{ Cal}$$

Equal volumes of the acid and alkali of the same strength at the same temperature are mixed in a calorimeter and the rise in temperature is noted. Water equivalent of calorimeter is determined. The heat of neutralisation is calculated.

Procedure :

(i) ***Determination of the water equivalent of calorimeter :*** Take a definite weight of cold water in the calorimeter and note its temperature. Add to it a definite amount of hot water of known temperature and note the temperature of the mixture. The water equivalent of calorimeter (W) is determined by the following equation.

→ (Weight of cold water + water equivalent) (Final temperature of mixture–temperature of cold water)

= (Weight of hot water) (Temperature of hot water–temperature of the mixture)

(ii) Take 100 c.c. of N NaOH in the calorimeter and add to it 100 c.c. of N HCl. Mix them well with the stirrer. Note the final temperature of the mixture.

Observations :

(i) ***Water equivalent of the calorimeter :***

Weight of cold water = m_1 g
Weight of hot water = m_2 g
Temp. of cold water = t_1° C
Temp. of hot water = t_2° C
Temp. of mixture = t_3° C

Water equivalent W is given by

$(m_1 + W)(t_3 - t_1) = m_2 (t_2 - t_3)$

(ii) Volume of acid = 100 c.c.
Volume of alkali = 100 c.c.
Initial temp. of acid = t° C
Initial temp. of alkali = t° C
Final temp. of the mixture = t_1° C
Rise in temperature = $(t_1 - t)$°C

The amount of heat produced on mixing acid and alkali = $(100 + 100 + W)(t_1 - t)$ = x calories

Here x is the heat of neutralisation

(II) To determine the heat of solution of copper sulphate

Theory :

The amount of heat evolved or absorbed when one mole of substance (solid/liquid) is dissolved in large quantity of water such that further dilution does not make any heat. Change is known as heat of solution.

Apparatus :

Dewar's vacuum flask, stirrer, thermometer physical balance, copper sulphate

Procedure:

(i) Determination of water equivalent of Dewar's vacuum flask. Take a definite weight of cold water in a Dewar's vacuum flask and note its temperature. Add to it a definite amount of hot water of known temperature and note the temperature of mixture. Determine the water equivalent by the following equation

(Weight of cold water+Water equivalent) (Final temperature of mixture-temperature of cold water)

= (Weight of hot water) (Temperature of hot water – temperature of mixture)

(ii) In second aperature again take a definite weight of cold water in Dewar's vacuum flask and note its temperature. Add to it definite amount of copper sulphate and stir the solution till the entire copper sulphate dissolves. Note down the final temperature of the solution

Initial temperature of water = T_1°C

Initial weight of water = W_1g

Final temperature of copper sulphate solution = T_2° C weight of copper sulphate = W_2 g

Water equivalent of Dewar's flask = W

Calculations :

Total mass of solution = $(W_1 + W_2)$g

Rise in temperature = $(T_2 - T_1)$°C

Heat gained by flask = $W(T_2 - T_1) \times 4.18$ J

Specific heat of water = 4.18 J/g°C

Heat gained by solution = $(W_1 + W_2)(T_2 - T_1) \times 4.18$ J

Total heat change during dissolution of copper sulphate

$$(W_2 g) = \left[W(T_2 - T_1) + (W_1 + W_2)(T_2 - T_1)\right] \times 4.18 = Q$$

Total heat change during dissolution of 1 mole of copper sulphate will be

$$= \frac{Q}{W_2} \times M \text{ J}$$

Where M is molecular weight of copper sulphate.

Hence heat of solution of copper sulphate $= \frac{Q \times M}{W_2}$ J / mole.

(III) Preparation of Lyophobic and lyophilic sols :

Preparation of arsenious sulphide sol :

Boil about 1 - 2 g pure As_2O_3 with about 500 ml of distilled water for about 10-12 minutes. Now cool the solution to room temperature and filter undissolved As_2O_3 if any. Dilute this solution and pass into it H_2S gas (free from HCl by passing through a tube containing soda lime and then through 3-4 wash bottles containing distilled water) till it is saturated. Then pass a stream of pure hydrogen washed through 3-4 wash bottles containing distilled water to remove the excess of H_2S. Filter the solution to remove the roarse precipitate of As_2S_3 if necessary.

Preparation of Gelatin sol.

Take about 400 ml of distilled water and heat it to 80-90° C . Add to it about 2 g of powdered gelatin and dissolve it. Allow the solution to cool to room temperature. This gives a clear sol. of gelatin.

(IV) Kinetic study of Iodide ions with H_2O_2

Theory: In acidic medium, hydrogen peroxide (H_2O_2) oxidises iodide ions (I^-) to iodine (I_2) which is detected by starch solution.

$$H_2O_2 + 2I^- + 2H^+ \longrightarrow 2H_2O + I_2$$

A known volume of sodium thiosulphate soln. and starch soln. is added to the reaction mixture for monitoring of reaction. I_2 liberated react with sodium thiosulphate solution and reduced to iodide ions and when thiosulphate ions are totally consumed, the liberated iodine reacts with starch solution and gives blue colour, which detect the presence of iodine.

$$I_2 + \underset{\text{Thiosulphate}}{2S_2O_3^{2-}} \xrightarrow{\text{fast}} S_4O_6^{2-} + 2I^-$$

$$I_2 + \text{starch solution} \longrightarrow \underset{\text{(Blue colour)}}{\text{starch -iodine complex}}$$

The time taken for the blue colour to first appear gives the idea about the rate of reaction.

***Chemical required*:-** 0.1. M.KI soln., 2M HCl soln. Starch soln. 1M sodium thiosulphate sol. 4V H_2O_2 Soln.

***Procedure*:** Take four different volume (apx. 25ml to 100ml) of 0.1M KI soln to four different flask and 50ml of 2M HCI is added to each flask. By dilution volume of soln. made upto 200ml and then 5ml starch soln., 2ml of 1M thiosulphate soln. and 25ml of H_2O_2 soln. is added to each flask.

Observation

Flask	0.1M KI solution	2M HCl	Water	Starch solution	1M sodium thiosulphate solution	4 volume hydrogen peroxide solution
A	25 cm^3	50 cm^3	125 cm^3	5 cm^3	2 cm^3	25 cm^3
B	50 cm^3	50 cm^3	100 cm^3	5 cm^3	2 cm^3	25 cm^3
C	75 cm^3	50 cm^3	75 cm^3	5 cm^3	2 cm^3	25 cm^3
D	100 cm^3	50 cm^3	50 cm^3	5 cm^3	2 cm^3	25 cm^3

Time required for the blue colour to first appear in :

Flask A — .... seconds
Flask B — .... seconds
Flask C — .... seconds
Flask D — .... seconds

Conclusion: It has been observed that time required for the blue colour to appear is decreases with increase in concentration of I^- ions. Thus. "The rate of reaction increases with increase in concentration of iodide ions."

Miscellaneous Solved Examples

1. An aqueous solution containing one mole of HgI_2 and two moles of NaI is orange in colour. On addition of excess of NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaOCl. Explain the equations

Sol. The orange colour is due to partial solubility of HgI_2. With excess of NaI colourless complex Na_2HgI_4 is formed which reappears on addition of NaOCl

$$\underset{\text{(orange)}}{HgI_2} + 2NaI \longrightarrow Na_2HgI_4$$

$$3Na_2HgI_4 + 2\,NaOCl + 2\,H_2O$$

$$\longrightarrow 3\,HgI_2 + 2NaCl + 4NaOH + 2\,NaI_3$$

2. A white solid is either Na_2O or Na_2O_2. A piece of red litmus paper turns white when it is dipped into freshly made aqueous solution of white solid

(i) Identify the substance and explain with balance equation

(ii) Explain what would happen to red litmus if white solid were the other compound

Sol. The compound is Na_2O or Na_2O_2 a powerful oxidant and bleaching agent.

$$Na_2O_2 + 2\,H_2O \longrightarrow 2\,NaOH + H_2O_2$$

$$H_2O_2 + \text{Red litmus} \longrightarrow \text{White (bleaching)}$$

The compound Na_2O gives NaOH in water. NaOH turns Red litmus blue.

3. Complete and balance the following equations

(i) $H_2SO_4 + HI \longrightarrow \text{-------} + \text{--------} +$

(ii) $CaOCl_2 + NaI + HCl$

$$\longrightarrow \text{------} + CaCl_2 + H_2O + NaCl$$

(iii) $Ag_2S + 2\,CuCl_2 + 2Hg$

$$\longrightarrow \text{---} + \text{-----} + S + 2Ag$$

Sol. (i) $H_2SO_4 + 2\,HI \longrightarrow I_2 + SO_2 + 2H_2O$

(ii) $CaOCl_2 + 2NaI + 2HCl$

$$\longrightarrow I_2 + CaCl_2 + H_2O + 2NaCl$$

(iii) $Ag_2S + 2\,CuCl_2 + 2\,Hg$

$$\longrightarrow Cu_2Cl_2 + Hg_2Cl_2 + 2\,Ag + S$$

4. (i) A black mineral (A) on heating in presence of air gives a gas (B)

(ii) The mineral (A) on reaction with H_2SO_4 gives a gas (C) and solution of a compound (D)

(iii) On passing gas (C) into an aqueous solution of (B) a white turbidity is obtained

(iv) The aqueous solution of (D) on reaction with potassium ferricyanide gives a blue compound (E). Identify (A) to (E) and give chemical equations for reactions at steps (i) to (iv)

Sol. (i) $\underset{A}{4\,FeS} + 7\,O_2 \longrightarrow \underset{B}{4\,SO_2} + 2\,Fe_2O_3$

(ii) $\underset{A}{FeS} + H_2SO_4 \longrightarrow \underset{D}{FeSO_4} + \underset{C}{H_2S}$

(iii) $2\,H_2S + SO_2\ (aq.) \longrightarrow 2\,H_2O + 3S$

or $\underset{C}{2\,H_2S} + H_2SO_3 \longrightarrow \underset{\text{Turbidity}}{3S} + 3\,H_2O$

(iv) $3\,Fe_2SO_4 + 2K_3[Fe(CN)_6]$

$$\longrightarrow Fe_3[Fe(CN)_6]_2 + 3\,K_2SO_4$$

5. Element A burns in nitrogen to give an ionic compound B. The compound B reacts with water to give C and D. A solution of C becomes milky on bubbling carbon dioxide. Identify A, B, C and D

Sol. $3Ca + N_2 \longrightarrow Ca_3N_2 \xrightarrow{6\,H_2O} 3Ca(OH)_2 + 2\,NH_3$

$$\begin{array}{lll} \text{or} & \text{or} & \text{or} \\ Ba & Ba_3N_2 & 3\,Ba(OH)_2 \\ A & B & C \end{array}$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O\,;$$

$$Ba(OH)_2 + CO_2 \longrightarrow BaCO_3 + H_2O$$

Exercise-1 | CONCEPTUAL MCQs

1. In sodium fusion test of organic compounds, the nitrogen of the organic compound is converted into
(a) sodamide (b) sodium cyanide
(c) sodium nitrite (d) sodium nitrate

2. The Lassaigne's extract is boiled with dil. HNO_3 before testing for halogens because
(a) silver halides are soluble in HNO_3
(b) Na_2S and NaCN are decomposed by HNO_3
(c) Ag_2S is soluble in HNO_3
(d) AgCN is soluble in HNO_3

3. In Lassaigne's test for nitrogen, the blue colour is due to the formation of
(a) potassium ferricyanide (b) sodium cyanide
(c) sodium ferrocyanide (d) ferri-ferrocyanide

4. Which of the following compounds does not show Lassaigne's test for nitrogen ?
(a) Urea (b) Hydrazine
(c) Phenylhydrazine (d) Azobenzene

5. When pieces of human hair are heated strongly with soda-lime, smell of ammonia can be detected. Which one of the following conclusion can be drawn form this observation?
(a) Ammonia is present in the human hair
(b) Ammonium salt is present in hair
(c) Hair contains amino acids
(d) None of the above

6. The Beilstein test for organic compounds is used to detect which of the followng ?
(a) Nitrogen (b) Sulphur
(c) Carbon (d) Halogens

7. A sample of $Na_2CO_3.H_2O$ weighing 0.62 g is added to 100 ml of 0.1 N – H_2SO_4 solution. The resulting solution would be:
(a) Acidic (b) Neutral
(c) Alkaline (d) None of these

8. The strength of an aqueous solution of I_2 can be determined by titrating the solution with standard solution of:
(a) oxalic acid (b) sodium thiosulphate
(c) sodium hydroxide (d) Mohr's salt

9. 10 mL of 1 M NaOH solution is neutralized by .... mL of 1 M H_2SO_4 solution:
(a) 2.5 (b) 2.0 (c) 10 (d) 5

10. A solution of 10 mL $\frac{M}{10}$ $FeSO_4$ is titrated with $KMnO_4$ solution in acidic medium the amount of $KMnO_4$ used will be :
(a) 5 mL of 0.1 M (b) 10 mL of 0.1 M
(c) 10 mL of 0.5 M (d) 10 mL of 0.02 M

11. The indicator used in the titration of acetic acid with sodium hydroxide for quantitative estimation is:
(a) phenolphthalein
(b) methyl orange
(c) methyl red
(d) a mixture of methyl red and methyl orange

12. What will be the molarity of a solution containing 5 g of sodium hydroxide in 250 mL solution:
(a) 0.5 (b) 1.0 (c) 2.0 (d) 0.1

13. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralize 10 mL of this solution is:
(a) 40 mL (b) 20 mL (c) 10 mL (d) 4 mL

14. Which of the following is true?
(a) Tollens' reagent gives a positive result with all aldehydes
(b) Tollens' reagent gives a negative result with all ketones
(c) Both (a) and (b)
(d) Neither (a) nor (b)

15. Precipitate(s) soluble in aqua regia is
(a) CoS (b) HgS
(c) NiS (d) All of these

16. A laboratory reagent imparts green colour to the flame. On heating with solid $K_2Cr_2O_7$ and conc. H_2SO_4 it evolves a red gas. Identify the reagent
(a) $CaCl_2$ (b) $BaCl_2$
(c) $CuCl_2$ (d) None of these

17. Preparation of Lyophobic sols by chemical method involves–
(a) double decomposition (b) oxidation & reduction
(c) hydrolysis (d) All of these

18. Acetaldehyde and acetone can be distinguished by :
(a) Iodoform test (b) Nitroprusside test
(c) Fehlings solution test (d) Any of these

19. In Lassaigne's test, the organic compound is fused with a piece of sodium metal in order to
(a) increase the ionisation of the compound
(b) decrease the melting point of the compound
(c) increase the reactivity of the compound
(d) convert the covalent compound into a mixture of ionic compounds

20. When excess of dilute NH_4OH is added to an aqueous solution of copper sulphate, an intense blue colour is obtained. This is due to the presence of
(a) $CuSO_4$ (b) $Cu(OH)_2$
(c) $[Cu(NH_3)_4]^{2+}$ (d) $(NH_4)_2SO_4$

21. An aqueous solution of colourless metal sulphate M gives a white precipitate with NH_4OH. This was soluble in excess of NH_4OH. On passing H_2S through this solution a white ppt. is formed. The metal M in the salt is

(a) Ca (b) Ba (c) Al (d) Zn

22. The reagent that can distinguish between silver and lead salt is

(a) H_2S gas

(b) hot dilute HCl solution

(c) NH_4Cl (solid) + NH_4OH (solution)

(d) NH_4Cl (solid) + $(NH_4)_2CO_3$ solution

23. A solution containing As^{3+}, Cd^{2+}, Ni^{2+} and Zn^{2+} is made alkaline with dilute NH_4OH and treated with H_2S. The precipitate obtained will consist of

(a) As_2S_3 and CdS (b) CdS, NiS and ZnS

(c) NiS and ZnS (d) Sulphide of all ions

24. Some pale green crystals are strongly heated. The gases given off are passed into a container surrounded by ice and then through a solution of acidified $KMnO_4$. The $KMnO_4$ is decolourized, a waxy white solid is formed in the ice container; this is dissolved in water. The solution will

(a) give a precipitate with silver nitrate solution

(b) give a precipitate with barium chloride solution

(c) turn red litmus blue

(d) give blue colour with starch solution

25. Which of the following will not be soluble in sodium bicarbonate?

(a) 2, 4, 6-Trinitrophenol (b) Benzoic acid

(c) *o*-Nitrophenol (d) Benzenesulphonic acid.

26. Phenol can be distinguished from ethyl alcohol by all reagents except

(a) NaOH (b) $FeCl_3$

(c) Br_2/H_2O (d) Na.

27. In the Victor-Meyer's test, the colour given by 1°, 2° and 3° alcohols are respectively.

(a) red, colourless, blue (b) red, blue, colourless

(c) blue, red, violet (d) red, blue, violet

28. Which of the following is not a preliminary test used to detect ions ?

(a) Borax bead test (b) Flame test

(c) Brown ring test (d) Permangante test

29. A metal chloride dissolves appreciably in cold water. When placed on a platinum wire in Bunsen flame no distinctive colour is noticed, the cation would be

(a) Mg^{2+} (b) Ba^{2+} (c) Pb^{2+} (d) Ca^{2+}

30. Potassium chromate solution is added to an aqueous solution of a metal chloride. The precipitate thus obtained is insoluble in acetic acid. When precipitate is subjected to flame test the colour of the flame is

(a) lilac (b) apple green

(c) crimson red (d) golden yellow

31. Which metal salt gives a violet coloured bead in the borax bead test?

(a) Fe^{2+} (b) Ni^{2+} (c) Co^{2+} (d) Mn^{2+}

32. In the borax bead test of Co^{2+}, the blue colour of bead is due to the formation of

(a) B_2O_3 (b) Co_3B_2 (c) $Co(BO_2)_2$(d) CoO

33. The compound formed in the borax bead test of Cu^{2+} ion in oxidising flame is

(a) Cu (b) CuBO

(c) $Cu(BO_2)_2$ (d) None of these

34. In borax bead test which compound is formed?

(a) Orthoborate (b) Metaborate

(c) Double oxide (d) Tetraborate

35. A salt on treatment with dil. HCl gives a pungent smelling gas and a yellow precipitate. The salt gives green flame when tested. The solution gives a yellow precipitate with potassium chromate. The salt is

(a) $NiSO_4$ (b) BaS_2O_3 (c) PbS_2O_3 (d) $CuSO_4$

36. When HNO_3 is dropped into the palm and washed with water, it turns yellow. It shows the presence of

(a) NO_2 (b) N_2O (c) NO (d) N_2O_3

37. The gas that turns lime water milky is

(a) CO_2 (b) SO_2

(c) Both of these (d) None of these

38. When $K_2Cr_2O_7$ crystals are heated with conc. HCl, the gas evolved is

(a) O_2 (b) Cl_2 (c) CrO_2Cl_2 (d) HCl

39. Which is most soluble in water?

(a) AgCl (b) AgBr (c) AgI (d) AgF

40. A white sodium salt dissolves readily in water to give a solution which is neutral to litmus. When silver nitrate solution is added to the solution, a white precipitate is obtained which does not dissolve in dil. HNO_3. The anion could be

(a) CO_3^{2-} (b) Cl^- (c) SO_4^{2-} (d) S^{2-}

41. Which is not dissolved by dil HCl?

(a) ZnS (b) MnS (c) $BaSO_3$ (d) $BaSO_4$

42. A one litre flask is full of brown bromine vapours. The intensity of brown colour of vapour will not decrease appreciably on adding to the flask some

(a) pieces of marble (b) animal charcoal powder

(c) carbon tetrachloride (d) carbon disulphide

43. The brown ring test for NO_2^- and NO_3^- is due to the formation of complex ion with formula

(a) $[Fe(H_2O)_6]^{2+}$ (b) $[Fe(NO)(CN)_5]^{2-}$

(c) $[Fe(H_2O)_5NO]^{2+}$ (d) $[Fe(H_2O)(NO)_5]^{2+}$

44. Which of the following gives blood red colour with KCNS?

(a) Cu^{2+} (b) Fe^{3+} (c) Al^{3+} (d) Zn^{2+}

45. Correct formula of the complex formed in the brown ring test for nitrates is

(a) $FeSO_4$. NO (b) $[Fe(H_2O)_5NO]^{2+}$

(c) $[Fe(H_2O)_5NO]^+$ (d) $[Fe(H_2O)_5NO]^{3+}$

46. AgCl is soulble in NH_4OH solution. The solubility is due to the formation of

(a) AgOH (b) Ag_2O
(c) $[Ag(NH_3)_2]^+$ (d) NH_4Cl

47. Which of the following does not react with AgCl?

(a) Na_2CO_3 (b) $NaNO_3$
(c) NH_4OH (d) $Na_2S_2O_3$

48. Which of the following gives a precipitate with $Pb(NO_3)_2$ but not with $Ba(NO_3)_2$?

(a) Sodium chloride
(b) Sodium acetate
(c) Sodium nitrate
(d) Sodium hyrogen phosphate

49. Mercurous ion is represented as

(a) Hg_2^{2+} (b) Hg^{2+}
(c) $Hg + Hg^{2+}$ (d) $3\ Hg^{3+}$

50. An aqueous solution of a substance gives a white precipitate on treatment with dil. HCl which dissolves on heating. When H_2S is passed through the hot acidic solution, a black precipitate is obtained. The substance is a

(a) Hg_2^{2+} salt (b) Cu^{2+} salt
(c) Ag^+ salt (d) Pb^{2+} salt

51. Consider the following observation :

$M^{n+} + HCl \rightarrow$ white precipitate $\xrightarrow{\Delta}$ water soluble
The metal ion M^{n+} will be

(a) Hg^{2+} (b) Ag^+ (c) Pb^{2+} (d) Sn^{2+}

52. On passing H_2S gas in II group sometimes the solution turns milky. It indicates the presence of

(a) oxidising agent (b) acidic salt
(c) thiosulphate (d) reducing agent

53. Which of the following pair is not distinguished by passing H_2S ?

(a) Hg, Pb (b) Cd, Pb (c) As, Cd (d) Zn, Mn

54. Which compound does not dissolve in hot dilute HNO_3?

(a) HgS (b) PbS (c) CuS (d) CdS

55. Which of the following is soluble in yellow ammonium sulphide?

(a) CuS (b) CdS (c) SnS (d) PbS

56. Three separate samples of a solution of a single salt gave these results. One formed a white precipitate with excess ammonia solution, one formed a white precipitate with dil. NaCl solution and one formed a black precipitate with H_2S. The salt could be

(a) $AgNO_3$ (b) $Pb(NO_3)_2$
(c) $Hg(NO_3)_2$ (d) $MnSO_4$

57. In the separation of Cu^{2+} and Cd^{2+} in 2nd group qualitative analysis of cations, tetrammine copper (II) sulphate and tetrammine cadmium (II) sulphate react with KCN to form the corresponding cyano complexes. Which one of the following pairs of the complexes and their relative stability enable the separation of Cu^{2+} and Cd^{2+}?

(a) $K_3[Cu(CN)_4]$ more stable and $K_2[Cd(CN)_4]$ less stable
(b) $K_2[Cu(CN)_4]$ less stable and $K_2[Cd(CN)_4]$ more stable
(c) $K_2[Cu(CN)_4]$ more stable and $K_2[Cd(CN)_4]$ less stable
(d) $K_3[Cu(CN)_4]$ less stable and $K_2[Cd(CN)_4]$ more stable

58. Which of the follwing is not precipitated as sulphide by passing H_2S in presence of conc. HCl

(a) Copper (b) Arsenic
(c) Cadmium (d) Lead

59. Which of the following sulphate is insoluble in water?

(a) $CuSO_4$ (b) $CdSO_4$ (c) $PbSO_4$ (d) $Bi_2(SO_4)_3$

60. Which of the following metal sulphides has maximum solubility in water?

(a) HgS, $K_{sp} = 10^{-54}$ (b) CdS, $K_{sp} = 10^{-30}$
(c) FeS, $K_{sp} = 10^{-20}$ (d) ZnS, $K_{sp} = 10^{-22}$

61. Identify the correct order of solubilty of Na_2S. CuS and ZnS in aqueous medium

(a) $CuS > ZnS > Na_2S$ (b) $ZnS > Na_2S > CuS$
(c) $Na_2S > CuS > ZnS$ (d) $Na_2S > ZnS > CuS$

62. A gas "X" is passed through water to form a saturated solution. The aqueous solutions on treatment with the $AgNO_3$ gives a white preciptate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas "Y". Identify 'X' and 'Y'.

(a) $X = CO_2, Y = Cl_2$ (b) $X = Cl_2, Y = CO_2$
(c) $X = Cl_2, Y = H_2$ (d) $X = H_2, Y = Cl_2$

63. A mixture of chlorides of copper, cadmium, chromium, iron and aluminium was dissolved in water acidified with HCl and hydrogen sulphide gas was passed for sufficient time. It was filtered, boiled and a few drops of nitric acid were added while boiling. To this solution ammonium chloride and sodium hydroxide were added and filtered. The filterate shall give test for.

(a) sodium and iron
(b) sodium and aluminium
(c) aluminium and iron
(d) sodium, iron, cadmium and Al

64. In qualitative analysis NH_4Cl is added before NH_4OH

(a) to decrease $[OH^-]$ conc. (b) to increase $[OH^-]$ conc.
(c) for making HCl (d) to increase $[Cl^-]$ conc.

65. Which of the following compound on reaction with NaOH and Na_2O_2 gives yellow colour?

(a) $Cr(OH)_3$ (b) $Zn(OH)_2$
(c) $Al(OH)_3$ (d) None of these

66. CrO_3 dissolves in aqueous NaOH to give

(a) $Cr_2O_7^{2-}$ (b) CrO_4^{2-} (c) $Cr(OH)_3$ (d) $Cr(OH)_2$

67. Which of the following cannot give iodometric titration?

(a) Fe^{3+} (b) Cu^{2+} (c) Pb^{2+} (d) Ag^{2+}

68. The only cations present in slightly acidic solution are Fe^{3+}, Zn^{2+} and Cu^{2+}. The reagent that when added in excess to this solution would identify and separate Fe^{3+} in one step is

(a) 2 M HCl (b) 6 M NH_3
(c) 6 M NaOH (d) H_2S gas

69. Which of the following statements is correct?
(a) Fe^{2+} gives brown colour with ammonium thiocyanate
(b) Fe^{2+} gives blue precipitate with potassium ferricyanide
(c) Fe^{3+} gives brown colour with potassium ferricyanide
(d) Fe^{3+} gives red colour with potassium ferrocyanide

70. Action of caustic soda on $Al(OH)_3$ gives a compound having formula
(a) Na_3AlO_3 (b) $NaAlO_2$
(c) $Na_2Al(OH)_4$ (d) $Al_2(OH)_4$

71. Dimethyl glyoxime in a suitable solvent was refluxed for 10 minutes with pure pieces of nickel sheet, it will result in
(a) red precipitate (b) blue precipitate
(c) yellow precipitate (d) no precipitate

72. When H_2S gas is passed through the HCl containing aqueous solution of $CuCl_2$, $HgCl_2$, $BiCl_3$ and $CoCl_2$ it does not precipitate out
(a) CuS (b) HgS (c) Bi_2S_3 (d) CoS

73. A metal is burnt in air and the ash on moistening smells of ammonia. The metal is
(a) Na (b) Fe (c) Mg (d) Al

74. A metal X on heating in nitrogen gas gives Y. Y on treatment with H_2O gives a colourless gas which when passed through $CuSO_4$ solution gives a blue colour. Y is
(a) $Mg(NO_3)_2$ (b) Mg_3N_2
(c) NH_3 (d) MgO

75. An aqueous solution of $FeSO_4$, $Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are
(a) a colourless filtrate and a green residue
(b) a yellow filtrate and a green residue
(c) a yellow filtrate and a brown residue
(d) a green filtrate and a brown residue

76. Which of the following is not efflorescent?
(a) Hydrated Na_2CO_3 (b) Hydrated $CuSO_4$
(c) NaOH (d) All of these

77. $K_2[HgI_4]$ detects the ion/group
(a) NH_2 (b) NO (c) NH_4^+ (d) Cl^-

78. By passing H_2S gas in acidified $KMnO_4$. we get
(a) K_2S (b) S (c) K_2SO_3 (d) MnO_2

79. Mark the correct statement
(a) I group basic radicals precipitate as chlorides
(b) IV group basic radicals precipitate as sulphides
(c) V group basic radicals precipitate as carbonates
(d) All the above statements are correct

80. A mixture of two salts is not water soluble but dissolves completely in dil. HCl to form a colourless solution. The mixture could be
(a) $AgNO_3$ and KBr (b) $BaCO_3$ and ZnS
(c) $FeCl_3$ and $CaCO_3$ (d) $Mn(NO_3)_2$ and $MgSO_4$

81. When a substance A reacts with water it produces a combustible gas B and a solution of substance C in water. When another substance D reacts with this solution of C, it also produces the same gas B on warming but D can produce gas B on reaction with dilute sulphuric acid at room temperature. A imparts a deep golden yellow colour to smokeless flame of Bunsen burner. A, B, C and D respectively are
(a) Na, H_2 NaOH, Zn (b) K, H_2, KOH, Al
(c) Ca, H_2, $Ca(OH)_2$, Sn (d) CaC_2, C_2H_2, $Ca(OH)_2$, Fe

82. In Nessler's reagent, the ion present is
(a) HgI^{2-} (b) $[HgI_4]^{2-}$ (c) Hg^+ (d) Hg^{2+}

83. Which of the following leaves no residue on heating?
(a) $Pb(NO_3)_2$ (b) NH_4NO_3
(c) $Cu(NO_3)_2$ (d) $NaNO_3$

84. The K_{sp} for HgS, Ag_2S and PbS are 10^{-31}, 10^{-45} and 10^{-50} respectively. The solubilities are in the order.
(a) $HgS > Ag_2S > PbS$ (b) $HgS < PbS < Ag_2S$
(c) $PbS > Ag_2S > HgS$ (d) $Ag_2S > HgS > PbS$

85. The phenomenon in which white transparent crystal changes into white powder is called
(a) Efflorescence (b) Allotropy
(c) Sublimation (d) None of these

Exercise-2 | PAST COMPETITION MCQs

1. When H_2S is passed through Hg_2S we get **[AIEEE 2002]**
(a) HgS (b) $HgS + Hg_2S$
(c) Hg_2S (d) None of these.

2. How do we differentiate between Fe^{3+} and Cr^{3+} in group III? **[AIEEE 2002]**
(a) By taking excess of NH_4OH solution
(b) By increasing NH_4^+ ion concentration
(c) By decreasing OH^- ion concentration
(d) Both (b) and (c).

3. Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in alkaline solutions but not in acidic solutions. What is the reason for it ? **[AIEEE 2003]**
(a) In acidic solutions protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available
(b) In alkaline solutions insoluble $Cu(OH)_2$ is precipitated which is soluble in excess of any alkali
(c) Copper hydroxide is an amphoteric substance
(d) In acidic solutions hydration protects copper ions

4. Which one of the following statements is correct ? **[AIEEE 2003]**

(a) From a mixed precipitate of AgCl and AgI, ammonia solution dissolves only AgCl

(b) Ferric ions give a deep green precipitate on adding potassium ferrocyanide solution

(c) On boiling a solution having K^+, Ca^{2+} and HCO_3^- ions we get a precipitate of $K_2Ca(CO_3)_2$

(d) Manganese salts give a violet borax bead test in the reducing flame

5. A red solid is insoluble in water. However it becomes soluble if some KI is added to water. Heating the red solid in a test tube results in liberation of some violet coloured fumes and droplets of a metal appear on the cooler parts of the test tube. The red solid is **[AIEEE 2003]**

(a) HgI_2 (b) HgO

(c) Pb_3O_4 (d) $(NH_4)_2Cr_2O_7$

6. 25ml of a solution of barium hydroxide on titration with a 0.1 molar solution of hydrochloric acid gave a litre value of 35ml. The molarity of barium hydroxide solution was **[AIEEE 2003]**

(a) 0.14 (b) 0.28

(c) 0.35 (d) 0.07

7. The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is **[AIEEE 2004]**

(a) $Fe_4[Fe(CN)_6]_3$ (b) $Na_3[Fe(CN)_6]$

(c) $Fe(CN)_3$ (d) $Na_4[Fe(CN)_5NOS]$

8. Excess of KI reacts with $CuSO_4$ solution and then $Na_2S_2O_3$ solution is added to it. Which of the statements is **incorrect** for this reaction ? **[AIEEE 2004]**

(a) $Na_2S_2O_3$ is oxidised (b) CuI_2 is formed

(c) Cu_2I_2 is formed (d) Evolved I_2 is reduced

9. The mass of potassium dichromate crystals required to oxidise 750 cm^3 of 0.6 M Mohr's salt solution is :

(Given molar mass potassium dichromate = 294, Mohr's salt = 392) **[AIEEE-2011]**

(a) 0.45 g (b) 22.05 g

(c) 2.2 g (d) 0.49 g

10. Which one among the following pairs of ions cannot be separated by H_2S in dilute hydrochloric acid? **[IITJEE-1986]**

(a) Bi^{3+}, Sn^{4+} (b) Al^{3+}, Hg^{2+}

(c) Zn^{2+}, Cu^{2+} (d) Ni^{2+}, Cu^{2+}

11. When concentrated H_2SO_4 is added to dry KNO_3, brown fumes evolves. These fumes are **[IIT 1987, CPMT 1988]**

(a) SO_2 (b) SO_3

(c) NO (d) NO_2

12. Sodium nitroprusside, when added to an alkaline solution of sulphide ions, produces purple colour ion due to the formation of **[IIT 1995, Orissa JEE 2008]**

(a) $Na[Fe(H_2O)_5 NOS]$ (b) $Na_2[Fe(H_2O)_5 NOS]$

(c) $Na_3[Fe(CN)_5NOS]$ (d) $Na_4[Fe(CN)_5NOS]$

13. In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is

(a) (Molecular weight)/2 **[IIT JEE-2001S]**

(b) (Molecular weight)/6

(c) (Molecular weight)/3

(d) Same as molecular weight

14. A metal nitrate reacts with KI to give a black precipitate which on addition of excess of KI convert into orange colour solution. The cation of the metal nitrate is **[IIT JEE-2005]**

(a) Hg^{2+} (b) Bi^{3+}

(c) Pb^{2+} (d) Cu^+

15. A solution when diluted with H_2O and boiled, it gives a white precipitate. On addition of excess NH_4Cl/NH_4OH the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in NH_4OH/NH_4Cl **[IIT JEE-2006]**

(a) $Zn(OH)_2$ (b) $Al(OH)_3$

(c) $Mg(OH)_2$ (d) $Ca(OH)_2$

16. $MgSO_4$ on reaction with NH_4OH and Na_2HPO_4 forms a white crystalline precipitate. What is its formula **[IIT JEE-2006]**

(a) $Mg(NH_4)PO_4$ (b) $Mg_3(PO_4)_2$

(c) $MgCl_2$, $MgSO_4$ (d) $MgSO_4$

17. A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt (II) thiocyanate gives rise to a deep blue crystalline precipitate. The metal ion is **[IITJEE-2007]**

(a) Pb^{2+} (b) Hg^{2+}

(c) Cu^{2+} (d) Co^{2+}

18. Passing H_2S gas into a mixture of Mn^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution precipitates **[IIT JEE-2011]**

(a) CuS and HgS (b) MnS and CuS

(c) MnS and NiS (d) NiS and HgS

19. The compound that does **NOT** liberate CO_2, on treatment with aqueous sodium bicarbonate solution, is **[JEE Advanced 2013]**

(a) Benzoic acid (b) Benzenesulphonic acid

(c) Salicylic acid (d) Carbolic acid (Phenol)

20. Upon treatment with ammonical H_2S, the metal ion that precipitates as a sulfide is **[JEE Advanced 2013]**

(a) Fe(III) (c) Mg(II)

(b) Al(III) (d) Zn(II)

Exercise-3 | Applied MCQs

1. Lassaigne's test for the detection of nitrogen will fail in case of
(a) NH_2CONH_2 (b) $H_2NCONHNH_2.HCl$
(c) $H_2N.NH_2.2HCl$ (d) $C_6H_5NHNH_2.2HCl$

2. For detection of sulphur in an organic compound sodium nitroprusside is added to the sodium extract. A violet colour is obtained due to formation of
(a) $Fe(CN)_2$ (b) $K_3Fe(CN)_5NS$
(c) $Na_4[Fe(CN)_5NOS]$ (d) $Na_4Fe(CN)_6$

3. The sodium extract prepared from sulphanilic acid, contains SCN^-. It gives blood red colouration with
(a) a mixture of Na_2S and CS_2
(b) $FeCl_3$
(c) $FeSO_4$ (d) Na_2SO_3

4. An organic compound is treated with $NaNO_2$ and dil. HCl at 0°C. The resulting solution is added to an alkaline solution of β-naphthol where by a brilliant red dye is produced. It shows the presence of
(a) $-NO_2$ group (b) aromatic $-NH_2$ group
(c) $-CONH_2$ group (d) aliphatic $-NH_2$ group

5. Beilstein's test is given by which of the following
(a) Halogens (b) Thio urea
(c) Pyridine (d) All of these

6. 0.45 g of acid (molecular weight 90) is neutralised by 20 ml of 0.5N caustic potash. The basicity of acid is
(a) 1 (b) 2
(c) 3 (d) 4

7. Volume of 3% solution of sodium carbonate necessary to neutralise a litre of 0.1 N sulphuric acid
(a) 176.66 ml (b) 156.6 ml
(c) 116.0 ml (d) 196.1 ml

8. 3.92 g of ferrous ammonium sulphate react completely with 50 ml $\frac{N}{10}$ $KMnO_4$ solution. The percentage purity of the sample is
(a) 50 (b) 78.4
(c) 80 (d) 39.2

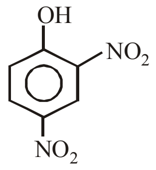
9. The strength of a 10 cc of 20 vol. solution of H_2O_2 in gm/ litre is
(a) 60.7 (b) 6.07
(c) 58.5 (d) 44

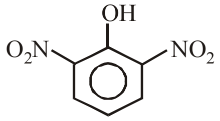
10. 1.25 g of a sample of Na_2CO_3 and Na_2SO_4 is dissolved in 250 ml solution. 25 ml of this solution neutralises 20 ml of 0.1N H_2SO_4. The % of Na_2CO_3 in this sample is
(a) 84.8% (b) 8.48%
(c) 15.2% (d) 42.4%

11. A solution containing Na_2CO_3 and NaOH requires 300 ml of 0.1N HCl using phenolphthalein as an indicator. Methyl orange is then added to above titrated solution when a further 25 ml of 0.2N HCl is required. The amount of NaOH present in solution is (NaOH = 40 , Na_2CO_3 = 106)
(a) 0.8 gm (b) 1.0 gm
(c) 1.5 gm (d) 2 gm

12. 0.5 g mixture of $K_2Cr_2O_7$ and $KMnO_4$ was treated with excess of KI in acidic medium. I_2 liberated required 100 cm^3 of 0.15 N $Na_2S_2O_3$ solution for titration. The percentage amount of $K_2Cr_2O_7$ in the mixture is
(a) 85.36% (b) 14.64%
(c) 58.63% (d) 26.14%

13. In the reaction of $KMnO_4$ with an oxalate in acidic medium, MnO_4^- is reduced to Mn^{2+} and $C_2O_4^{2-}$ is oxidised to CO_2. Hence, 50 ml of 0.02 M $KMnO_4$ is equivalent to
(a) 100 ml of 0.05 M $H_2C_2O_4$
(b) 50 ml of 0.05 M $H_2C_2O_4$
(c) 25 ml of 0.2 M $H_2C_2O_4$
(d) 50 ml of 0.10 M $H_2C_2O_4$

14. Which of the following does not give effervescences of CO_2 with aq. $NaHCO_3$ solution?
(a) H_2CO_3 (b)


(c)


(d) None of these

15. $KMnO_4$ reacts with oxalic acid as :
$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$
Hence, 50 ml of 0.04 M $KMnO_4$ is acidic medium is chemically equivalent to
(a) 100 ml of 0.1 M $H_2C_2O_4$
(b) 50 ml of 0.2 M $H_2C_2O_4$
(c) 50 ml of 0.1 M $H_2C_2O_4$
(d) 25 ml of 0.1 M $H_2C_2O_4$

16. In the preparation of p-nitro acetanilide from aniline nitration is not done by nitrating mixture (a mixture of conc. H_2SO_4 and conc. HNO_3) because
(a) on nitration it gives o-nitro acetanilide
(b) it gives a mixture of o and p-nitro aniline
(c) $-NH_2$ group gets oxidised
(d) it forms a mixture of o and p-nitro acetanilide.

17. Leveling bulb is used during experiment to study kinetics of the dissociation of hydrogen peroxide to ensure –
(a) Pressure within the reaction vessel is same as that in the room
(b) Uniform pressure difference between the room and the gases in the system
(c) Same temperature as that of room
(d) None of these

18. If during experiment to calculate enthalpy of copper sulphate temperature is recorded for every half minute for 2½ minute than zinc powder should be added in cup at –
(a) precisely 3 minutes (b) anytime after 2½ minute
(c) after 3 minutes (d) None of these

19. During experiment to calculate heat of neutralization of strong acid and base concentration temperature should be recorded till–
(a) constant temperature is achieved
(b) maximum temperature is achieved
(c) minimum temperature is achieved
(d) None of these

20. For preparing 250 ml of N/20 solution of Mohr's salt, the amount of Mohr's salt needed is
(a) 9.8 g (b) 4.9 g
(c) 19.6 g (d) 3.2 g

21. Prussian blue is formed when
(a) ferrous sulphate reacts with $FeCl_3$
(b) ferric sulphate reacts with $K_4Fe(CN)_6$
(c) ferrous ammonium sulphate reacts with $FeCl_3$
(d) ammonium sulphate reacts with NO_2

22. A substance on treatment with dil.H_2SO_4 liberates a colourless gas which produces
(I) turbidity with baryta water and
(II) turns acidified dichromate solution green. The reaction indicates the presence of
(a) CO_3^{2-} (b) S^{2-}
(c) SO_3^{2-} (d) NO_3^-

23. A green mass is formed in the charcoal cavity test when a colourless salt (x) is fused with cobalt nitrate. (x) may contain
(a) aluminium (b) copper
(c) barium (d) zinc

24. The presence of magnesium is confirmed in the qualitative analysis by the formation of a white crystalline precipitate of
(a) $Mg(HCO_3)_2$ (b) $MgNH_4PO_4$
(c) $MgNH_4(HCO_3)_3$ (d) $MgCO_3$

25. A salt which gives CO_2 with hot conc.H_2SO_4 and also decolourizes acidified $KMnO_4$ on warming is:
(a) HCO_3^- (b) CO_3^{2-}
(c) Oxalate (d) Acetate

26. Na_2CO_3 cannot be used in place of $(NH_4)_2CO_3$ for the precipitation of V group because
(a) Na^+ interferes in the detection of V group
(b) Conc. of CO_3^{2-} is very low
(c) Na will react with acid radicals
(d) Mg will be precipitated

27. Chemical volcano is produced on heating
(a) $K_2Cr_2O_7$ (b) $(NH_4)_2Cr_2O_7$
(c) $ZnCr_2O_7$ (d) K_2CrO_4

28. Reddish-brown (chocolate) ppt. is formed with
(a) Cu^{2+} and $Fe(CN)_6^{4-}$ (b) Ba^{2+} and SO_4^{2-}
(c) Pb^{2+} and I^- (d) None of these

29. Few drops of HNO_3 are added to II group before proceeding to III group in order to
(a) convert Fe^{2+} to Fe^{3+} (b) convert Fe^{3+} to Fe^{2+}
(c) Ppt. III group (a) None of these

30. Which pair would be expected to form precipitate when solutions are mixed
(a) K^+, SO_4^{2-} (b) Na^+, S^{2-}
(c) Ag^+, NO_3^- (d) Al^{3+}, OH^-

31. H_2S will precipitate the sulphides of all the metals from the solution of chlorides of Cu, Zn and Cd if
(a) the solution is aqueous
(b) the solution is acidic
(c) the solution is dilute acidic
(d) the solution is concentrated and basic

32. Addition of solution of oxalate to an aqueous solution of mixture of Ba^{2+}, Sr^{2+} and Ca^{2+} will precipitate
(a) Ca^{2+} (b) Ca^{2+} and Sr^{2+}
(c) Ba^{2+} and Sr^{2+} (d) All the three

33. The salt used for performing 'bead' test in qualitative inorganic analysis is
(a) $K_2SO_4.Al_2(SO_4)_3.24H_2O$
(b) $FeSO_4.(NH_4)_2SO_4 4H_2O$
(c) $Na(NH_4)HPO_4.4H_2O$
(d) $CaSO_4.2H_2O$

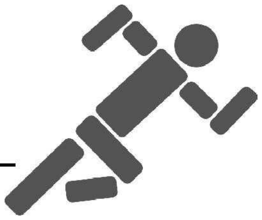
34. Concentrated aqueous sodium hydroxide can separate a mixture of
(a) Al^{3+} and Sn^{2+} (b) Al^{3+} and Fe^{3+}
(c) Al^{3+} and Zn^{2+} (d) Zn^{2+} and Pb^{2+}

35. An orange precipitate of II group is dissolved in conc. HCl; the solution when treated with excess of water turns milky due to formation of
(a) $Sn(OH)Cl$ (b) $Sb(OH)Cl_2$
(c) $SbOCl$ (d) $Sb(OH)_2Cl$

36. Lead has been placed in qualitative group analysis Ist and 2nd because
(a) it shows the valency one and two
(b) it forms insoluble $PbCl_2$
(c) it forms lead sulphide
(d) it is partly soluble in water

37. $[X] + H_2SO_4 \longrightarrow [Y]$ a colourless gas with irritating smell,
$[Y] + K_2Cr_2O_7 + H_2SO_4 \longrightarrow$ green solution. [X] and [Y] is:
(a) SO_3^{2-}, SO_2 (b) Cl^-, HCl
(c) S^{2-}, H_2S (d) CO_3^{2-}, CO_2

Hints & Solutions



EXERCISE 1

1. **(b)** $Na + C + N \rightarrow NaCN$ from organic compound

2. **(b)** Na_2S and NaCN, formed during fusion with metallic sodium, must be removed before adding $AgNO_3$, otherwise black ppt. due to Na_2S or white precipitate due to AgCN will be formed and thus white precipitate of AgCl will not be identified easily.

$$Na_2S + 2AgNO_3 \longrightarrow 2NaNO_3 + \underset{\text{Black}}{Ag_2S\downarrow}$$

$$NaCN + AgNO_3 \longrightarrow NaNO_3 + \underset{\text{White}}{AgCN\downarrow}$$

$$NaCl + AgNO_3 \longrightarrow NaNO_3 + \underset{\text{white}}{AgCl\downarrow}$$

$$Na_2S + 2HNO_3 \xrightarrow{\text{boil}} 2NaNO_3 + H_2S\uparrow$$

$$NaCN + HNO_3 \xrightarrow{\text{boil}} NaNO_3 + HCN\uparrow$$

3. **(d)**

4. **(b)** Hydrazine (NH_2NH_2) does not contain carbon and hence on fusion with Na metal, it cannot form NaCN; consequently hydrazine does not show Lassaigne's test for nitrogen.

5. **(c)** Hair contains amino acids which upon fusion with soda lime (NaOH + CaO) evolve NH_3.

6. **(d)**

7. **(b)** Geq of $Na_2CO_3.H_2O = \dfrac{0.62}{62} = 0.01$

Geq of $H_2SO_4 = \dfrac{100 \times 0.1}{1000} = 0.01$

Hence solution will be neutral

8. **(b)** $I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$

9. **(d)** $N_1V_1 = N_2V_2 \therefore 10 \times 1 = V \times 2 \therefore V = 5$ ml

10. **(d)** Meq of $FeSO_4 = 10 \times \dfrac{1}{10} = 1$

Meq. of $KMnO_4$ needed = 1

$\therefore$ Meq of 10 ml of 0.02 M = 10 × 0.1 = 1 (1 M $KMnO_4$ = 5 $KMnO_4$ in acid medium)

11. **(a)** NaOH is strong base hence indicator used is phenolphthalein.

12. **(a)** $M = \dfrac{Wt \times 1000}{M.Wt \times V} = \dfrac{5 \times 1000}{40 \times 250} = 0.5$

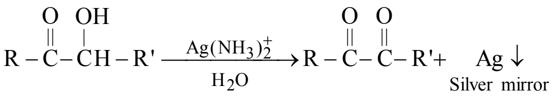
13. **(a)** Normality of oxalic acid $= \dfrac{6.3 \times 1000}{63 \times 250} = 0.4$;

$N_1V_1 = N_2V_2$

$V_1 \times 0.1 = 10 \times 0.4$

$\therefore V_1 = 40$ mL

14. **(a)** Tollens' reagent also oxidises α-hydroxyketones, hence positive result is observed in such case.



$$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{CH}-R' \xrightarrow[H_2O]{Ag(NH_3)_2^+} R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R' + \underset{\text{Silver mirror}}{Ag\downarrow}$$

15. **(d)**

16. **(b)** The reagent is $BaCl_2$ which imparts green colour to flame. $BaCl_2$ forms chromyl chloride (which is red in colour), when treated with $K_2Cr_2O_7$ and conc. H_2SO_4.

$$2BaCl_2 + K_2Cr_2O_7 + 3H_2SO_4$$

$$\longrightarrow K_2SO_4 + 2BaSO_4 + \underset{\substack{\text{Chromyl chloride} \\ \text{(red gas)}}}{2CrO_2Cl_2} + 3H_2O$$

17. **(d)**

18. **(c)** Acetaldehyde is easily oxidised to acetic acid by a mild oxidising agent like Fehling solution. Acetone is not easily oxidised.

Both acetone and acetaldehyde give iodoform test. Other two conditions are not relevant to aldehydes and ketones.

19. **(d)** To convert covalent compounds into ionic compounds such as NaCN, Na_2S, NaX etc.

20. **(c)** $$CuSO_4 + 4NH_4OH \longrightarrow \underset{\text{Intense blue colour}}{[Cu(NH_3)_4]^{2+}}$$

$$+ SO_4^{2-} + 2H_2O$$

21. **(d)** $$Zn^{2+} + 2NH_4OH \longrightarrow \underset{\text{White ppt.}}{Zn(OH)_2} + 2NH_4^+$$

$$Zn(OH)_2 + 2NH_4OH \longrightarrow \underset{\text{Soluble}}{(NH_4)_2ZnO_2} + 2H_2O$$

$$(NH_4)_2ZnO_2 + H_2S \longrightarrow \underset{\text{White ppt.}}{ZnS} + 2NH_4OH$$

22. **(b)** Hot HCl will produce precipitate of AgCl with Ag^+ only. $PbCl_2$ will not precipitate because it is soluble in hot solution.

23. **(d)** As^{3+} and Cd^{2+} are the radicals of group II, whereas Ni^{2+} & Zn^{2+} are the radicals of group IV. The solubility product of group IV radicals is higher as compared to group II. NH_4OH increases the ionisation of H_2S by removing H^+ of H_2S as unionisable water.

$$H_2S \rightleftharpoons 2H^+ + S^{2-};\ H^+ + OH^- \longrightarrow H_2O$$

Thus excess of sulphide ions are present which leads to the precipitation of all the four ions.

Note : HCl decreases ionisation of H_2S whereas NH_4OH increases the ionisation of H_2S.

24. **(b)** The salt can be $FeSO_4.7H_2O$ which produces SO_2. SO_2 decolourises $KMnO_4$ and gets oxidised to SO_3 which dissolves in water to give H_2SO_4 which gives white ppt. of $BaSO_4$ with $BaCl_2$ solution.

25. **(c)**

26. **(d)**

27. **(b)**

28. **(c)** Brown ring test is not preliminary test. It is confirmatory test.

29. **(a)** $MgCl_2$ is soluble in water and does not give flame test. Other give flame test.

30. **(b)** $BaCl_2 + K_2CrO_4 \rightarrow BaCrO_4 + 2KCl$. $BaCrO_4$ is insoluble in acetic acid and Ba gives apple green colour in flame test.

31. **(d)** Mn^{2+} gives violet coloured bead in borax bead test

32. **(c)** $Co(BO_2)_2$ blue bead

33. **(c)** $Cu(BO_2)_2$ is formed in oxidising flame and $CuBO_2$ or Cu in reducing flame

34. **(b)** See text $NaBO_2$ Sodium metaborate is fomed

35. **(b)** Gas evolved is SO_2

36. **(a)** Xanthoprotein test - skin protein is oxidised to yellow colour and HNO_3 is reduced to NO_2

37. **(c)** Both CO_2 and SO_2 turn lime water milky due to formation of $CaCO_3$ and $CaSO_3$.

38. **(c)** Chromyl chloride is formed CrO_2Cl_2

39. **(d)** AgF is most soluble in water, others are insoluble

40. **(b)** NaCl is a salt of strong acid and strong base hence on dissolution will give neutral solution.

$NaCl + AgNO_3 \rightarrow AgCl\downarrow + HNO_3$

41. **(d)** $BaSO_4$ is insoluble in HCl

42. **(a)** CCl_4 and CS_2 disslove bromine very much, animal charcoal will adsorb it. Only marble will not effect

43. **(c)** Complex formed in ring test is $[Fe(H_2O)_5NO]^{2+}$

44. **(b)** $Fe(CNS)_3$ is blood red in colour

45. **(b)**

46. **(c)** $AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl + 2H_2O$ soluble complex

47. **(b)** $NaNO_3$ does not react with AgCl in any way. Other forms Ag, $[Ag(NH_3)_2]Cl$ and $Ag_2S_2O_3$

48. **(a)** $Pb(NO_3)_2 + 2NaCl \rightarrow PbCl_2\downarrow + 2NaNO_3$;

$BaCl_2$ is soluble in water

49. **(a)** Hg_2^{2+} or $\overset{+}{Hg}-\overset{+}{Hg}$

50. **(d)** $PbCl_2$ is insoluble in cold water, soluble in hot water and PbS is black ppt in acidic medium

51. **(c)**

52. **(a)** H_2S is oxidised to colloidal sulphur by oxidising agent

53. **(a)** Both Hg and Pb gives black ppt with H_2S (HgS and PbS) see table for colour of others

54. **(a)** HgS does not dissolve in hot dil HNO_3. It dissolves in aquaregia

55. **(c)** $SnS + (NH_4)_2S_2 \rightarrow (NH_4)_2SnS_3$ soluble

56. **(b)** $Pb(NO_3)_2 + 2NH_4OH \rightarrow \underset{\text{(white ppt)}}{Pb(OH)_2\downarrow} + 2NH_4NO_3$

$Pb(NO_3)_2 + 2HCl \rightarrow \underset{\text{(white ppt)}}{PbCl_2\downarrow} + 2HNO_3$

$Pb(NO_3)_2 + H_2S \rightarrow \underset{\text{(black)}}{PbS\downarrow} + 2HNO_3$

57. **(a)** $K_3[Cu(CN)_4]$ more stable $K_2[Cd(CN)_4]$ less stable

58. **(c)** CdS is precipitated in dil soln only due to its higher K_{sp}

59. **(c)** $PbSO_4$ is insoluble in water

60. **(c)** The higher the value of K_{sp}, the more is the solublity

61. **(d)** The correct order of solubility of sulphides is

$Na_2S > ZnS > CuS$

62. **(c)** $Cl_2 + H_2O \rightarrow HCl + HClO$

$HCl + AgNO_3 \rightarrow \underset{\text{White ppt}}{AgCl\downarrow} + HNO_3$

$Mg + 2HCl \rightarrow MgCl_2 + H_2\uparrow$

Hence X is Cl_2 and y is H_2

63. **(b)** CuS and CdS are precipitated by H_2S. Hydroxide of Al will pass into the solution in the form of $NaAlO_2$ being amphoteric in nature hence filtrate will give test for sodium and aluminium

64. **(a)** HCl is added before NH_4OH to decrease conc. of $[OH^-]$ (see text)

65. **(a)** $2Cr(OH)_3 + 4NaOH + 3O \rightarrow \underset{\substack{\text{sodium chromate}\\ \text{(yellow)}}}{2Na_2CrO_4} + 5H_2O$

66. **(b)** $CrO_3 + 2NaOH \rightarrow Na_2CrO_4 + H_2O$

67. **(a)** There is no reaction between I^- and Fe^{3+}

68. **(b)** When NH_3 is added to Fe^{3+}, Zn^{2+}, and Cu^{2+} we get $Fe(OH)_3$ brown ppt. $[Zn(NH_3)_4]^{2+}$ soluble $[Cu(NH_3)_4]^{2+}$ soluble

69. **(b)**

70. **(b)** $Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$

71. **(d)** DMG forms a complex of red colour with Ni^{2+} ions and not metallic Ni.

72. **(d)** CoS is not precipitated in acidic medium (see text)

73. **(c)** $3Mg + 2N_2 \rightarrow Mg_3N_2 \xrightarrow{H_2O} NH_3 + Mg(OH)_2$

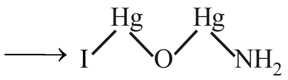
$Mg_3N_2 \xrightarrow{H_2O} NH_3 + Mg(OH)_2$

74. **(b)** $CuSO_4 + 4NH_3 \rightarrow \underset{\text{deep blue colour}}{Cu[(NH_3)_4]\,SO_4}$

75. **(b)** Green residue is due to $Fe(OH)_2$ and yellow filtrate is due to chromate ions CrO_4^{2-}

76. **(c)** NaOH is hygroscopic in nature

77. **(c)** $\underset{\text{Nesslers reagent}}{2K_2(HgI_4)} + NH_4OH + 3NaOH$



$+ 4KI + 3NaI + 3H_2O$

Brown ppt (Millon's base)

78. **(b)** $2KMnO_4 + 3H_2SO_4 \rightarrow$

$K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$

$H_2S + O \rightarrow H_2O + \underset{\text{colloidal sulphur}}{S}$

79. **(d)** All statements are correct

80. **(b)** $BaCO_3$ and ZnS are insoluble in water but soluble in HCl

$BaCO_3 + 2HCl \rightarrow BaCl_2 + CO_2 + 2H_2O$

$ZnS + 2HCl \rightarrow ZnCl_2 + H_2S$

81. **(a)** $\underset{A}{2Na} + 2H_2O \rightarrow \underset{C}{2NaOH} + \underset{B}{H_2}$

$\underset{D}{Zn} + 2NaOH \rightarrow Na_2ZnO_2 + \underset{B}{H_2}$

Hence A, B, C and D are Na, H_2, NaOH and Zn respectively.

82. **(b)** Nessler's reagent is $K_2[HgI_4]$ hence ion $[HgI_4]^{2-}$

83. **(b)** $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$ hence no residue left

84. **(a)** The higher the K_{sp}, the higher is the solubility

85. **(a)** Efflorescence is loss of water of crystallisation to change into lower hydrate or anhydrous form

EXERCISE 2

1. **(b)** $Hg_2^{2+} + H_2S \rightarrow HgS + Hg + 2H^+$

2. **(d)** NH_4^+ ions are increased to suppress release of OH^- ions, hence solubility product of $Fe(OH)_3$ is attained. Colour of precipitate is different.

3. **(a)** $\dot{N}H_3 + H^+ \text{(acid medium)} \rightleftharpoons \overset{+}{N}H_4$

4. **(a)** Ammonia can dissolve ppt. of AgCl only due to formation of complex as given below:

$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$

5. **(a)** $\underset{\text{(insoluble)}}{HgI_2} + KI \rightarrow \underset{\text{(soluble)}}{K_2HgI_4}$

On heating HgI_2 decomposes as

$HgI_2 \rightleftharpoons Hg + I_2$

6. **(d)** $25 \times N = 0.1 \times 35\,;\, N = 0.14 \therefore M = 0.07\,M$

$Ba(OH)_2$ is diacid base

7. **(a)** Prussian blue $Fe_4[Fe(CN)_6]_3$ is formed in Lassaignei's test for nitrogen

8. **(c)** $4KI^{-1} + 2CuSO_4 \rightarrow I_2^0 + Cu_2I_2 + 2K_2SO_4$

$\overset{0}{I_2} + 2Na_2\overset{2+}{S_2}O_3 \rightarrow Na_2\overset{+2.5}{S_4}O_6 + 2NaI^{-1}$

9. **(b)** Potassium dichromate oxidise Fe^{++} to Fe^{+++} as

$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow$

$K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$

i.e., change in O.S. of Cr per atom = 6

Therefore the eq.wt. of $K_2Cr_2O_7 = \frac{294}{6}$

Now, since

Normality = Gram Eq. / volume of solution in litre

or $N \times V = \frac{W}{E}$

$0.6 \times 0.75 \times 1 = \frac{W}{294} \times 6$

$W = 22.05$ g

10. **(a)** The ions of group II of salt analysis are precipitated by HCl and H_2S whereas members of group IV are precipitated by H_2S in alkaline medium.

$\because Bi^{3+}$ and Sn^{4+} both belong to group II

$\therefore$ They will be precipitated by HCl in presence of H_2S.

11. **(d)** $2KNO_3 + H_2SO_4 \rightarrow 2KHSO_4 + \underset{\text{(Brown gas)}}{2NO_2 \uparrow}$

12. **(d)** $Na_2[Fe(CN)_5NO] + S^{2-} \rightarrow \underset{\substack{\text{Sodium thio-nitroprusside} \\ \text{(violet)}}}{Na_4[Fe(CN)_5NOS]}$

13. **(b)** Hypo solution are used as the reducing agent with potassium dicromate solution

$K_2\overset{+6}{Cr_2}O_7 = \frac{\text{Molecular weight}}{6}$

14. **(b)**

15. **(a)** Due to formation tetraamine of zinc (II) complex;

$Zn^{+2} + NH_4OH \rightarrow [Zn(NH_3)_4]^{+2}$

16. (a) Test of Mg^{+2} ion

$Mg^{+2} + NH_4OH + Na_2HPO_4 \rightarrow Mg(NH_4)PO_4$.

17. (b) $Hg^{2+} + 2KI \rightarrow \underset{\text{(red ppt)}}{HgI_2} \downarrow + 2K^+$

$HgI_2 + 2KI \rightarrow K_2HgI_4$

$$Hg^{2+} + Co^{2+} + 4SCN^- \longrightarrow \underset{\text{(deep blue crystalline)}}{CoHg(SCN)_4 \downarrow}$$

18. (a) In presence of acid, ionisation of H_2S is supressed, so less number of S^{2-} are furnished. Hence only those sulphides are precipitated which has low solubility product (K_{sp}); thus only CuS and HgS are precipitated.

19. (d) Carbolic acid (Phenol) is weaker acid than carbonic acid and hence does not liberate CO_2 on treatment with aq. $NaHCO_3$ solution.

20. (d) The group reagent of fourth group is ammonical H_2S by which Zn^{2+} ion will be precipitated as ZnS, whereas Fe^{3+} ion and Al^{3+} ions will be precipitated as hydroxides.

EXERCISE 3

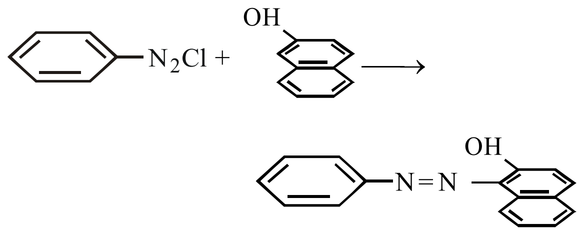
1. (c) For detection of nitrogen by lassaigne's method, the compound must contain C and N both to form NaCN.

2. (c) $\underset{\text{Soda nitroprusside}}{Na_2S + Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{Soda.thio nitroprusside}}{Na_4[Fe(CN)_5NOS]}$

3. (b) $SCN^- + Fe^{+++} \longrightarrow Fe(SCN)_3$

blood red ppt.

4. (b)



Red dye

5. (d) Pyridine and thiourea form volatile cupric cyanide and also give bluish green flame like volatile cupric halides.

6. (b) Eq. of acid = Eq of base,

$$\therefore \frac{0.45}{E.wt} = \frac{20 \times 0.5}{1000}, = E.wt = 45$$

$$\text{Basicity} = \frac{M.wt}{E.wt} = \frac{90}{45} = 2$$

7. (a) Normality of 3% Na_2CO_3. $N = \frac{3 \times 100}{53 \times 100} = 0.566N$

For H_2SO_4 sol. $N_1 = 0.1, V_1 = 100$ ml

For Na_2CO_3 sol. $N_2 = 0.566$. N_2 ?

Now apply $N_1V_1 = N_2V_2$

$$V_2 = \frac{N_1V_1}{N_2} = \frac{0.1 \times 100ml}{0.566} = 176.66ml$$

8. (a) Eq of $KMnO_4$ used $= \frac{50 \times 1}{1000 \times 10} = 0.005$

$\therefore$ Eq of FAS reacted = 0.005

$\therefore$ weight of FAS needed = 0.005 × 392 = 1.96 g

Thus percentage purity of FAS is 50%

9. (a) The strength of H_2O_2 in g/litre

$$= \frac{68 \times \text{Volume}}{22.4} = \frac{68 \times 20}{22.4} = 60.7 g/l$$

10. (a) Let the amount of Na_2CO_3 present in the mixture be x g . Na_2SO_4 will not react with H_2SO_4. Then

$$\frac{x}{53} = \frac{20 \times 0.1 \times 10}{1000} \therefore x = 1.06g$$

$$\therefore \text{Percentage of } Na_2CO_3 = \frac{1.06 \times 100}{1.25} = 84.8\%$$

11. (b) Let *x* Eq of Na_2CO_3 and y Eq of NaOH be present in the solution. In presence of phenolphthalein the reaction are

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

$NaOH + HCl \rightarrow NaCl + H_2O$

$$\therefore \frac{x}{2} + x = \frac{300 \times 0.1}{1000} = 0.03$$

In presence of methyl orange rest of Na_2CO_3 reacts

$$\frac{x}{2} = \frac{25 \times 0.2}{1000} = 0.005$$

$\therefore$ x = 0.01 Then weight of = 0.01 then weight of $Na_2CO_3 = 0.01 \times 53 = 0.53$ g

are y = 0.03 – 0.005 = 0.025 thus weight of NaOH = 0.025 × 40 = 1g

12. (b) Let the amount of the $K_2Cr_2O_7$ in the mixture be x g, then amount of $KMnO_4$ will be (0.5 – x) g

$$\therefore \left(\frac{x}{49} + \frac{0.5 - x}{31.6}\right) = \frac{100 \times 0.15}{1000}$$

where 49 is Eq. wt. of $K_2Cr_2O_7$ and 31.6 is Eq. wt. of $KMnO_4$.

On solving, we get x = 0.073 g

$$\text{Percentage of } K_2Cr_2O_7 = \frac{0.0732 \times 100}{0.5} = 14.64\%$$

13. (b)

14. (d) Each of them decompose aqueous solution of $NaHCO_3$. Recall that when at least two $-NO_2$ groups are present in *ortho* and *para* positions with respect to phenolic –OH group, it becomes highly acidic and gives effervescences of CO_2 with aq. $NaHCO_3$ solution.

15. **(c)** Equiv. mass of

$$MnO_4^- = \frac{\text{molar mass}}{7-2} = \frac{\text{molar mass}}{5}.$$

Equiv. mass of

$$C_2O_4^{2-} = \frac{\text{molar mass}}{2(4-3)} = \frac{\text{molar mass}}{2}$$

Meq. of $KMnO_4 = 50 \times 5 \times 0.04 = 10 =$ meq of $H_2C_2O_4 = 50 \times 2 \times 0.1 = 10$. Hence (c).

16. **(c)** The nitation of aniline is difficult to carry out with nitrating mixture since $-NH_2$ group get oxidised which is not required. So the amino group is first protected by acylation to form acetanilide which is then nitrated to give p-nitro acetanilide as a major product.

17. **(a)** **18.** **(a)** **19.** **(a)**

20. **(b)** The ionic equation for oxidation of Mohr's salt is

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

$$\text{Now Eq. of Mohr's salt} = \frac{392}{1} = 392$$

$$\text{Strength} = \text{Normality} \times \text{Eq. mass} = \frac{1}{20} \times 392 = 19.6\,g/lit$$

Thus for preparing 250 ml of N/20 Mohr's salt solution,

$$\text{Mohr's salt needed} = \frac{19.6}{1000} \times 250 = 4.9\,g$$

21. **(b)** $$2Fe_2(SO_4)_3 + 3K_4[(Fe(CN)_6] \rightarrow \underset{\text{prussian blue}}{Fe_4[Fe(CN)_6]_3} + 6K_2SO_4$$

22. **(c)** $$Na_2SO_3 + 2HCl(dil) \rightarrow 2NaCl + H_2O + SO_2$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + H_2O$$

23. **(d)** Salt of Zn : $ZnSO_4 + Na_2CO_3 \rightarrow ZnCO_3 + Na_2SO_4$

$$ZnCO_3 \rightarrow ZnO + CO_2$$

$$2Co(NO_3)_2 \rightarrow 2CoO + 4NO_2 + O_2$$

$$CoO + ZnO \rightarrow \underset{\text{green}}{Co.ZnO_2}$$

24. **(b)** $$MgCl_2 + Na_2HPO_4 + NH_4OH \rightarrow \underset{\text{white ppt.}}{Mg(NH_4)PO_4} + 2NaCl + H_2O$$

25. **(c)** $$Na_2C_2O_4 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO + CO_2$$

CO burns with blue flame $2CO + O_2 \rightarrow 2CO_2$

$$Na_2C_2O_4 + H_2SO_4(dil) \rightarrow Na_2SO_4 + H_2C_2O_4$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

26. **(d)** Na_2CO_3 will furnish appreciable CO_3^{2-} ions to precipitate Mg

27. **(b)** $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$

It is violent reaction with flashes of light (volcano)

28. **(a)** $Cu_2[Fe(CN)_6]$ is chocolate colour and insoluble compound

29. **(a)** Fe^{2+} is oxidised to Fe^{3+} in order to precipitate $Fe(OH)_3$

30. **(d)** $Al(OH)_3$ is insoluble ppt.

31. **(a)** In aqueous solution the H_2S will provide sufficient S^{2-} ions to precipitate CuS, ZnS and CdS.

32. **(d)** The oxalates of Ba^{2+}, Ca^{2+} and Sr^{2+} are insoluble in water

33. **(c)** Microcosmic salt. $Na(NH_4)HPO_4.4H_2O$ is used for bead test

$$Na.(NH_4)HPO_4 \rightarrow NaPO_3 + NH_3 + H_2O$$

$$NaPO_3 + CoO \rightarrow NaCo.PO_4\,(\text{blue})$$

34. **(b)** Al^{3+} is soluble in NaOH.It forms $[Al(OH)_4^-]$ soluble complex

35. **(c)** $$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2S$$

$$SbCl_3 + 6H_2O \rightarrow \underset{\text{ppt (White)}}{SbOCl} + 2HCl$$

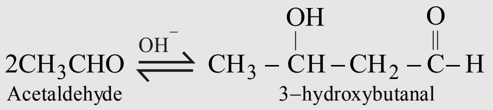
36. **(d)** Lead forms $PbCl_2$ in group I and PbS in group II which are partially soluble in water

37. **(a)** SO_2 and H_2S both being reducing agents, can turn acidified dichromate solution green. SO_2 can be obtained by the action of acid upon sulphite while H_2S is evolved by the action of acid upon sulphide. However, SO_2 has a burning sulphur smell which is irritating. H_2S has rotten egg like smell.

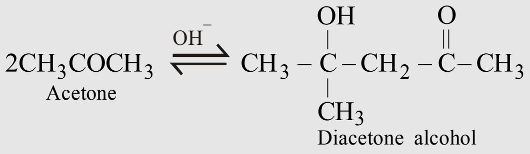
APPENDIX - I

REACTION MECHANISMS

1. **Aldol Condensation :** Reversible self addition of aldehydes or ketones containing α-hydrogen atom in presence of dilute base. The product obtained is both an aldehyde or ketone and alcohol

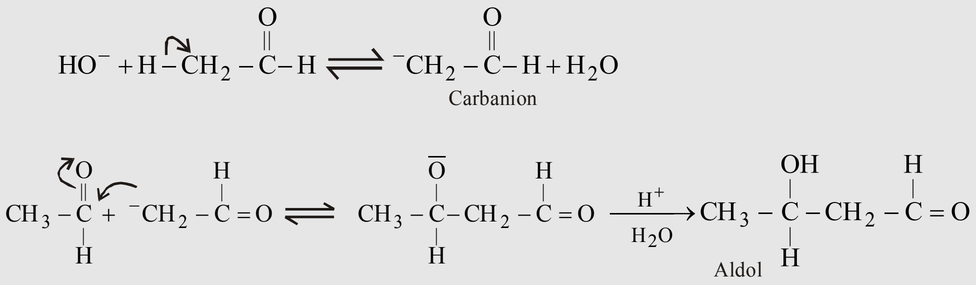


$$\underset{\text{Acetaldehyde}}{2CH_3CHO} \overset{OH^-}{\rightleftharpoons} \underset{\text{3-hydroxybutanal}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-\overset{\overset{O}{||}}{C}-H}$$



$$\underset{\text{Acetone}}{2CH_3COCH_3} \overset{OH^-}{\rightleftharpoons} \underset{\text{Diacetone alcohol}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-\overset{\overset{O}{||}}{C}-CH_3}$$

Mechanism:



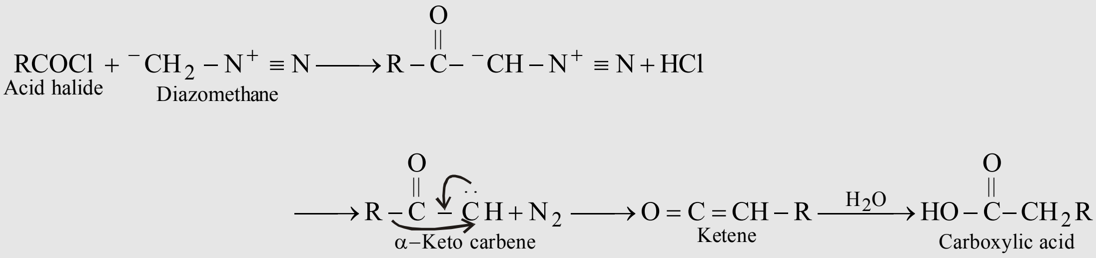
$$HO^- + H-CH_2-\overset{\overset{O}{||}}{C}-H \rightleftharpoons \underset{\text{Carbanion}}{{}^-CH_2-\overset{\overset{O}{||}}{C}-H} + H_2O$$

$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{O}{||}}{C}} + {}^-CH_2-\overset{\overset{H}{|}}{C}=O \rightleftharpoons CH_3-\underset{\underset{H}{|}}{\overset{\overset{\bar{O}}{|}}{C}}-CH_2-\overset{\overset{H}{|}}{C}=O \xrightarrow[H_2O]{H^+} \underset{\text{Aldol}}{CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-\overset{\overset{H}{|}}{C}=O}$$

2. **Arndt-Eistert Synthesis :** The conversion of an acid to next higher homologue via acyl chloride reacting with diazomethane

$$RCOCl \xrightarrow[H_2O]{CH_2N_2\Delta} RCH_2COOH$$

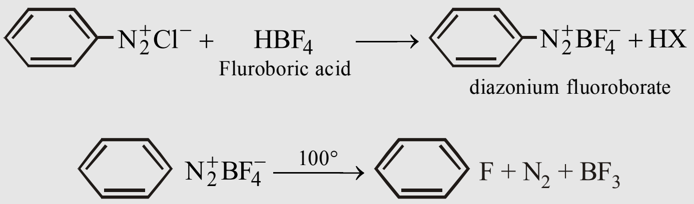
Mechanism :



$$\underset{\text{Acid halide}}{RCOCl} + \underset{\text{Diazomethane}}{{}^-CH_2-N^+\equiv N} \longrightarrow R-\overset{\overset{O}{||}}{C}-{}^-CH-N^+\equiv N + HCl$$

$$\longrightarrow \underset{\alpha\text{-Keto carbene}}{R-\overset{\overset{O}{||}}{C}-\ddot{C}H} + N_2 \longrightarrow \underset{\text{Ketene}}{O=C=CH-R} \xrightarrow{H_2O} \underset{\text{Carboxylic acid}}{HO-\overset{\overset{O}{||}}{C}-CH_2R}$$

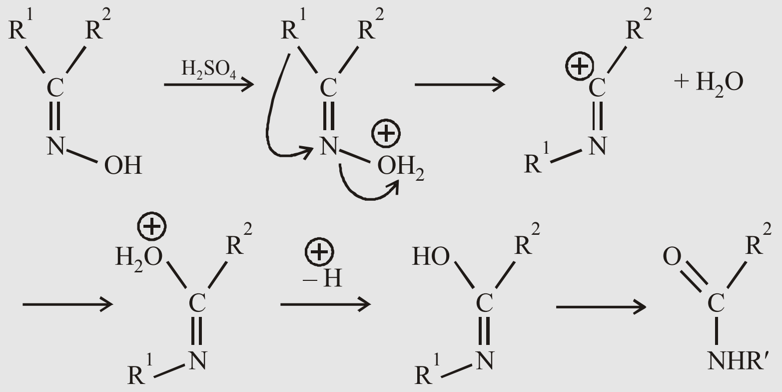
3. **Balz-Schiemann Reaction :** Replacement of $-N_2X$ by F.



4. **Beckmann rearrangement :** Ketoximes on treatment with reagents like PCl_5, H_2SO_4, H_3PO_4 etc. undergo Beckmann rearrangement to form an acid amide.

$$\underset{\text{Ketoxime}}{Ar_2C = NOH} \longrightarrow \underset{\text{Acid Amide}}{Ar.CONHAr}$$

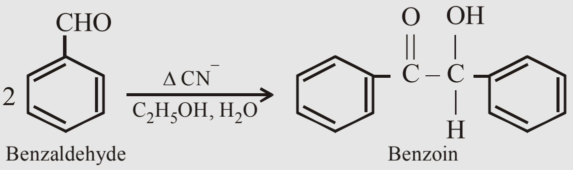
Mechanism : The rearrangement is intramolecular involving 1,2-shift as follows



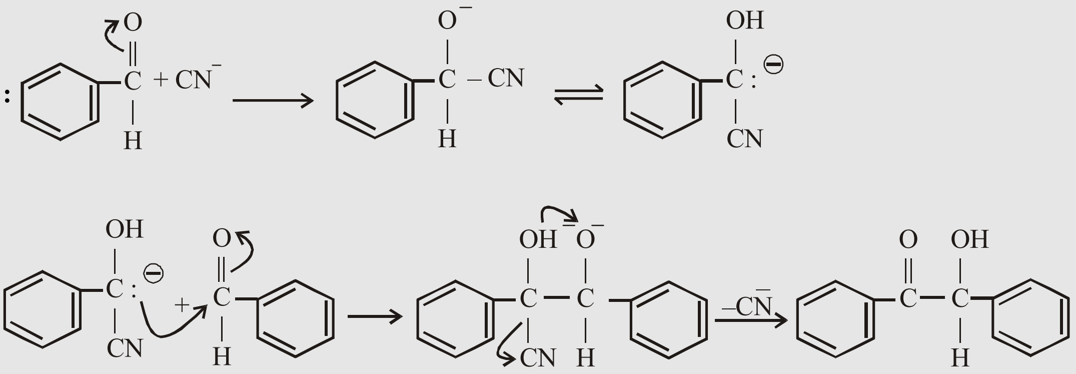
when PCl_5 is used, replace $\overset{+}{O}H_2$ by $OPCl_4$.

It is always the anti R group that migrates in the Backmann rearrangement.

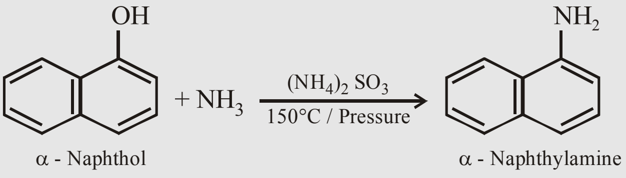
5. **Benzoin Condensation :** Dimerisation of benzaldehyde to α-hydroxy Ketone called benzoin when heated with ethanolic NaCN or KCN, is known as benzoin condensation.



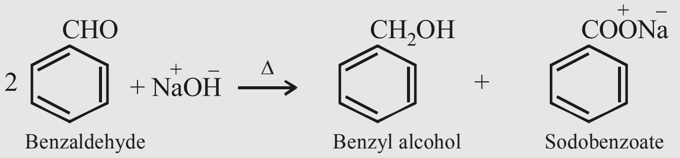
Mechanism :



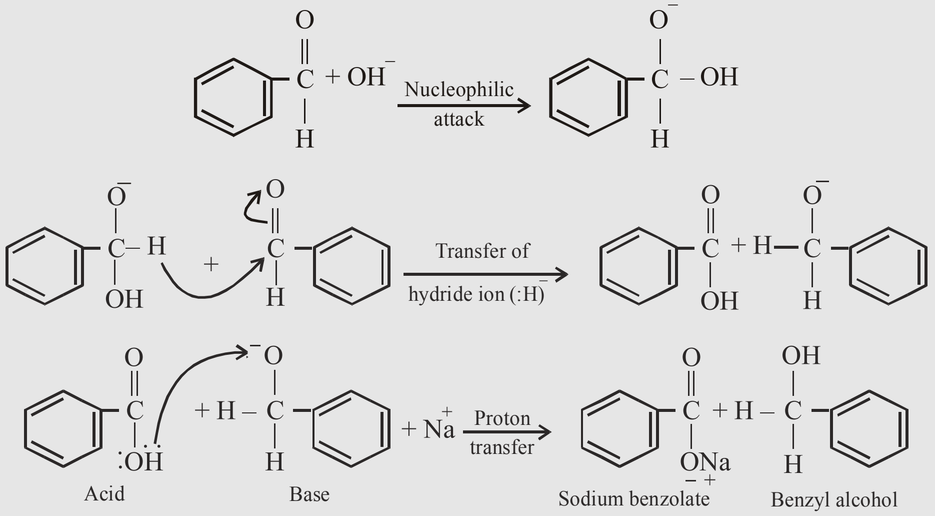
6. **Bucherer Reaction:** The reversible conversion of a naphthol into corresponding naphthylamine is called Bucherer reaction.



7. **Cannizzaro Reaction :** Aldehydes containing no α-hydrogen atom when heated with conc. Sodium or potassium hydroxide solution, undergo intermolecular oxidation-reduction reaction.



Mechanism :



8. **Carbylamine Reaction** (Isocyanide reaction) : A primary amine (aliphatic or aromatic) when warmed with an ethanlic solution of potassium hydroxide, forms an isonitrile (carbylamine).

$$RNH_2 + 3KOH + CHCl_3 \longrightarrow R - N \overset{\rightarrow}{=} C + 3KCl + 3H_2O$$

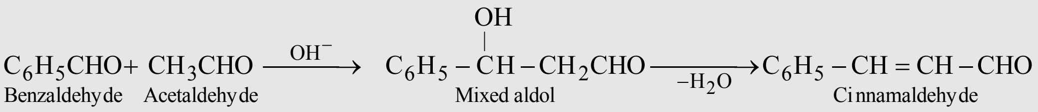
Mechanism : The reaction proceeds through the intermediate formation of dichloro carbene (:CCl_2)

$$CHCl_3 + OH^- \longrightarrow {}^-CCl_3 + H_2O \longrightarrow :CCl_2 + Cl^-$$

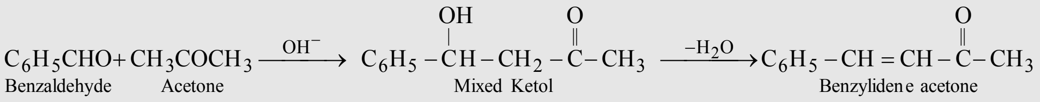
$$R - NH_2 + :CCl_2 \longrightarrow R - NH - CHCl_2$$

$$R - NH - CHCl_2 + 2OH^- \longrightarrow R - \overset{+}{N} \equiv \overset{-}{C} : + 2Cl^- + 2H_2O$$

9. **Claisen Schmidt Condensation :** It is condensation of benzaldehyde or methyl Ketones in presence of dilute alkali at room temperature to form unsaturated aldehyde or Ketone. It is a type of mixed aldol condensation



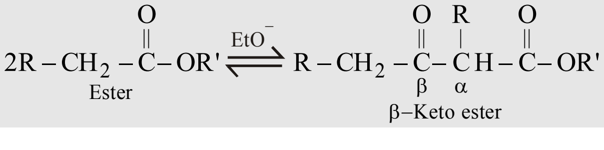
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{OH^-} \underset{\text{Mixed aldol}}{C_6H_5 - \overset{\overset{\displaystyle OH}{|}}{C}H - CH_2CHO} \xrightarrow[-H_2O]{} \underset{\text{Cinnamaldehyde}}{C_6H_5 - CH = CH - CHO}$$



$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{OH^-} \underset{\text{Mixed Ketol}}{C_6H_5 - \overset{\overset{\displaystyle OH}{|}}{C}H - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3} \xrightarrow{-H_2O} \underset{\text{Benzylidene acetone}}{C_6H_5 - CH = CH - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3}$$

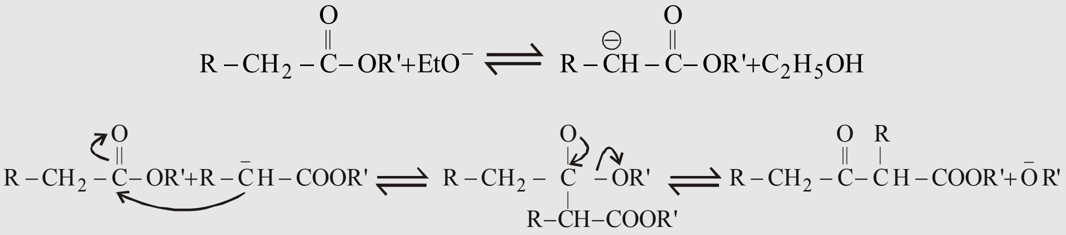
Mechanism : Similar to aldol condensation.

10. **Claisen Condensation :** when esters containing α-hydrogen are treated with a strong base such as sodium ethoxide, a β-ketoester is formed. The reaction is called claisen condensation.



$$\underset{\text{Ester}}{2R - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - OR'} \overset{EtO^-}{\rightleftharpoons} \underset{\beta\text{–Keto ester}}{R - CH_2 - \underset{\beta}{\overset{\overset{\displaystyle O}{\|}}{C}} - \underset{\alpha}{\overset{\overset{\displaystyle R}{|}}{C}}H - \overset{\overset{\displaystyle O}{\|}}{C} - OR'}$$

Mechanism :



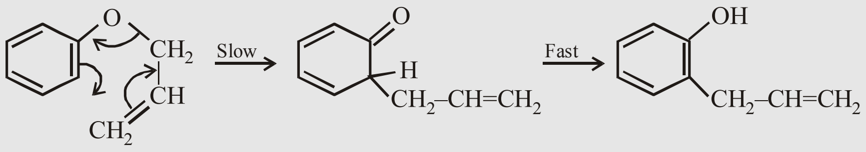
$$R-CH_2-\overset{O}{\overset{\|}{C}}-OR'+EtO^- \rightleftharpoons R-\overset{\ominus}{C}H-\overset{O}{\overset{\|}{C}}-OR'+C_2H_5OH$$

$$R-CH_2-\overset{O}{\overset{\|}{C}}-OR'+R-\bar{C}H-COOR' \rightleftharpoons R-CH_2-\underset{R-CH-COOR'}{\overset{O}{C}}-OR' \rightleftharpoons R-CH_2-\overset{O}{\overset{\|}{C}}-\overset{R}{\overset{|}{C}}H-COOR'+\bar{O}R'$$

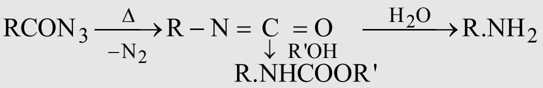
The ester can also be condensed with compounds containing active methylene group eg. certain aldehydes, Ketones, nitriles, nitro alkanes, diphenyl methane etc.

11. **Claisen Rearrangement :** Allyl arylethers, when heated, rearrange to O-allylphenols and reaction is called Claisen rearrangement.

Mechanism : The mechanism is concerted pericyclic [3.3] segmatropic rearrangement.

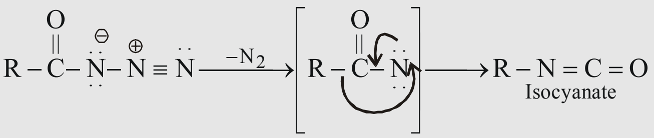


12. **Curtius Reaction :** The Curtius rearrangement involves the pyrolysis of acyl azide to give Isocyanates which can be hydrolysed by water or alcohol to give amines as carbamates (urethan derivatives) respectively.



$$RCON_3 \xrightarrow[-N_2]{\Delta} \underset{\underset{R.NHCOOR'}{\downarrow R'OH}}{R-N=C=O} \xrightarrow{H_2O} R.NH_2$$

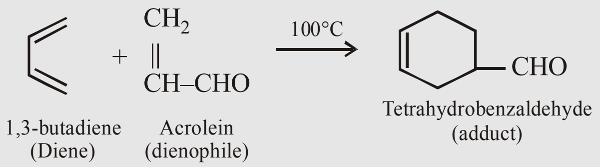
Mechanism :



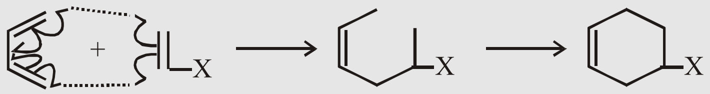
$$R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{\ddot{N}}-\overset{\oplus}{N}\equiv N \xrightarrow{-N_2} \left[R-\overset{O}{\overset{\|}{C}}-\ddot{N}\right] \longrightarrow \underset{\text{Isocyanate}}{R-N=C=O}$$

The reaction may be used to step down a series and for preparing 1° amines free from 2° and 3° amines, and urethanes.

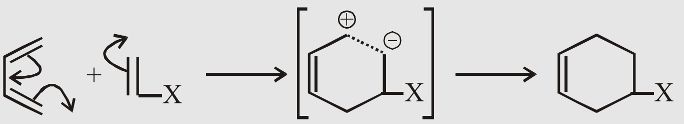
13. **Diel's Alder reaction :** The reaction involves the addition of dienophile across 1,4-positions of a conjugated diene to form a cyclohexane derivative.



Mechanism : *(a) Free radical mechanism*



(b) Polar mechanism :



Here X is some electron withdrawing atom a group which activates dienophile.

14. Finkelstein Reaction : Halogen exchange

$$RCl + NaI \xrightarrow{\text{acetone}} RI + NaCl$$

$$2RCl + HgF_2 \xrightarrow{0°C} 2RF + HgCl_2$$

15. Frankland's reaction : Similar to Wurtz reaction. Here zinc is used in place of sodium.

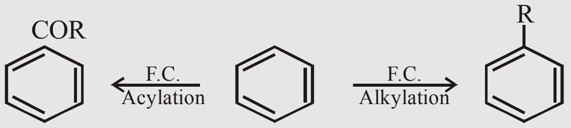
Mechanism :

$$C_2H_5I + Zn \longrightarrow C_2H_5ZnI$$

$$2C_2H_5ZnI \longrightarrow Zn(C_2H_5)_2 + ZnI_2$$

$$Zn(C_2H_5)_2 + 2C_2H_5I \longrightarrow 2C_2H_5 - C_2H_5 + ZnI_2$$

16. Friedel-Craft's reaction : The process of introducing alkyl or acyl groups in the aromatic compounds under the influence of a suitable catalyst is known as F.C. alkylation or acylation.

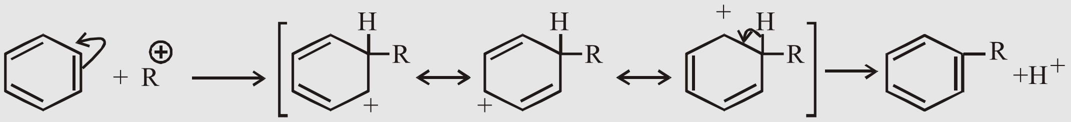


Alkylating agents : RX, ROH, ROR, Olefins or alkyl esters

Acylating agents : aacid chlorides, anhydrides, acids or esters

Catalysts : Anhy $AlCl_3$, BF_3, $SbCl_5$, $FeCl_3$, $SnCl_4$, $ZnCl_2$

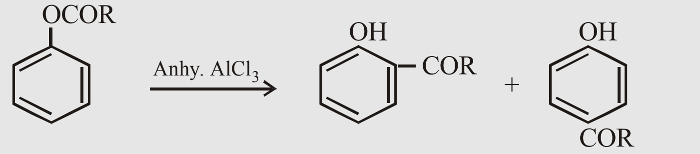
Mechanism : $RCl + AlCl_3 \longrightarrow R^+ + Al^-Cl_4$



$$H^+ + Al^-Cl_4 \longrightarrow HCl + AlCl_3$$

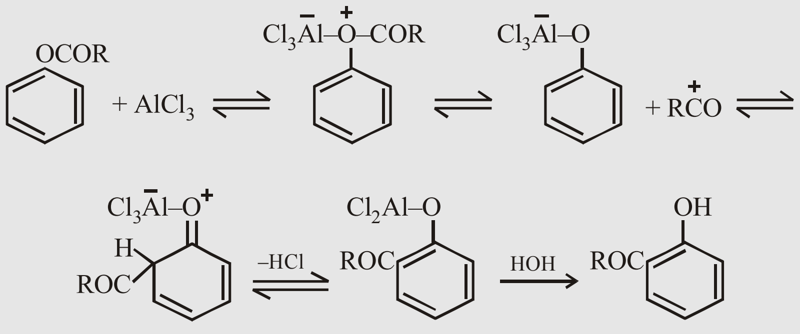
In case of acylation the electrophile is $R\overset{+}{C}O$, acylium ion.

17. Fries Rearrangement : Phenolic esters of both the aliphatic or aromatic acids when heated with any. $AlCl_3$ undergo rearrangment to form aromatic Ketones.

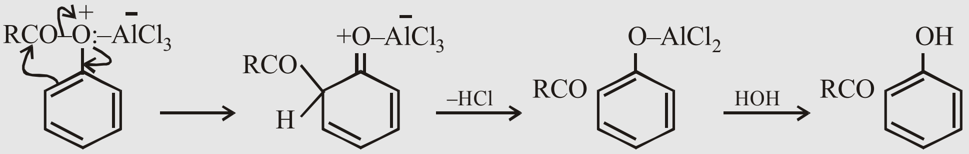


Phenyl ester O-hydroxy Ketone p-hydroxy Ketone

Mechanism : (a) Intermolecular mechanism.

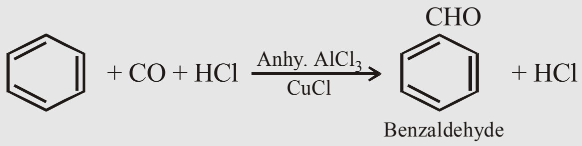


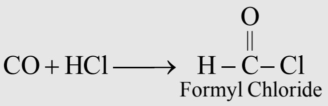
Intramolecular mechanism :



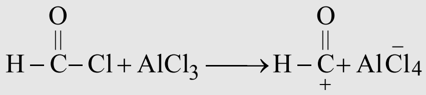
18. **Gatterman Reaction :** In place of Cuprous salts Cu powder is used. The mechanism is the same as Sandmeyer's reaction.

19. **Gattermann-Koch reaction :** Formylation with CO and HCl

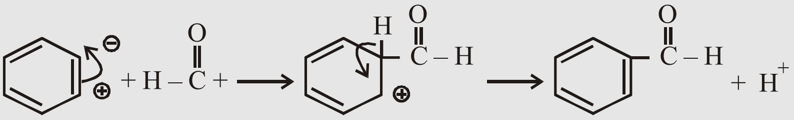


Mechanism : 

$$CO + HCl \longrightarrow \underset{\text{Formyl Chloride}}{H-\overset{\overset{\displaystyle O}{||}}{C}-Cl}$$

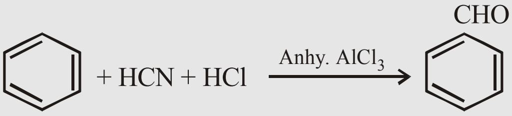


$$H-\overset{\overset{\displaystyle O}{||}}{C}-Cl + AlCl_3 \longrightarrow H-\underset{+}{\overset{\overset{\displaystyle O}{||}}{C}} + Al\overset{-}{C}l_4$$

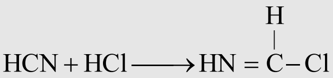


$$H^+ + \overset{-}{A}lCl_4 \longrightarrow HCl + AlCl_3$$

20. **Gattermann Aldehyde reaction :** Formylation with HCl and HCN

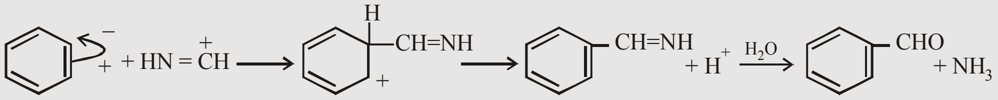


Mechanism :

(i) 

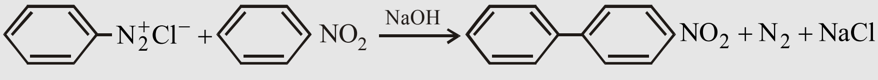
$$HCN + HCl \longrightarrow HN = \overset{\overset{\displaystyle H}{|}}{C}-Cl$$

(ii) $HN = CHCl + AlCl_3 \longrightarrow HN = \overset{\oplus}{C}H + \overset{-}{A}lCl_4$

(iii) 

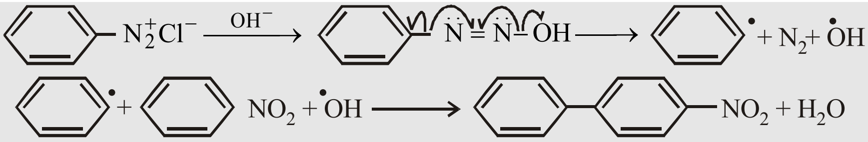
(iv) $H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$

21. **Gomberg Reaction :** Replacement of $-N_2X$ by Ar



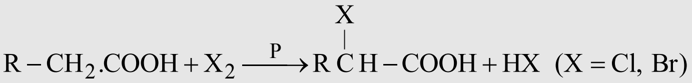
p-nitrobiphenyl

Mechanism :



22. Hell-Volhard-Zelinsky reaction : HVZ reaction

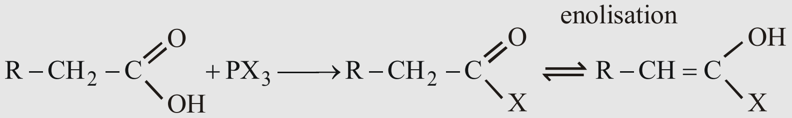
It is α-substitution when a carboxylic acid having α-hydrogens is treated with chlorine or bromine is presence of small amount of red phosphorous.



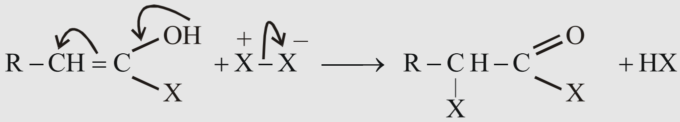
$$R-CH_2.COOH + X_2 \xrightarrow{P} R\overset{\overset{X}{|}}{C}H-COOH + HX \quad (X = Cl, Br)$$

Mechanism :

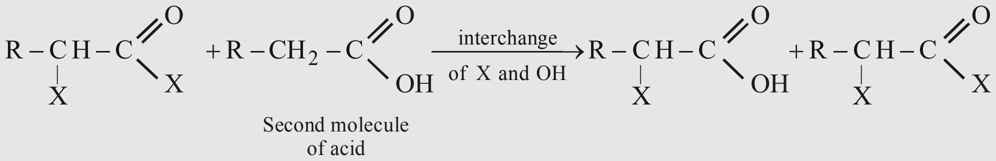
(i) $2P + 3X_2 \longrightarrow 2PX_3$



(ii)



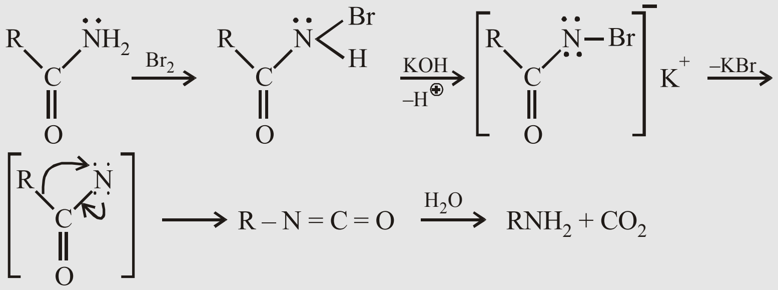
(iii)



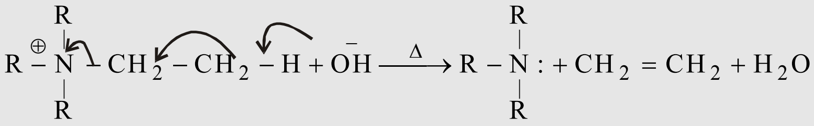
23. Hofmann Degradation or Hofmann bromamide reaction : This is the conversion of an amide into 1° amine by means of bromine (or chlorine) and alkali.

$RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$

Mechanism :

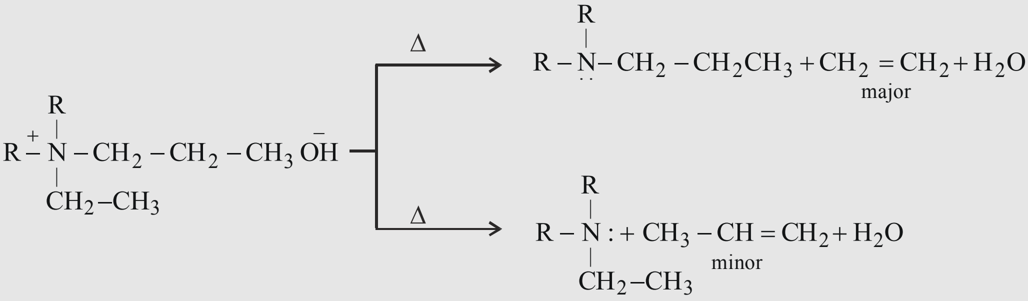


24. Hofmann Elimination : The tetraalkyl ammonium hydroxides having one of the substituent groups on the nitrogen bearing one β-hydrogen, on pyrolysis form a tertiary amine and an alkene by E_2 mechanism.



$$R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{\overset{\oplus}{N}}}-CH_2-CH_2-H + \overset{-}{O}H \xrightarrow{\Delta} R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{N}}: + CH_2 = CH_2 + H_2O$$

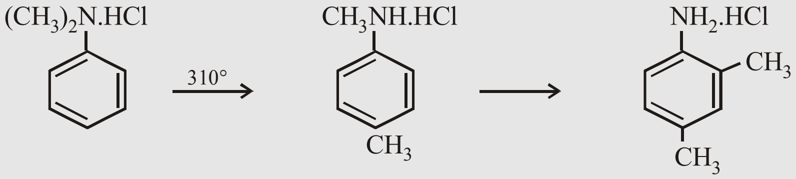
Hofmann Rule : When theoretically more than one type of alkenes are possible, in such case alkene containing least alkylated double bond is the major product.



$$(CH_3)_4\overset{+}{N}OH \xrightarrow{\Delta} (CH_3)_3\ddot{N} + CH_3OH$$

Tetramethylammonium hydroxide give trimethylamine and methyl alcohol.

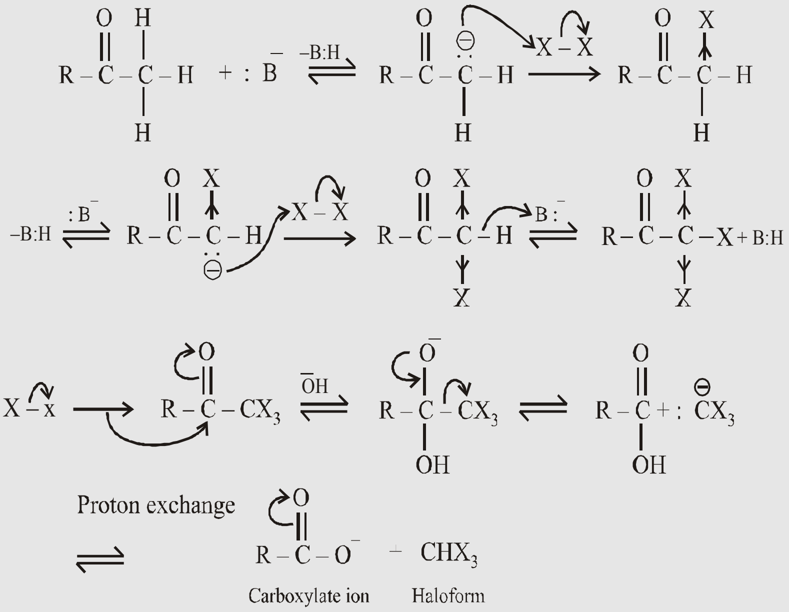
25. Hofmann-Martius Rearrangement : When N-alkyl or N, N-dialkyl anilines are heated in strong acid medium at 310°C, intermolecular migration of alkyl groups occurs, preferentially to para position.



N, N-dimethylaniline hydrochloride — 4-methyl-N-methyl aniline hydrochloride — 2,4-dimethyl aniline Hydrochloride

26. The Haloform Reaction : Reaction of methyl ketone with X_2/NaOH to give HCX_3 (haloform)

Machanism :



27. Hunsdiecker Reaction or Borodine-Hunsdiecker Reaction :

When silver salts of the carboxylic acids in CCl_4 are decomposed by chlorine or bromine, alkyl halides are formed.

$$RCOOAg + Br_2 \xrightarrow[\Delta]{CCl_4} RBr + CO_2 + AgBr$$

The yield of halides 1° > 2° > 3° and bromine is generally used, chlorine gives poor yield.

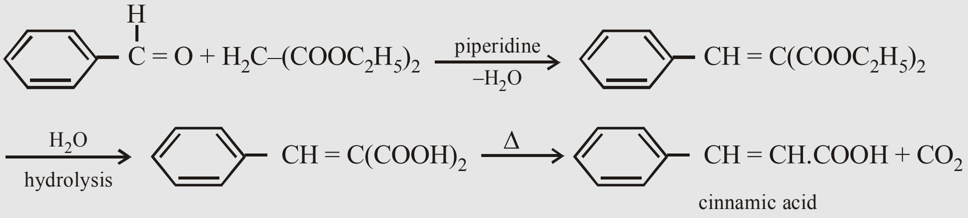
Mechanism :

(i) $RCO\overset{-}{O}\overset{+}{Ag} \xrightarrow[-AgBr]{Br_2} RCOOBr \longrightarrow RCO\dot{O} + \dot{B}r$

(ii) $RCO\dot{O} \longrightarrow R^{\bullet} + CO_2$

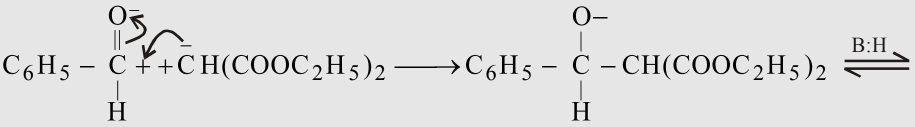
(iii) $R^{\bullet} + RCOOBr \longrightarrow R-Br + RCO\dot{O}$

28. Knoevenagel Condensation : It is condensation of benzaldehyde with compounds containing active methylene group e.g. diethyl-malonate, acetoacetic ester etc.

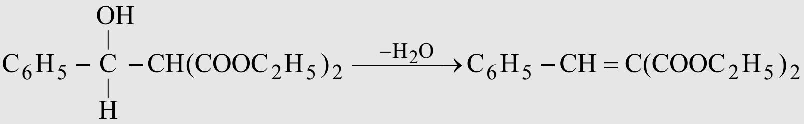


Mechanism :

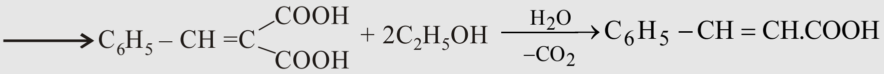
$$CH_2(COOC_2H_5) + :B^- \longrightarrow B:H + \bar{C}H(COOC_2H_5)_2$$



$$C_6H_5-\overset{\overset{\displaystyle O^-}{\|}}{\underset{\underset{\displaystyle H}{|}}{C^+}} + \bar{C}H(COOC_2H_5)_2 \longrightarrow C_6H_5-\overset{\overset{\displaystyle O-}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH(COOC_2H_5)_2 \xrightleftharpoons{B:H}$$

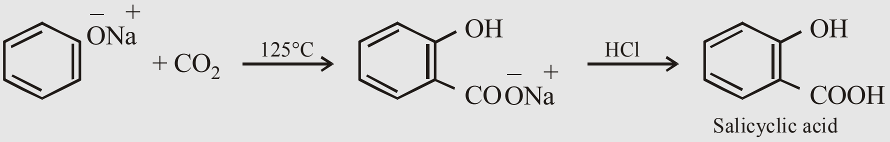


$$C_6H_5-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH(COOC_2H_5)_2 \xrightarrow{-H_2O} C_6H_5-CH=C(COOC_2H_5)_2$$



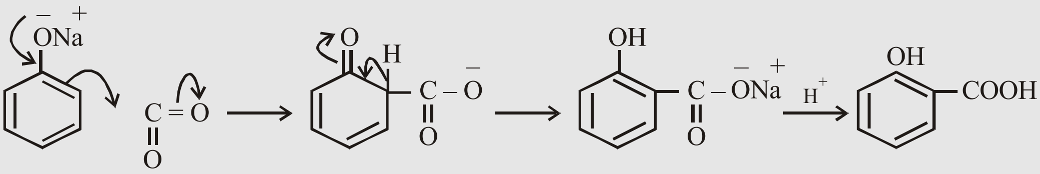
$$\longrightarrow C_6H_5-CH=C\begin{matrix}COOH\\COOH\end{matrix} + 2C_2H_5OH \xrightarrow[-CO_2]{H_2O} C_6H_5-CH=CH.COOH$$

29. Kobe's Reaction : When CO_2 is passed over sodium phenoxide at 125°C and 6-9 Atm. COOH is introduced at ortho position.



Small amount of p-isomer is also formed. At 250-300°C p-isomer is the main product.

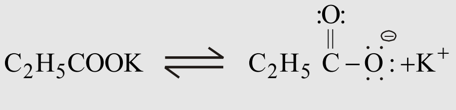
Mechanism :



30. Kolbe's Electrolysis : Electrolysis of Na or K salt of saturated mono-carboxylic acid to get alkane at anode.

$$2RCOOK + 2H_2O \xrightarrow{\text{Electrolysis}} R-R + 2CO_2 + 2KOH + H_2$$

Mechanism :



$$C_2H_5COOK \rightleftharpoons C_2H_5\overset{\overset{\displaystyle :O:}{\|}}{C}-\ddot{\underset{\cdot\cdot}{O}}:^{\ominus} + K^+$$

At Anode $$C_2H_5COO^- \xrightarrow{-e} \underset{\text{A free radical}}{C_2H_5COO^{\bullet}} \xrightarrow{\text{Fractionation}} {}^{\bullet}C_2H_5 + \ddot{\underset{\cdot\cdot}{O}} = C = \ddot{\underset{\cdot\cdot}{O}}$$

$$\dot{C}_2H_5 + \dot{C}_2H_5 \longrightarrow C_2H_5-C_2H_5 \quad n-\text{Butane}$$

$$\dot{C}_2H_5 + \dot{C}_2H_5 \longrightarrow C_2H_4 + C_2H_6 \quad \text{(Small quantity)}$$

$$CH_3CH_2CO\dot{O} + \dot{C}_2H_5 \longrightarrow CH_3CH_2COOC_2H_5 \quad \text{(Small quantity)}$$

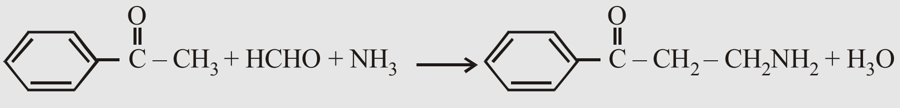
At Cathode $2K^+ + 2e^- \longrightarrow 2K$

$$2K + 2H_2O \longrightarrow 2KOH + H_2$$

Electrolysis of Pot. Succinate guives ethene while Pot. Salts of maleic acid and fumaric acid give acetylene.

Electrolysis of alkyl derivatives of Pot. Succinate gives Alkenes and alkyl derivatives of Pots. Salts of maleic acid and fumaric acid give Alkynes.

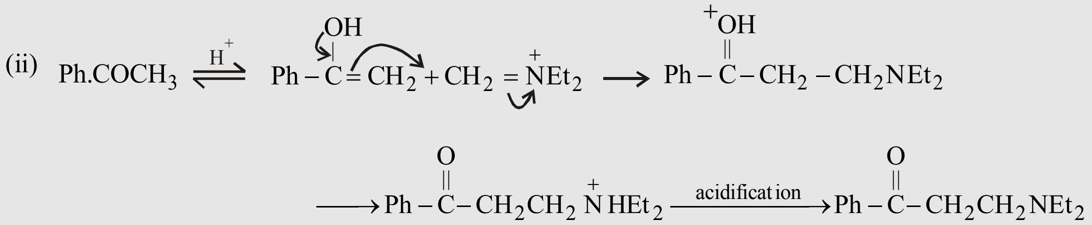
31. **Mannich reaction :** The condensation of formaldehyde (other aldehydes may also be used), ammonia or a 1° or 2° amine (preferably the hydrochloride) and a compound containing at leaset one active hydrogen atom eg. Ketones, β-Keto-ester, β-cyanoesters, nitroalkanes, alkynes etc. The condesnation product is known as Mannich base.



Acetophenone β-amino ketone

Mechanism :

(i) $2Et_2NH + CH_2O \rightleftharpoons Et_2N-CH_2-NEt_2 \overset{H^+}{\rightleftharpoons} Et_2\overset{+}{N}=CH_2 \longleftrightarrow Et_2N-\overset{+}{C}H_2$

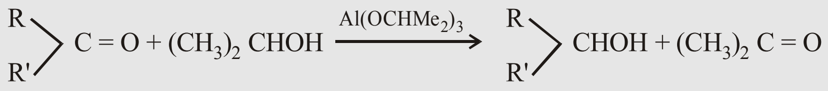


(ii) $Ph.COCH_3 \overset{H^+}{\rightleftharpoons} Ph-\overset{OH}{\overset{|}{C}}=CH_2 + CH_2=\overset{+}{N}Et_2 \longrightarrow Ph-\overset{{}^+OH}{\overset{||}{C}}-CH_2-CH_2NEt_2$

$$\longrightarrow Ph-\overset{O}{\overset{||}{C}}-CH_2CH_2\overset{+}{N}HEt_2 \xrightarrow{\text{acidification}} Ph-\overset{O}{\overset{||}{C}}-CH_2CH_2NEt_2$$

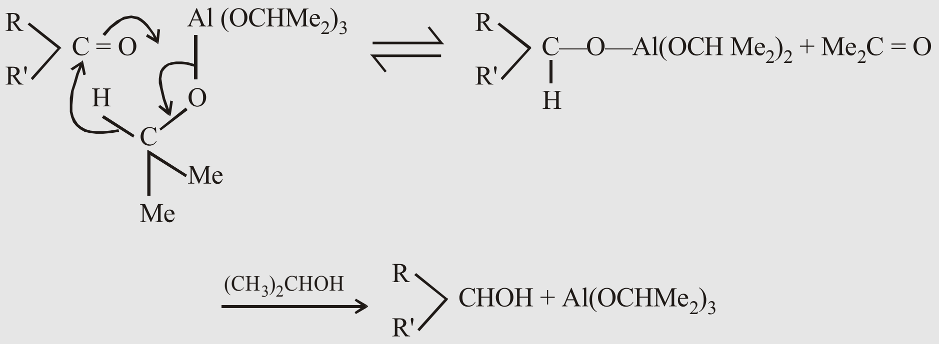
32. **Meerwein Ponndorf-Verley Reduction** (MPV reduction):

The reduction of ketones into alcohols with aluminium isopropoxide in isopropanol.This is hydride ion transfer reaction.

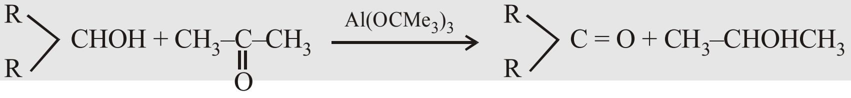


$$\begin{matrix}R\\R'\end{matrix}\!\!>C=O + (CH_3)_2CHOH \xrightarrow{Al(OCHMe_2)_3} \begin{matrix}R\\R'\end{matrix}\!\!>CHOH + (CH_3)_2C=O$$

Mechanism:

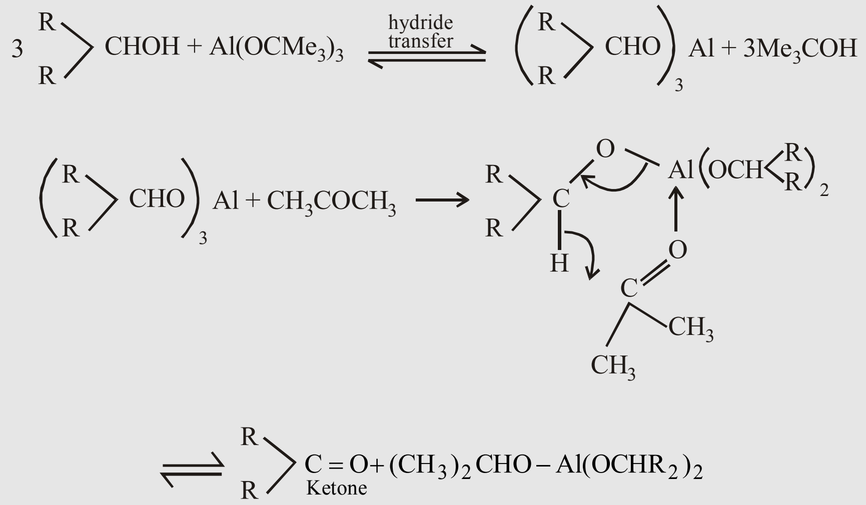


33. **Oppenauer Oxidation :** This reaction is reverse of MPV reduction. It is oxidation of alcohols to Ketone in presence of aluminium tertiary butoxide in presence of benzene or toluene.



$$\begin{matrix}R\\R\end{matrix}\!\!>CHOH + CH_3-\underset{O}{\underset{||}{C}}-CH_3 \xrightarrow{Al(OCMe_3)_3} \begin{matrix}R\\R\end{matrix}\!\!>C=O + CH_3-CHOHCH_3$$

Mechanism:

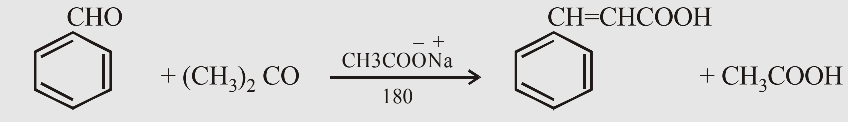


$$3\begin{matrix}R\\R\end{matrix}\!\!>CHOH+Al(OCMe_3)_3 \overset{\text{hydride transfer}}{\rightleftharpoons} \left(\begin{matrix}R\\R\end{matrix}\!\!>CHO\right)_3 Al+3Me_3COH$$

$$\left(\begin{matrix}R\\R\end{matrix}\!\!>CHO\right)_3 Al+CH_3COCH_3 \longrightarrow$$

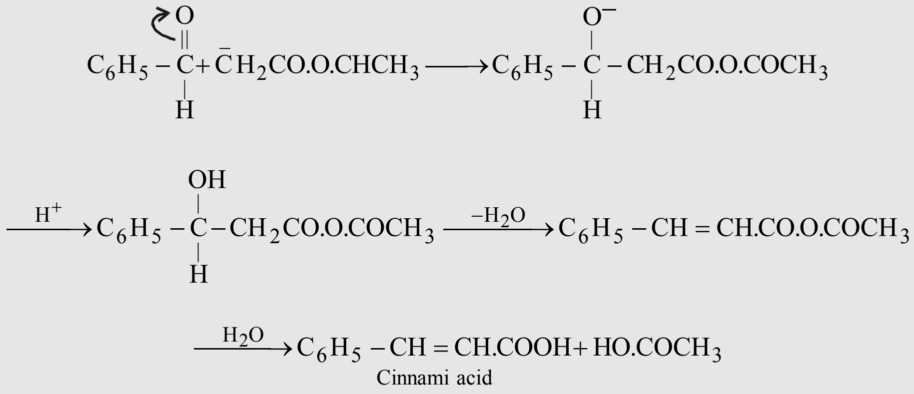
$$\rightleftharpoons \begin{matrix}R\\R\end{matrix}\!\!>\underset{\text{Ketone}}{C=O}+(CH_3)_2CHO-Al(OCHR_2)_2$$

34. Perkins Rection : It is the condensation of an aromatic aldehyde with anhydride of an aliphatic acid in presence of sodium salt of the same acid (catalyst) to form α, β-unsaturated acid.



Mechanism :

$$CH_3COO^- + H.CH_2CO.O.COCH_3 \longrightarrow CH_3COOH + \bar{C}H_2CO.O.COCH_3$$

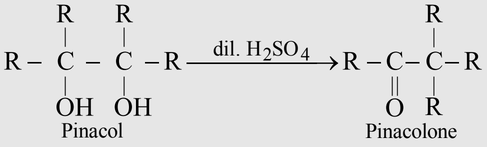


$$C_6H_5-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{C}}+\bar{C}H_2CO.O.CHCH_3 \longrightarrow C_6H_5-\overset{\overset{O^-}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CO.O.COCH_3$$

$$\xrightarrow{H^+} C_6H_5-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CO.O.COCH_3 \xrightarrow{-H_2O} C_6H_5-CH=CH.CO.O.COCH_3$$

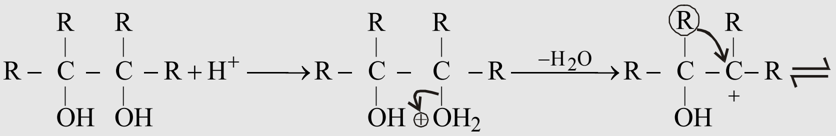
$$\xrightarrow{H_2O} \underset{\text{Cinnami acid}}{C_6H_5-CH=CH.COOH}+HO.COCH_3$$

35. Pinacol-Pinacolone Rearrangement : It is the conversion of pinacol to pinacolone by dehydration with hot dil. H_2SO_4

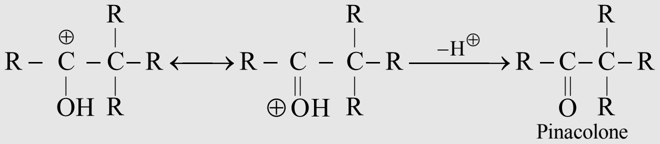


$$\underset{\text{Pinacol}}{R-\overset{\overset{R}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{\overset{R}{|}}{\underset{\underset{OH}{|}}{C}}-R} \xrightarrow{\text{dil. }H_2SO_4} \underset{\text{Pinacolone}}{R-\underset{\underset{O}{\|}}{C}-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}-R}$$

Mechanism :

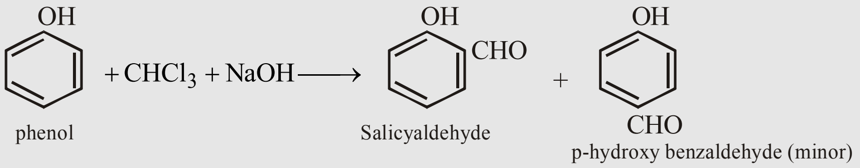


$$R-\overset{\overset{R}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{\overset{R}{|}}{\underset{\underset{OH}{|}}{C}}-R+H^+ \longrightarrow R-\overset{\overset{R}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{\overset{R}{|}}{\underset{\underset{\oplus OH_2}{|}}{C}}-R \xrightarrow{-H_2O} R-\overset{\overset{Ⓡ}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{\overset{R}{|}}{\underset{+}{C}}-R \rightleftharpoons$$

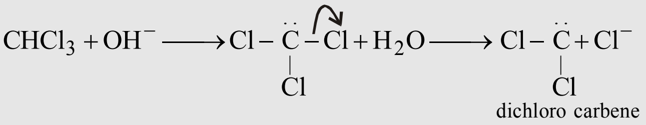


$$R-\underset{OH}{\overset{\oplus}{C}}-\underset{R}{\overset{R}{\underset{|}{\overset{|}{C}}}}-R \longleftrightarrow R-\underset{\oplus OH}{\overset{\|}{C}}\!\!\!\!\!-\underset{R}{\overset{R}{C}}-R \xrightarrow{-H^{\oplus}} R-\underset{O}{\overset{\|}{C}}\!\!\!\!\!-\underset{R}{\overset{R}{C}}-R$$

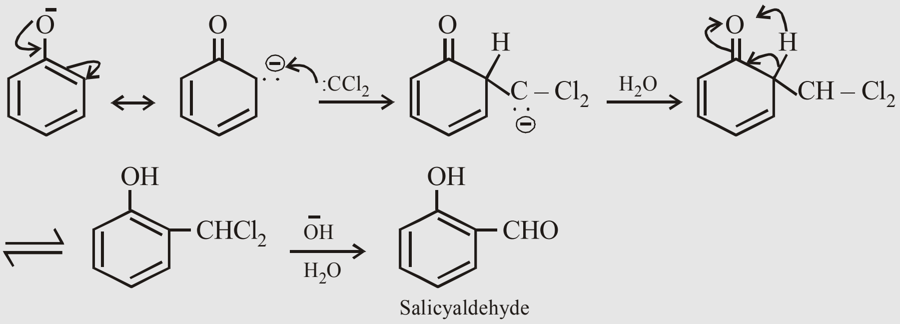
36. Reimer-Tiemann Reaction : Formylation with chloroform in presence of hydroxide ion e.g.



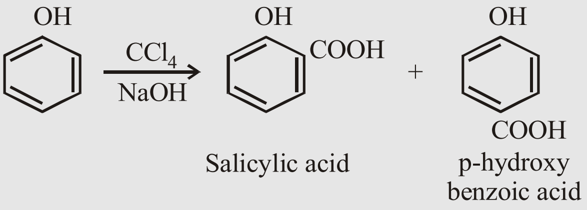
Mechanism:



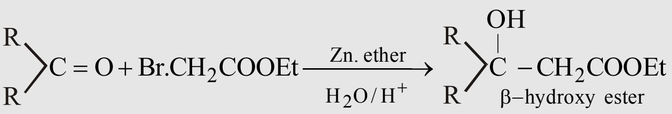
$$CHCl_3+OH^- \longrightarrow Cl-\underset{Cl}{\overset{..}{C}}-Cl+H_2O \longrightarrow Cl-\underset{Cl}{\overset{..}{C}}+Cl^-$$



Phenol with CCl_4 and NaOH gives salicylic acid (main product) and p-hydroxy benzoic acid (minor product)

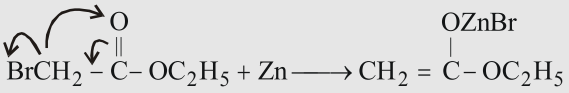


37. Reformatsky Reaction : It is the reaction between an α-bromoacid ester and a carbonyl compound (aldehyde or ketone) in the presence of Zn to form a β-hydroxy ester.



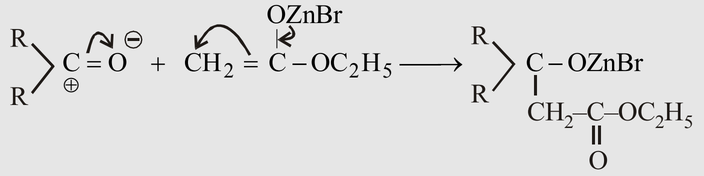
$$\begin{matrix}R\\R\end{matrix}\!\!>C=O+Br.CH_2COOEt \xrightarrow[H_2O/H^+]{Zn.\ ether} \begin{matrix}R\\R\end{matrix}\!\!>\overset{OH}{\overset{|}{C}}-CH_2COOEt$$

Mechanism :

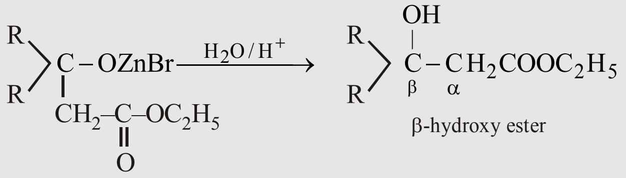


(i) $$BrCH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5+Zn\longrightarrow CH_2=\overset{OZnBr}{\overset{|}{C}}-OC_2H_5$$

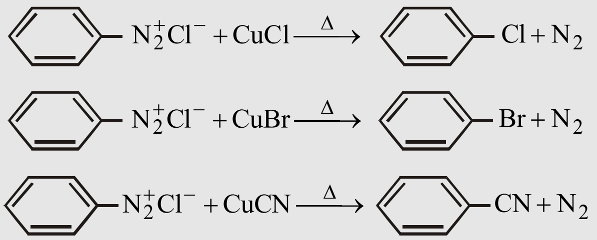
(ii)



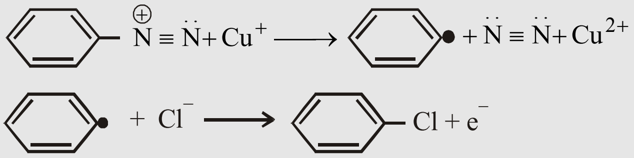
(iii) Acid hydrolysis



38. Sandmeyer Reaction : It is replacement of–N_2X by Cl, Br or CN by treating cold $ArN_2^+Cl^-$ solution with CuCl/HCl, CuBr/HBr or CuCN.



Mechanism

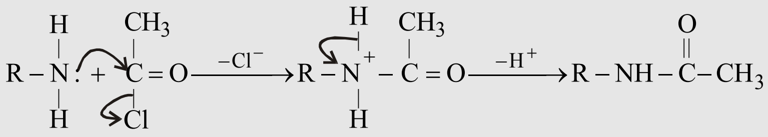


$$Cu^{2+} + e^- \longrightarrow Cu^+$$

39. Schotten Baumann Reaction : It is acylation of amines in presence of cold aqueous base (NaOH or Na_2CO_3)

$$RNH_2 + CH_3COCl + NaOH \xrightarrow{\text{Cold}} R-NHCOCH_3 + NaCl + H_2O$$

Mechanism :

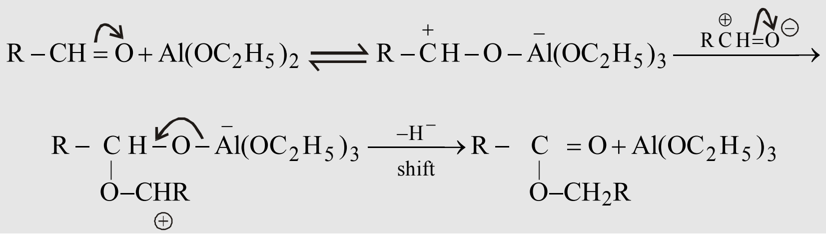


$$R-\underset{H}{\overset{H}{N}}: + \underset{Cl}{\overset{CH_3}{C}}=O \xrightarrow{-Cl^-} R-\underset{H}{\overset{H}{\overset{+}{N}}}-\overset{CH_3}{C}=O \xrightarrow{-H^+} R-NH-\overset{O}{\overset{\|}{C}}-CH_3$$

40. Tischenko reaction : All aldehydes can be made to undergo the Cannizzaro reaction by treatment with aluminium ethoxide. The acid and alcohol formed, combine to give ester e.g. acetaldehyde gives ethyl acetate.

$$2CH_3CHO \xrightarrow{Al(OC_2H_5)_3} CH_3COOC_2H_5$$

Mechanism :



$$R-CH=O + Al(OC_2H_5)_2 \rightleftharpoons R-\overset{+}{C}H-O-\overset{-}{Al}(OC_2H_5)_3 \xrightarrow{R\overset{\oplus}{C}H=O^{\ominus}}$$

$$R-\underset{\underset{\oplus}{O-CHR}}{CH}-O-\overset{-}{Al}(OC_2H_5)_3 \xrightarrow[\text{shift}]{-H^-} R-\underset{O-CH_2R}{C}=O+Al(OC_2H_5)_3$$

41. **Wurtz Reaction :** When an alkyl halide (preferably bromide and iodide) is heated with metallic sodium in dry ether, a paraffin is formed.

$$RI + 2Na + IR \xrightarrow[\text{dry ether}]{\text{Heat}} R - R + 2NaI$$

Mechanism:

(a) Intermediate formation of Organo metallic compound

$$C_2H_5I + 2Na \longrightarrow C_2H_5^{-}Na^{+} + Na^{+}I^{-}$$

$$C_2H_5I + Na^{+}C_2^{-}H_5 \longrightarrow C_2H_5.C_2H_5 + Na^{+}I^{-}$$

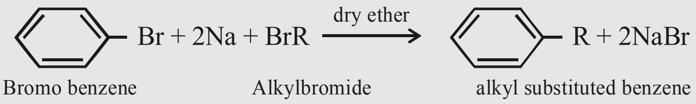
(b) Intermediate formation of free radicals

$$C_2H_5I + Na \longrightarrow Na^{+}I^{-} + \overset{\circ}{C}_2H_5$$

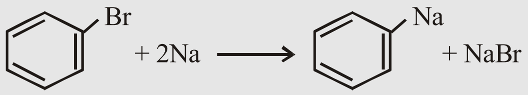
$$C_2H_5^{\circ} + \overset{\circ}{C}_2H_5 \longrightarrow C_2H_5 - C_2H_5 \text{ (Main reaction)}$$

$$\overset{\circ}{C}_2H_5 + \overset{\circ}{C}_2H_5 \longrightarrow C_2H_4 + C_2H_6 \text{ (Disproportionation)}$$

42. **Wurtz-Fittig Reaction :** It is coupling reaction between aryl halides and alkyl halides in presence of sodium and ether.

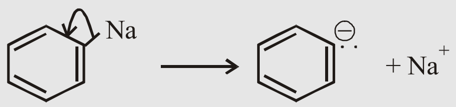


Mechanism:



$$R - Br + 2Na \longrightarrow RNa + NaBr$$

The C–Na bond is conic in nature



$$R - Na \longrightarrow R:^{-} + Na^{+}$$

Phenyl carbanion is stabilised by resonance and is strong nucleophile and displaces halogen of alkyl halide.