CHAPTER 1

Solid State

Chapter Analysis with respect to Last 3 Years' Board Exams

List of Topics	**2016**		**2017**		**2018**	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Classification of solids based on different binding forces: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids	(1, 1 mark)					
Unit cell in two-dimensional and three-dimensional lattices					(3 marks)	(3 marks)
Calculation of density of unit cell, packing in solids, packing efficiency, voids, number of atoms per unit cell in a cubic unit cell	(1 mark)	(3 marks)	(3 marks)	(2 marks)		
Point defects, electrical and magnetic properties.						
Band theory of metals, conductors, semiconductors and insulators and n & p type semiconductors	(3 marks)		(1 mark)			

Topic 1: Classification of Solids, Crystal Lattices and Unit Cells, Close Packed Structures

Summary

Substances which have a definite shape, mass and volume.

General Characteristics of solids:

- Very less intermolecular space and strong intermolecular force.
- The constituents particles (atoms, molecules or ions) can only oscillate about their mean position.
- High boiling and melting point.
- Solids have rigidity, low compressibility and high density.

Types of solid:

- Crystalline solid: Particles with definite shapes and made of huge number of small crystals arranged in order.
  - ➢ Molecular solid
    - Non-polar molecular solids
    - Polar molecular solids
    - Hydrogen bonded molecular solids
  - ➢ Covalent solid
  - ➢ Metallic solids
  - ➢ Ionic solids

Types of Crystalline Solid	Constituent particles	Bonding/ Attractive forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
• Molecular solids	Molecules					
➢ Non-polar		Dispersion or London forces	Ar, CCl_2, H_2, I_2, CO_2	Soft	Insulator	Very low
➢ Polar		Dipole-Dipole interaction	HCl, SO_2	Soft	Insulator	Low
➢ Hydrogen bonded		Hydrogen bonding	H_2O (ice	Hard	Insulator	Low
Ionic solids	Ions	Coulombic or Electrostatic	NaCl, MgO, Zns, CaF	Hard but brittle	Insulators in solid state but conductors in molten state and aqueous solutions	High
Metallic solids	Positive ions in a sea of delocalized electrons	Metallic bonding	Fe, Cu Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
Covalent or network solids	Atoms	Covalent bonding	SiO_2(quartz), SiC, C(diamond), AlN C_{Graphite}	Hard Soft	Insulators Conductor (exception)	Very high

- Amorphous solid: They lack ordered arrangement.

Properties of solid:

- Anisotropy: When the properties of a material vary with different direction in same crystal.
- Isotropy: When the properties of a material are the same in all directions.

Crystal lattice: The symmetrical three-dimensional arrangement of atoms in a crystal.

Unit cell: Smallest three-dimensional unit of crystal lattice.

Types of Unit Cell:

- Primitive unit cell
- Non- primitive unit cell

Types of Non- primitive unit cell:

- Face-centered: Particles at corners and at centre of all faces
- Body-centered: Particles at corners and at centre in the body
- End centered::Particles at corners and at centre of two opposite end faces.

System	Lengths and Angles	Number of Lattices
Cubic	$a = b = c$; $\alpha = \beta = \gamma = 90°$	3
Tetragonal	$a = b \neq c$; $\alpha = \beta = \gamma = 90°$	2
Orthorhombic	$a \neq b \neq c$; $\alpha = \beta = \gamma = 120°$	4
Rhombohedral	$a = b = c$; $\alpha = \beta = 90°, \gamma = 120°$	1
Monoclinic	$a \neq b \neq c$; $\alpha = \gamma = 90°, \neq \beta$	2
Triclinic	$a \neq b \neq c$; $\alpha \neq \gamma \neq \beta$	1
Hexagonal	$a = b \neq c$; $\alpha = \beta = 90°, \gamma = 120°$	1

Number of atoms in a unit cell:

- Simple cubic: Z = 1
- bcc: Z = 2
- fcc: Z = 4
- ecc: Z = 2

Closed packed structures:

- Close packing in one dimension: Spheres touch each other in a row.
- Close packing in two dimensions: Square close packing: each sphere is in touch with four other

Close packing in three dimensions:

- Cubic Close packed (ccp):In such packing, the spheres of molecules are adjacent to each other in a way that each row is a repetition of the previous row. Lattice of this cubic close packed is simple cubic and its unit cell is primitive cubic unit cell.
- Hexagonal Close packed (hcp):In such packing, the spheres of a row in a particular dimension fit into depressions between adjacent spheres of the previous row

Coordination number:

The number of spheres which are touching a particular sphere.Coordination number for hcp and ccp is 12 and for bcc it is 8.

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 1

1 Mark Questions

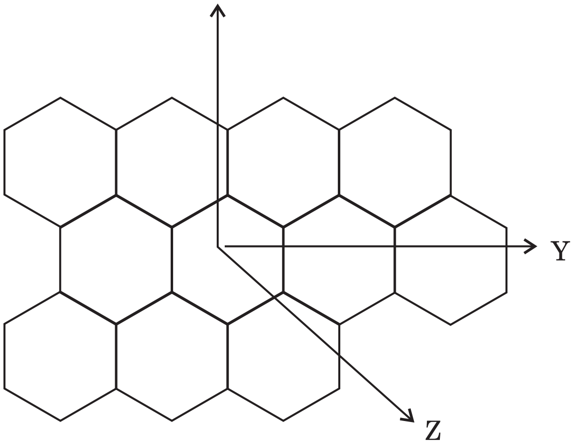
1. 'Crystalline solids are anisotropic in nature'. What does this statement mean? **[DELHI 2011]**
2. Write a point of distinction between a metallic solid and an ionic solid other than metallic luster. **[DELHI 2012]**
3. What type of inter molecular attractive interaction exists in the pair of methanol and acetone? **[DELHI 2014]**
4. What is the coordination number of each type of ions in a rock-salt type crystal structure? **[DELHI 2016]**
5. Give an example each of a molecular solid and an ionic solid. **[DELHI 2016]**
6. 'Crystalline solids are anisotropic in nature'. What does this statement mean? **[DELHI 2016]**
7. How do metallic and ionic substances differ in conducting electricity? **[DELHI 2017]**
8. Write a feature which will distinguish a metallic solid from an ionic solid.

3 Marks Questions

9. An element with molar mass $27\ g\ mol^{-1}$ forms a cubic unit cell with edge length 4.05×10^{-8} cm. If its density is $2.7\ g\ cm^{-3}$, what is the nature of the cubic unit cell? **[DELHI 2015]**

Solutions

1. Anisotropic means when properties of crystal is viewed from different x, y and z coordinates, it shows different properties. It means that some of the physical properties of crystalline solids such as refractive index, electrical conductivity, thermal expansion, etc. show different values when measured along different directions in the same crystal. **[1]**



Crystalline – Anisotropic nature –properties are different in all directions.

2. Metallic solids do not ionize in aqueous state but ionic solids ionize immediately.

   Metallic solids conducts electricity in its solid due to free electrons, where as ionic solids conduct electricity only in its molten or aqueous form due to free ions. **[1]**
3. Hydrogen bonding (intermolecular) **[1]**
4. 6 : 6 or 6 **[1]**
5. Molecular solids: Ice (H_2O) and Solid Ammonia
   Ionic solids: Sodium chloride ($NaCl$), Magnesium oxide (MgO) and Zinc Sulphide (ZnS) **[1]**
6. It means that some of the properties of crystalline solids such as refractive index, electrical conductivity, thermal expansion, optical properties etc. show different values when measured along different directions in the same crystal. **[1]**
7. Metallic substances are conductors in solid state as well as in molten state. Ionic substances are insulators in solid state as no free ions are available, but conductors in molten state and in aqueous solution due to free ions. **[1]**

8.

Metallic solids	Ionic solids
Metallic solids are conductors of electricity in solid state as well as in molten state. Metals are malleable and ductile	Ionic solids are insulators in solid state, but conductors in a molten state and in aqueous solutions. Ionic solids are hard and brittle.

[1]

9. Given, Molar mass of the given element,

$M = 27\,g\,mol^{-1} = 0.027 kg\,mol^{-1}$

Edge length, $a = 4.05 \times 10^{-8} cm = 4.05 \times 10^{-10} m$

[1]

Density, $d = 2.7\ g\ cm^{-3} = 2.7 \times 10^{3} kg\,m^{3}$

We know that $d = \dfrac{Z \times M}{a^3 \times N_A}$ **[1]**

Where, Z is the number of atoms in the unit cell and N_A is the Avogadro number.

Thus, $Z = \dfrac{d \times a^3 \times N_A}{M}$

$$Z = \frac{2.7 \times 10^3 \left(4.05 \times 10^{-10}\right)^3 \times 6.022 \times 10^{23}}{0.027}$$

$Z = 4$ *or* $Z \approx 4(f.c.c.)$ **[1]**

Since the number of atoms in the unit cell is 4, the given cubic unit cell has a face-centred cubic (fcc) or cubic-closed packed (ccp) structure.

Topic 2: Packing Efficiency, Calculations Involving Unit Cell Dimensions

Summary

Atomic radius:

Half the space between the nuclei of two identical neighboring atoms in its solid form.

Relationship between radius of atom (r) and unit cell edge length (a):

The following formulas show how the sphere (atom) radius, r, is related to the unit cell edge length, a:

Simple Cubic	**Body Centered Cubic**	**Face-Centered Cubic**
$a = 2r$	$a = \sqrt{\frac{16}{3}}r$	$a = \sqrt{8}r$

	Radius	Atoms/ unit cell	Packing density	# Neighbors
Simple cubic	$\frac{a}{2}$	1	$\frac{\pi}{6} = 52\%$	6
Body-centered cubic	$\frac{\sqrt{3}a}{4}$	2	$\frac{\pi\sqrt{3}}{8} = 68\%$	8
Face-centered cubic	$\frac{\sqrt{2}a}{4}$	4	$\frac{\pi\sqrt{2}}{6} = 74\%$	12
Diamond	$\frac{\sqrt{3}a}{8}$	8	$\frac{\pi\sqrt{3}}{16} = 34\%$	4

Voids:

The vacant space between the particles in a closed packed structure.

- Triangular voids: It is the two dimensional void.
- Tetrahedral voids: In cubic close packed structure, spheres of the second layer lie above the triangular voids of the first layer. The number of tetrahedral voids is two times the number of spheres.
- Octahedral voids: The vacant space formed by combining the triangular voids of the first layer and that of the second layer. The number of tetrahedral voids is same as the number of spheres.

Packing efficiency:

Packing efficiency is defined as the percentage of total space occupied by the particles packed inside the lattice.

$$\text{Packing efficiency of } hcp = \frac{\text{Volume occupied by four spheres in the unit cell}}{\text{Total volume of the unit cell } (a^3)} \times 100 = 74\%$$

$$\text{Packing efficiency of bcc} = \frac{\text{Volume occupied by two spheres in the unit cell}}{\text{Total volume of the unit cell } (a^3)} \times 100 = 68\%$$

$$\text{Packing efficiency of simple cubic lattice} = \frac{\text{Volume occupied by one spheres in the unit cell}}{\text{Total volume of the unit cell } (a^3)} \times 100 = 52.4\ \%$$

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 2

1 Mark Questions

1. How many atoms constitute one unit cell of a face-centered cubic crystal? **[DELHI 2013]**

2. Write the formula of a compound in which the element Y forms ccp lattice and atoms of X occupy 1/3rd of tetrahedral voids.

[ALL INDIA 2015]

2 Marks Questions

3. Explain how you can determine the atomic mass of an unknown metal if you know its mass density and the dimensions of unit cell of its crystal. **[DELHI 2011]**

4. Calculate the packing efficiency of a metal crystal for a simple cubic lattice.

[ALL INDIA 2011]

5. Aluminium crystalizes in an fcc structure. Atomic radius of the metal is 125pm. What is the length of the side of the unit cell of the metal? **[ALL INDIA 2013]**

6. An element with density 2.8 g cm^{-3} forms a f.c.c. unit cell with edge length 4 x 10^{-8} cm. Calculate the molar mass of the element.
(Given: N_A = 6.022 x 10^{23} mol^{-1})

[ALL INDIA 2014]

7. Calculate the number of unit cells in 8.1 g of aluminum if it crystallizes in a face-centered cubic (f.c.c.) structure. (Atomic mass of Al = 27 g mol^{-1}) **[ALL INDIA 2017]**

3 Marks Questions

8. Silver crystallizes in face-centered cubic unit cell. Each side of this unit cell has a length of 400 pm. Calculate the radius of the silver atom. (Assume the atoms just touch each other on the diagonal across the face of the unit cell. That is each face atom is touching the four corner atoms). **[DELHI 2011]**

9. The density of lead is 11.35 $g\ cm^{-3}$ and the metal crystallizes with fcc unit cell. Estimate the radius of lead atom. (Atomic mass of lead = 207 $g\ mol^{-1}$ and $N_A = 6.02 \times 10^{23}\ mol^{-1}$)

[DELHI 2011]

10. Tungsten crystallizes in body centered cubic unit cell. if the edge of the unit cell is 316.5 pm, what is the radius of tungsten atom?

[ALL INDIA 2012]

11. Iron has a body centred cubic unit cell with a cell dimension of 286.65 pm. The density of iron is 7.874 $g\ cm^{-3}$. Use this information to calculate Avogadro's number (At. Mass of Fe = 55.845 u) **[ALL INDIA 2012]**

12. An element crystallizes in a b.c.c. lattice with cell edge of 500pm. The density of the element is 7.5 $g\ cm^{-3}$. How many atoms are present in 300 g of the element? **[ALL INDIA 2016]**

13. Silver crystallizes with face- centered cubic unit cells. Each side of the unit cell has a length of 409 pm. What is the radius of an atom of silver? (Assume that each face atom is touching the four corner atoms.) **[DELHI 2017]**

14. An element '*X*' (Atomic mass = 40 $g\ mol^{-1}$) having FCC structure, has unit cell edge length of 400 pm. Calculate the density of '*X*' and the number of unit cells in 4g of '*X*'.
$\left(N_A = 6.022 \times 10^{23} mol^{-1}\right)$ **[ALL INDIA 2018]**

Solutions

1. **4 atoms** constitute one unit cell of a face centered cubic crystal. It can be determined from the number of atoms contributed from the faces and the corners of the unit cell as:

$(8 \text{ corners} \times \frac{1}{8} \text{ atom per corner} = 1 \text{ atom}) +$

$(6 \text{ faces} \times \frac{1}{2} \text{ atom per unit face} = 3 \text{ atoms})$

Total number of atoms per unit cell $= 1 + 3 = 4$

atoms. **[1]**

2. Y is present in CCP,

Let, the number of close packed spheres be N,

Then:

The number of octahedral voids generated = N

The number of tetrahedral voids generated = 2N

Number of atoms of Y= N $= \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$

X is present at $\frac{1}{3}$ of tetrahedral voids,

$$X = \frac{1}{3} \times 2N$$

$$\therefore X = \frac{1}{3} \times 8$$

Ratio of number of atoms $X : Y = \frac{8}{3} : 4 = 2 : 3$

So, Formula is $X : Y \; or \; X_2Y_3$ **[1]**

3. We can determine the atomic mass of an unknown metal by using the formula.

$M = \frac{d \times a^3 \times N_A}{Z}$ [1]

By knowing d, a, N_A & Z, We can calculate the M

Where, [1]

$d =$ density of the element

$N_A =$ Avogadro number

$a =$ cell edge or edge length

$Z =$ no. of atoms present in one unit

4. $\textit{Packing efficiency} = \frac{Z \times \text{Volume of one atom}}{\text{Volume of cubic unit cell}}$

$= \frac{1 \times \frac{4}{3}\pi r^3}{a^3}$ **[1]**

For simple cubic lattice, $a = 2r$

therefore, packing efficiency

$= \frac{1 \times \frac{4}{3}\pi r^3}{8r^3} = 0.524$ or 52.4% **[1]**

5. For F.C.C. **[1]**

$\sqrt{2}a = 4r$

$\sqrt{2}a = 4 \times 125\,\text{pm}$

$a = \frac{500}{\sqrt{2}} = 353.5\,\text{pm}$ **[1]**

6. We know $d = \frac{Z \times M}{a^3 \times N_A}$ **[1]**

$d = 2.8\ g/cm^3,\ Z = 4,\ a = 4 \times 10^{-8}\ cm$

$$2.8 = \frac{4 \times M}{\left(4 \times 10^{-8}\right)^3 \times 6.02 \times 10^{23}}$$

$2.8 = \frac{4 \times M}{4^3 \times 6.02 \times 10^{-1}}$ **[1]**

$M = 26.97$ g mol^{-1}

7. Moles of Al $= \frac{\text{Mass}}{\text{Molecular mass}}$ **[1]**

$n_{Al} = \frac{8.1}{27} = 0.3$ moles

We know that one unit of FCC,
No. of atoms = 4
4 - atoms are there in unit cell = 1
1 - atoms are there in unit cell $= \frac{1}{4}$ (1 mole)

1 mole atoms are found in unit cell $= \frac{N_A}{4}$

0.3 moles atoms are found in unit cell $= \frac{N_A}{4} \times 0.3 = 0.75 \times N_A$ **[1]**

$= 4.51 \times 10^{22}$ number of atoms

8. Given $a = 400\,pm,\ r = ?$ **[1]**

For FCC unit cell: $r = \frac{a}{2\sqrt{2}}$ **[1]**

$r = \frac{400}{2 \times 1.4142} = \frac{400}{2.828}$ **[1]**

$r = 141.4\,pm$

Hence, radius of the silver is 141.4 pm

9. Given: $d = 11.35\,g\,cm^{-3}$

According to the formula

$d = \frac{Z \times M}{a^3 \times N_A} \quad or \quad a^3 = \frac{Z \times M}{d \times N_A}$ **[1]**

For FCC lattice $Z = 4$

$a^3 = \frac{828}{68.327 \times 10^{23}} = 12.118 \times 10^{-23}$

$a^3 = 1.212 \times 10^{-22}\,cm^3$ **[1]**

$a = \sqrt[3]{1.212 \times 10^{-22}}\,cm^3$

For fcc unit cell

$r = \frac{a}{2\sqrt{2}}$

$r = \frac{495 \times 10^{-8}}{2 \times 1.414} = \frac{495 \times 10^{-8}}{2.828}$

Radius $r = 1.75 \times 10^{-10}\,cm = 175\,pm$ **[1]**

10. It is body centered cubic cell for which radius, $r = \frac{\sqrt{3}}{4}a$ **[1]**

$a = 316.5 pm$ (Given)

Radius $= \frac{\sqrt{3}}{4} \times 316.5 pm$ **[1]**

$= \frac{1.732}{4} \times 316.5 \ = 137.04 pm$ **[1]**

11. $a = \ 286.65 \ pm$ **[1]**

$= 286.65 \ \times 10^{-10} cm$

Density $(\rho) = 7.874 \ g \ cm^{-3}$

At mass of Fe $= 55.845 \ u$

$Z = 2$ (For body centric cubic unit cell)
Avogadro number $(N_A) = ?$

$$\rho = \frac{Z \times M}{a^3 \times N_A}$$ **[1]**

$$N_A = \frac{Z \times M}{a^3 \times d}$$

$$= \frac{2 \times 55.845}{\left[\left(286.65 \times 10^{-10}\right)^3 \times 7.874\right]} = \frac{111.69}{18.5} \times 10^{23}$$

$N_A = 6.037 \times 10^{23}$ **[1]**

12. Given, $a = 500 pm = 500 \ \times 10^{-10} cm$ **,** $Z = 2$**,**

$m = 300 \ g$

$m = \frac{M}{N_A}$ (M is molar mass)

Density, $d = \frac{ZM}{a^3 N_A}$ **[1]**

$$7.5 = \frac{2 \times M}{(500)^3 \times 10^{-30} \times 6.02 \times 10^{23}}$$

$$M = \frac{7.5 \times (500)^3 \times 10^{-30} \times 6.02 \times 10^{23}}{2}$$

$= 282.1 \ g/mol$ **[1]**

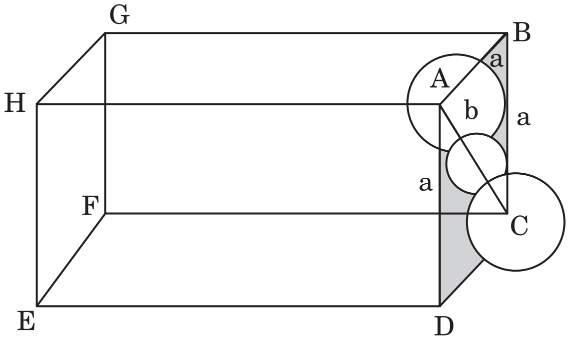
Molar mass, $M = \frac{Mass\,of\ compound \times N_A}{No.\,of\ atoms}$

$$282.1 = \frac{300 \times 6.02 \times 10^{23}}{No.\,of\ atoms}$$

No. of atoms $= 6.4 \ \times \ 10^{23}$

Therefore, the number of atoms present in 300g of compound is $6.4 \ \times \ 10^{23}$ **[1]**

13.



[1]

The relation between the edge length of the unit cell and the radius of the atom in a fcc lattice is given as:

$a = \frac{4r}{\sqrt{2}}$

where, a = edge length

$= \ 409 pm \ = \ 409 \ \times 10^{-12} m$ **[1]**

r = radius of the atom

$r = \frac{a\sqrt{2}}{4}$

$r = \frac{409 \times 10^{-12} \times 1.414}{2} = 289.2 \times 10^{-12}$ m **[1]**

14. We know $d = \frac{Z \times M}{N_A \times a^3}$ **[1]**

For FCC, Z is 4.

$$a = \frac{4 \times 40}{6.022 \times 10^{23} \times \left(400 \times 10^{-10}\right)^3} = 4.1514 \, gcm^{-3}$$

Volume of 4 gm X is $\frac{4}{4.1514} cm^3 = 0.96 \, cm^3$ **[1]**

Volume of 1 unit cell is

$= \left(400 \times 10^{-10}\right)^3 cm^3 = 64 \times 10^{-24} cm^3$

Number of unit cell $= \frac{0.96}{64 \times 10^{-24}} = 1.5 \times 10^{22}$ **[1]**

Topic 3: Imperfections in Solids, Electrical and Magnetic Properties

Summary

Defects in solids:

Points defects:

- ➢ Stoichiometric defects
  Vacancy defect: vacant lattice sites
  Interstitial defect
  Frenkel defect
  Schottky defect
- ➢ Impurity defects
- ➢ Non-stoichiometric defects

Metal excess defect

1. Metal excess defect due to anion vacancies
2. F-centers
3. Metal excess defect due to interstitial cation

Metal deficiency defect.

Types of solid based on its conductivity:

- Conductor
- Semi-conductor
- 13-15 compound
- 12-16 compound
- Doping
- N-type
- P-type
- Insulators

Classification on the basis of magnetic properties:

- Parametric: weakly attracted, unpaired electrons
- Diamagnetic: weakly repelled, paired electrons
- Ferromagnetic: All the domains in same direction
- Anti-Ferromagnetic: Equal and opposite domains
- Ferrimagnetic: Unequal domains

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 3

▶ 1 Mark Questions

1. Which stoichiometric defect in crystals decreases the density of a solid? **[DELHI 2011]**

2. What is meant by 'doping' in a semiconductor? **[ALL INDIA 2012]**

3. What type of stoichiometric defect is shown by AgCl? **[DELHI 2013]**

4. What type of substances would make better Permanent Magnets, Ferromagnetic or Ferrimagnetic? **[DELHI 2013]**

▶ 2 Marks Questions

5. (*a*) Why does presence of excess of lithium makes *LiCl* crystals pink?

(*b*) A solid with cubic crystal is made of two elements *P* and *Q*. Atoms of *Q* are at the corners of the cube and *P* at the body-centre. What is the formula of the compound?

[ALL INDIA 2013]

6. (*i*) Write the type of magnetism observed when the magnetic moments are aligned in parallel and anti-parallel directions in unequal numbers.

(*ii*) Which stoichiometric defect decreases the density of the crystal ?

[ALL INDIA 2014]

7. Examine the given defective crystal

A^+ B^- A^+ B^- A^+
B O B A^+ B
A^+ B A^+ O A^+
B A^+ B A^+ B

Answer the following questions:

(*i*) What type of stoichiometric defect is shown by crystal?

(*ii*) How is the density of the crystal affected by this defect?

(*iii*) What type of ionic substances show such defect? **[DELHI 2014]**

3 Marks Questions

8. Examine the given defective crystal:

X^+ Y^- X^+ Y^- X^+
Y^- X^+ Y^- X^+ Y^- X^+
X^+ Y^- X^+ e^- X^+
Y^- X^+ Y^- X^+ Y^-

Answer the following questions:

(*i*) Is the above defect stoichiometric or non-stoichiometric?

(*ii*) Write the term used for the electron occupied site.

(*iii*) Give an example of the compound which shows this type of defect. **[ALL INDIA 2012]**

9. What is a semiconductor? Describe the two main types of semiconductors and explain mechanisms for their conduction. **[DELHI 2016]**

Solutions

1. Schottky defect. (As Schottky defect is due to missing of cation and anion from its position.) **[1]**

2. Doping is the process of adding impurities into semiconductor to alter its electrical properties. **[1]**

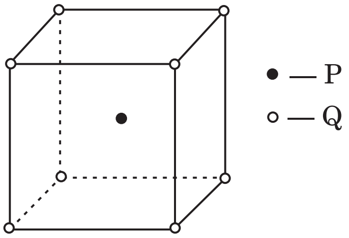
3. Frenkel defect is shown by *AgCl*. **[1]**

4. Ferromagnetic substance would make better permanent magnets than ferri-magnetic substances because in the first case, the spins due to all unpaired electrons are aligned parallel. On the other hand, in ferri-magnetic substances, the electron spins are aligned both in the parallel and antiparallel directions in unequal number, so when the ferromagnetic substance is placed in a magnetic field, all the domains get oriented in the direction of the magnetic field producing strong magnetic effect. This arrangement of domains persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet. **[1]**

5. (a) Presence of metal excess defect results due to presence of e– at the position of –ve ions this results in Formation of F-centre and *LiCl* become pink **[1]**

Excess Lithium atoms loses electron to form Li^+ ions, Cl^- ions from the crystal diffuse on the surface and combine with ionized Li to form LiCl. The released unpaired electrons occupy the anionic sites known as F-centres. The pink color is formed because of the excitation of these electrons when they absorb energy from visible light falling on them.

(b) **[1]**



Effective number of P atoms = 1

$$\text{Effective number of Q atoms} = \frac{1}{8} \times 8 = 1$$

Formula of compound is **PQ**

6. (i) Ferrimagnetism is observed when the magnetic moments are aligned in parallel and anti-parallel directions in unequal numbers. **[1]**

(ii) Due to Schottky defect vacancies are formed and density decreases **[1]**

Vacancy Defects: When some lattice sites left vacant during the formation of crystal, the defect is called vacancy defects. In vacancy defects, an atom is missing from its regular atomic site. Because of missing of atom the density of substance decreases, i.e., because of vacancy defects.

7. (i) Schottky defect, as equal number of cations and anions are missing. **[½]**

(ii) The density of the crystal decreases as ions are missing from crystal lattice. **[½]**

(iii) Highly ionic substances with almost comparable size of cation and anion show this defect, e.g. *KCl*. **[1]**

8. (i) Non-stoichiometric defect, because ratio of cation and anion changes after the formation of defect. **[1]**

(ii) F-centre, The site at which e– is present is called as F-centre or Farbe centre, which means colour because free e– absorb energy and transit to higher energy state that makes compound coloured. **[1]**

(iii) *NaCl*, when *NaCl* appears yellow on heating in the presence of Na vapours this defect is formed. **[1]**

9. The solids with intermediate conductivities between insulators and conductors are termed semiconductors. **[1]**

(i) n-type semiconductor: It is obtained by doping Si or Ge with a group 15 element like P. Out of 5 valence electrons, only 4 are involved in bond formation and the fifth electron is delocalized and can be easily provided to the conduction band. The conduction is thus mainly caused by the movement of electron. **[1]**

(ii) p-type semiconductor: It is obtained by doping Si or Ge with a group 13 element like Gallium which contains only 3 valence electrons. Due to missing of 4th valence electron, electron hole or electron vacancy is created The movement of these positively charged holes is responsible for the conduction. **[1]**

Smart Notes ....

Smart Notes ....

CHAPTER 2

Solutions

Chapter Analysis with respect to Last 3 Years' Board Exams

List of Topics	**2016**		**2017**		**2018**	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Types of solutions, expression of concentration of solutions of solids in liquids						
Solubility of gases in liquids, solid solutions	(2 marks)	(2 marks)				
Colligative properties - relative lowering of vapour pressure						
Raoult's law, elevation of boiling point, depression of freezing point, osmotic pressure	(3 marks)		(5 marks)	(5 marks)	(2 marks)	(2 marks)
Determination of molecular masses using colligative properties, abnormal molecular mass, van't Hoff factor	(3 marks)					

Topic 1: Types of Solutions, Expressing Concentration of Solutions and Solubility

Summary

- **Solution:** A homogeneous mixture of two (or more) substances.
- **Binary solution:** A solution consisting of two components. The component which is present in larger quantity is called **solvent** and the component which is small in quantity is called **solute.**

Solute	Solvent	Example
Gas	Gas	Air
Gas	Liquid	Aerated water
Gas	Solid	Hydrogen in palladium
Liquid	Liquid	Alcohol in water, benzene in toluene
Liquid	Solid	Mercury in zinc amalgam
Liquid	Gas	CO_2 dissolved in water
Solid	Liquid	Sugar in water, common salt in water
Solid	Gas	Smoke
Solid	Solid	Various alloys

Types of solutions:

- **Unsaturated solution:** A solution in which more solute can be dissolved without raising temperature.
  - **Saturated solution:** A solution in which no solute can be dissolved any more at a given temperature.
  - **Supersaturated solution:** A solution which contains more solute than that would be required to do saturation at a given temperature.
  - **Aqueous solution:** In this type of solution, water is present as solvent. For example, salt solution.
  - **Non-aqueous solution:** In this type of solution, there is another solvent apart from water. For example, iodine dissolved in alcohol.
- **Solubility:** The maximum amount of a solute that can be dissolved in a given amount of solvent at a given temperature.

  The solubility of a solute in a solvent depends upon the following:
  - Nature of the solute
  - Nature of the solvent
  - Temperature of the solution: If the dissolution process is endothermic, solubility of solid in liquid increases with increase in temperature, and in endothermic process, solubility decreases.
  - Pressure (in case of gases): Solubility of gases increase with increase in pressure but it has no effect on solids in liquids.

Methods of Expressing Concentration of Solutions:

- **Mass Percentage (W / w)**

$$\text{W/ w\%} = \frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 100$$

- **Percentage by volume (V / v%)**

$$\text{V/ v\%} = \frac{\text{Volume of solute}}{\text{Total volume of solution}} \times 100$$

- **Mass by volume percentage (*w/v*)**

$$\text{w / v\%} = \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

- **Mole fraction (x)**: It is defined as the ratio of the number of moles of a component to the total number of moles of all the components. For a binary solution, if the number of moles of A and B are n_A and n_B respectively, the mole fraction of A will be

$$\chi_A = \frac{n_A}{n_A + n_B}, \chi_B = \frac{n_B}{n_A + n_B}$$

- **Parts per million (ppm):** It is defined as the parts of a component per million parts of the solution.

$$\text{ppm} = \frac{\text{number of parts of the component}}{\text{total number of parts of all the components}} \times 10^6$$

It can be expressed in different ways like mass to mass, volume to volume and mass to volume.

$$\text{ppm}\left(\text{mass to mass}\right) = \frac{\text{Mass of a component}}{\text{Total mass of solution}} \times 10^6 \quad \text{ppm}\left(\text{volume to volume}\right) = \frac{\text{Volume of a component}}{\text{Total volume of solution}} \times 10^6$$

$$\text{ppm}\left(\text{mass to volume}\right) = \frac{\text{Mass of a component}}{\text{Volume of solution}} \times 10^6$$

- **Molarity (M):** It is the number of moles of solute present in 1L (dm^3) of the solution.

$$\text{M} = \frac{\text{Number of moles of solute}}{\text{Volume of solution}} = \frac{W_B \times 1000}{M_B \times V(\text{ml})}$$

- **Molality (m):** It is the number of moles of solute per kilogram of the solvent.

$$\text{m} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent}} = \frac{W_B \times 1000}{W \times W_A}$$

- **Normality (N):** The number of gram equivalents of solute present in 1 L of solution.

$$\text{Normality} = \frac{\text{Number of gram equivalent of solute}}{\text{Volume of solution in L}}$$

Number of gram equivalents of solute = $\frac{\text{Mass of solute in gram}}{\text{Equivalent weight}}$

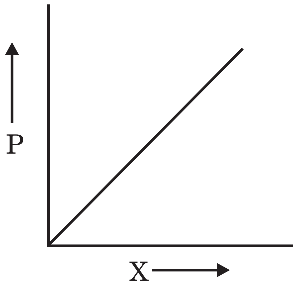
- **Relationship between Molarity and Molality:**

$$\text{m} = \frac{1000\text{M}}{\text{M} \times \text{M}_B - 1000\text{d}}$$

- **Henry's law**: The partial pressure of a gas in vapour phase (p) is proportional to the mole fraction of the gas (χ) in a solution. It is a special case of Raoult's law.

$\rho = K_H\chi$ **,** K_H is the Henry's constant

Higher the value of K_H, lower the solubility of gas in the liquid.



Slope of the line gives the value of K_H

- **Limitations of Henry's law:** This law is applicable only when
  The law does not apply for gases which undergo association or dissociation in the solution.
  This law is not applied for gases at high pressure and low temperature.
  The law does not apply for gases which undergo any chemical change.
- **Applications of Henry's law:**
  At high altitudes, low blood oxygen makes people weak and cause a problem called anoxia.
  Bottles of soft drinks are sealed under high pressure to increase the solubility of CO_2
  Scuba divers use air diluted with helium, nitrogen and oxygen to avoid toxic effects of nitrogen in blood.

PREVIOUS YEARS'
EXAMINATION QUESTIONS
TOPIC 1

▶ 1 Mark Questions

1. Give one example each of lyophobic sol and lyophilic sol. **[DELHI 2014]**

▶ 2 Mark Questions

[DELHI 2013]

2. State Henry's law. What is the effect of temperature on the solubility of a gas in a liquid. **[DELHI 2014]**
3. Define an ideal solution and write, one of its characteristics. **[DELHI 2014]**
4. State Henry's law correlating the pressure of a gas and its solubility in a solvent and mention two applications for the law. **[DELHI 2016]**
5. (i) Gas (A) is more soluble in water than Gas (B) at the same temperature. Which of the two gases will have the higher value of K_H (Henry's constant) and why?
   (ii) In non-ideal solution, what type of deviation shows the formation of maximum boiling azeotropes? **[ALL INDIA 2016]**

▶ 5 Mark Questions

6. (a) Differentiate between molality and molarity of a solution. How does a change in temperature influence their values?
   (b) Calculate the freezing point of an aqueous solution containing 10.50 g of $MgBr_2$ in 200 g of water. (Molar mass of $MgBr_2$ = 184 g) (K_f for water $= 1.86K\ kgmol^{-1}$)

   OR

   (a) Define the terms osmosis and osmotic pressure. Is the osmotic pressure of a solution a colligative property? Explain
   (b) Calculate the boiling point of a solution prepared by adding 15.00 g of NaCl to 250.0 g of water. (K_b for water $= 0.512K\ kgmol^{-1}$, Molar mass of $NaCl = 58.44g$)

   [DELHI 2011]
7. (a) State the following:
   1. Henry's law about partial pressure of a gas in a mixture.
   2. Raoult's law in its general form in reference to solutions.

   (b) A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr at 25°C. Assuming the gene fragment is non-electrolyte, find its molar mass.

OR

(a) Difference between molarity and molality in a solution. What is the effect of temperature change on molarity and molality in a solution?

(b) What would be the molar mass of a compound if 6.21 g of it is dissolved in 24.0g of chloroform to form a solution that has a boiling point of 68.04°C. The boiling point of pure chloroform is 61.7°C and the boiling point elevation constant, for chloroform is 3.63°C/m. **[DELHI 2011]**

8. (a) Define the following terms:

(i) Ideal solution

(ii) Azeotrope

(iii) Osmotic pressure

(b) A solution of glucose $\left(C_6H_{12}O_6\right)$ in water is labelled as 10% by weight. What would be the molality of the solution? (Molar mass of glucose $= 180\ g\ mol^{-1}$)

[ALL INDIA 2013]

9. (a) Define the following terms :

(i) Molarity

(ii) Molal elevation constant $\left(K_b\right)$

(b) A solution containing 15 g urea (molar mass = 60 $g\ mol^{-1}$) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 190 $g\ mol^{-1}$) in water. Calculate the mass of glucose present in one litre of its solution.

OR

(a) What type of deviation is shown by a mixture of ethanol and acetone? Give reason.

(b) A solution of glucose (molar mass = 180 $g\ mol^{-1}$) in water is labeled as 10% (by mass). What would be the molality and molarity of the solution? (Density of solution = 1.2 $g\ mL^{-1}$) **[DELHI 2015]**

10. (a) A 10% solution (by mass) of sucrose in water has a freezing point of 269.15 K.

Calculate the freezing point of 10% glucose in water if the freezing point of pure water is 273.15 K. Given: (Molar mass of sucrose = 342 $g\ mol^{-1}$)

(Molar mass of glucose = 180 $g\ mol^{-1}$)

(b) Define the following terms:

(i) Molality (m)

(ii) Abnormal molar mass

[ALL INDIA 2017]

Solutions

1. Lyophobic sol: Metal sol or metal sulphide. Lyophilic sol: Gum, Starch, gelatin. **[1]**

2. Henry's law states that "the partial pressure of the gas in vapour phase (p) is directly proportional to the mole fraction of gas (x) in the solution." **[1]**

$p = K_H x$ (K_H—Henry's law constant)

The solubility of a gas in liquid decreases with rise in temperature as dissolution of a gas in a liquid is an exothermic process. **[1]**

3. A solution which obeys Raoult's law at all temperatures and concentrations is called an ideal solution **[1]**

i.e. $P_A = P^o{}_A$ and $P_B = P^o{}_B$

Where, P = Total pressure and P_A, P_B, P_A^o, P_B^o and X_A, X_B are partial pressure, pressure of pure component and mole fraction of component A and B respectively.

Characteristics: In ideal solution, no volume change or enthalpy change takes place while mixing to form such a solution, **[1]**

i.e., $\Delta H_{mix} = 0\, and\, \Delta V_{mix} = 0$

4. Henry's law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas over the solution. [1]

Applications:

(i) To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure. **[½]**

(ii) Scuba divers must cope with high concentrations of dissolved nitrogen with breathing air at high pressure underwater. To avoid this air is diluted with He. **[½]**

(iii) At high altitudes, the partial pressure of oxygen is less than that at the ground level. Low blood oxygen causes hypoxia.

5. (i) As per Henry's law, the solubility of a gas is inversely related to the Henry's constant (K_H) for that gas. Hence gas (B) being less soluble, would have a higher K_H value. **[1]**

(ii) A maximum boiling azeotrope shows negative deviation from the Raoult's law.

[1]

6. (a) Molarity is the number of moles of solute dissolved in 1 litre of solution. It is temperature dependent. **[1]**

$$M = \frac{W \times 1000}{\text{Molecular mass} \times V}$$

Molality is the number of moles of solute dissolved per 1 kg of the solvent. It is temperature independent.

$$M = \frac{W \times 1000}{M_2 \times W}$$

Molality is independent of temperature, whereas molarity is a function of temperature because volume depends on temperature and mass does not. **[1]**

(b) Since $MgBr_2$ is an isotonic compound. Hence undergoes complete dissociation

	$MgBr_2 \longrightarrow$	Mg^{2+}	$+ 2Br^-$
Initial moles	1	0	0
After Dissociation	0	1	2

Total number of moles = 1 + 2 = 3 **[1]**

Thus, $i = \frac{3}{1} = 3$

Using the formula

$\Delta T_f = iK_f m$ $\qquad T_f^{\circ} - T_f = iK_f m$

$$0°C - T_f = 3 \times 1.86 \times \frac{10.50}{184} \times \frac{1000}{200}$$ **[1]**

$$-T_f = \frac{58590}{30800} = 1.59°C$$

$$T_f = -1.59°C \; or \; 271.41K$$ **[1]**

OR

(a) Osmosis is the phenomenon of flow of solvent through a semi-permeable membrane from the region of higher concentration to the region of lower concentration. **[1]**

The osmotic pressure of a solution is the excess pressure that must be applied to the solution to prevent the passage of solvent molecule through a semi-permeable membrane into the solution.

Yes, osmotic pressure is a colligative property as it depends only on the amount of solute present in the solution. **[1]**

(b) Initial moles after dissociation

$NaCl \longrightarrow$	Na^+	$+ Cl^-$
1	0	0
0	1	1

[1]

(Total no. of moles 1 + 2 = 2)

$\therefore \; i = \frac{2}{1} = 2$

We know that, **[1]**

$$\Delta T_b = iK_b m$$

$$T_b - T_b^{\circ} = 2 \times 0.512 \times \frac{15 \times 1000}{58.44 \times 250}$$

$$T_b - 373K = \frac{15360}{14610} = 1.05K$$

$$T_b = 1.05K + 373K$$

$$\therefore T_b = 374.05K$$ **[1]**

7. (a)

1. Henry's law states that the partial pressure of gas in vapour phase is directly proportional to its mole fraction in the solution **[1]**
2. Raoult's law states that for a solution with volatile components, the partial vapour pressure of each component present in the solution is proportional to its mole fraction in the solution. **[1]**

(b) Given: $w_2 = 8.95\,mg = 8.95 \times 10^{-3}\,g$ **[1]**

$V = 35\,mL$

$\pi = 0.335\,\text{torr}$

$T = 25°C = 298K$

$M_2 = ?$

Substituting all the values in the given formula

$\pi = CRT$ **[1]**

$$\pi = \frac{w_2 RT}{M_2 V}$$

$$\text{Or } M_2 = \frac{w_2 RT}{\pi V}$$

$$M_2 = \frac{8.95 \times 10^{-3} \times 0.0821 \times 298 \times 760}{0.335 \times 35}$$

So, Molar mass,

$$M_2 = 1.42 \times 10^4\,g\,mol^{-1}$$ **[1**]

OR

(a) Molarity is defined as the number of moles of solute present in 1 liter of solution, while molality is defined as the number of moles of solute present in 1 kg of solvent. **[1]**

Molality does not have any effect of change in temperature because mass does not change with temperature, whereas molarity changes with temperature. **[1]**

(b) Given: $w_2 = 6.21\,g$ **[1]**

$w_1 = 24\,g$

$K_b = 3.63°C/m$

$\Delta T_b = T_b - T_b° = 68.04 - 61.7 = 6.34°C$

$M_2 = ?$

From the formula,

$$M_2 = \frac{1000 \times K_b \times w_2}{\Delta T_b \times w_1}$$ **[1]**

$$= \frac{1000 \times 3.63 \times 6.21}{6.34 \times 24}$$

$$= 148.14\,g\,mol^{-1}$$

So, molar mass of the compound,

$M = 148.14\,g\,mol^{-1}$ **[1]**

8. (a)

(i) Ideal solution: Ideal solution is that solution which follows Raoult's law. In ideal solutions like force of attraction are equals to unlike force of attraction and therefore

(i) $\Delta H_{mixing} = 0$

(ii) $\Delta V_{mixing} = 0$

(iii) $\Delta S_{mixing} > 0$

(i) Azeotrope: At a particular conc. the mixture of two or more than two components boils at constant temp. Such mixture is called as azeotropic mixture. The components of the azeotropic mixture cannot be separated by distillation.

(ii) Osmotic pressure: When two solution (of same solvent) having different conc. are separated by semipermeable membrane the solvent particles moves from less conc. to more conc. It results in rising of liquid level on more conc. side so amount of external pressure required to be applied on more conc. side to stop the movement of solvent particles in called as osmotic pressure.

(b) $$\text{Molality} = \frac{\%\,by\,wt}{mol.mass} \times \frac{1000}{\left(100 - \%\frac{w}{w}\right)}$$

$$= \frac{10}{180} \times \frac{(1000)}{(100-10)}$$

$$= \frac{10}{180} \times \frac{1000}{90}$$

$$= 0.617\,m$$

9. (a)

(i) **Molarity (M):** Molarity can be defined as no. of moles of solute dissolved per litre of solution **[1]**

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

(ii) Molal elevation constant (K_b) : When 1 molal solution is prepared, the elevation in boiling point is called as molal boiling point elevation constant. **[1]**

(b) For isotonic solution:

$\pi_1 = \pi_2$ **[1]**

$C_1 = C_2$ {at same temp.}

or $n_1 = n_2$ (As volume is same)

$$\therefore \frac{15}{60} = \frac{x}{180}$$ **[1]**

$x = 45\,g$, mass of glucose per liter of solution. **[1]**

OR

(a) Ethanol and acetone shows positive deviation because both are non polar compounds and after mixing force of attraction decreases **[1]**

Like particle force of attraction > unlike particle force of attraction **[1]**

(b) $$\text{Molarity} = \frac{10}{180} \times \frac{1000}{180} = 0.66M$$ **[1]**

$$\text{Molality} = \frac{\%\,\text{mass}}{\text{mol. mass of solute}}$$

$$\text{Molality} = \frac{\%\,\text{mass}}{\text{mol. mass of solute}} \times \frac{100}{100 - \%\,\text{Mass}}$$

[1]

$$= \frac{10}{180} \times \frac{1000}{90}$$

$= 0.617m$ **[1]**

10. (a) For Sucrose:

$n = \frac{10}{342} = 0.0292\ mol$ **[1]**

$n = 0.292\ mol$

Now, $m = \frac{0.0292 \times 1000}{90}$

$= 0.3244$

We know that,

$K_f = \frac{\Delta T_f}{m} = \frac{4}{0.3244}$

$= 12.33$ kg/mol

Now for glucose,

$n = \frac{10}{180} = 0.055$ mol

Now, $m = \frac{0.055 \times 1000}{90}$

$= 0.6160$ mol/kg **[1]**

Again we know that,

$\Delta T_f = K_f \times m$

$= 12.33 \times 0.616 = 7.60$

$T_f = 273.15 - 7.60 = 265.55$ K

So, freezing point of 10% glucose in water is **265.55** K **[1]**

(b) (i) Molality is defined as the number of moles of solute per kilogram of solvent. The SI unit for molality is mol/kg. **[1]**

(ii) Abnormal molar masses for the solute which undergo association or dissociation. Observed value of colligative property is different from the calculated value of colligative property. **[1]**

OR

(a) Vapour pressure of water,

$p_1 = 23.8\ mm\ of\ Hg$

Weight of water = 846 *g*

Weight of urea = 30 *g*

Molecular weight of water

$(H_2O) = 1 \times 2 + 16 = 18\ g\ mol^{-1}$

Molecular weight of urea

$(NH_2CONH_2) = 2N + 4H + C + O$

$= 2 \times 14 + 4 \times 1 + 12 + 16$

$= 60$ g mol^{-1} **[1]**

Number of moles of water, $n_1 = \frac{846}{18} = 47$

Number of mole of urea, $n_2 = \frac{30}{60} = 0.5$ **[1]**

Now, we have to calculate vapour pressure of water in the solution. We take vapour pressure as $p_{1.}$

Use the formula of Raoult's law

$$\frac{(P_1^0 - P_1)}{P_1^0} = \frac{n_2}{(n_1 - n_2)}$$

Plug the values we get

$$\frac{(23.8 - P_1)}{23.8} = \frac{0.5}{(47 + 0.5)}$$

$$\frac{(23.8 - P_1)}{23.8} = 0.5106$$

After cross multiply

$23.8 - p_1 = 23.8 \times 0.5106$

Solving it, we get $p_1 = 11.6\ mm\ Hg$

So, Vapour pressure of water in the given solution $= 11.6\ mm\ of\ Hg$ **[1]**

(b) **Ideal Solution**: Obey Raoult's law at every range of concentration. Non-ideal Solution: Do not obey Raoult's law. **[1]**

Neither heat is evolved nor absorbed during dissolution of Ideal Solution for N$_m$ ideal solution.

$\Delta H_{mixing} > 0$ or < 0. **[1]**

Topic 2: Vapour Pressure of Liquid Solutions, Ideal and Non-ideal Solutions

Summary

- **Vapour Pressure:** Vapour pressure of a liquid solution is the amount of pressure that the vapours exert on the liquid solvent when they are in equilibrium and at a fixed temperature. It changes with the temperature of the surroundings and the nature of the liquid.
- **Raoult's Law:** The law states that the partial pressure is directly proportional to the mole fraction of the solute component. So, according to Raoult's Law, the partial pressure of A will be

  $$P_A \propto x_A$$

  $$P_A = P_A{}^0 x_A$$

  Where $P_A{}^0$ is the vapour pressure of pure liquid component A.

  Similarly partial pressure of B will be

  $$P_B \propto x_B$$

  $$P_B = P_B{}^0 x_B$$

  Where $P_B{}^0$ is the vapour pressure of pure liquid component B. The total pressure (P_{total}) of the solution placed in a container is the sum of partial pressures of its respective components. That is

  $$P_{total} = P_A + P_B$$

  $$P_{total} = P_A{}^0 x_a + P_B{}^0 x_B$$

- **Raoult's Law as a Special Case of Henry's Law:**

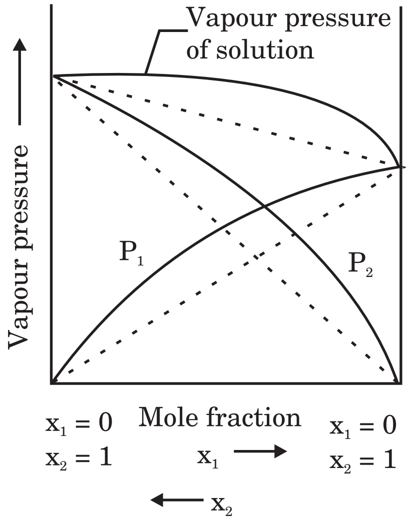
  According to Raoult's law, vapour pressure of volatile component is given by, $p_i = x_i p_i^o$

  According to Henry's law, the gaseous component is volatile that it exist as a gas and solubility depends on Henry's law:

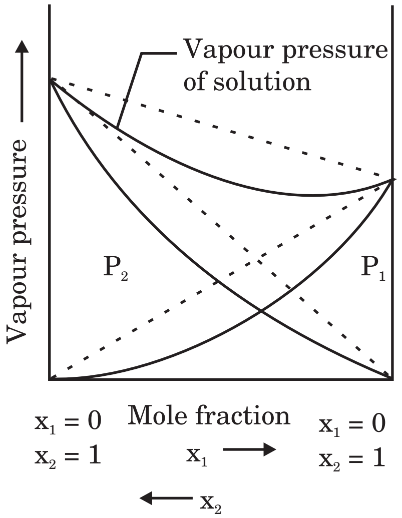
  $$p_A = K_H x_A$$

- **Positive and negative deviation from Raoult's law:**

  Positive deviation leads to increase in vapour pressure. In positive deviation, A-B interactions are weaker than interaction between B-B or A-B. Examples: Acetic acid and toluene, Methanol and chloroform, etc.



Negative deviation leads to decrease in vapour pressure. In negative deviation, A-A and B-B intermolecular forces are weaker than interaction between A-B. Examples: Chloroform and benzene, chloroform and methyl acetate, etc.



- **Ideal Solution:** These are the solutions which obey Raoult's law over the entire range of concentration.

  Two properties of Raoult's law:

  $\Delta_{mix}H = 0$ and $\Delta_{mix}V = 0$

  Examples of ideal solutions are: Ethyl bromide and ethyl chloride, benzene and toluene.
- **Non-ideal Solutions:** These solutions do not obey Raoult's law over the range of concentration.

  If the vapour pressure of such a solution is higher, then the solution exhibits positive deviation and if it is lower, then the solution exhibits negative deviation.
- **Azeotropes:** Binary mixtures which have same composition in liquid and vapour phase and boil at constant temperature are called azeotropes.
- **Minimum boiling azeotrope:** Solutions which show large positive deviation from Raoult's law. For example: Ethanol-water mixture.
- **Maximum boiling azeotrope:** Solutions which show large negative deviation from Raoult's law. For example: Nitric acid and water.

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 2

1 Mark Questions

1. Some liquids on mixing form 'azeotropes'. What are 'azeotropes'? **[DELHI 2014]**

2 Mark Questions

2. State the following:
   (i) Raoult's law in its general form in reference to solutions.
   (ii) Henry's law about partial pressure of a gas in a mixture. **[ALL INDIA 201]**
3. State Raoult's law for the solution containing volatile components. What is the similarity between Raoult's law and Henry's law? **[DELHI 2014]**
4. What is meant by positive deviations from Raoult's law? Give an example. What is the sign of $\Delta_{mix}H$ for positive deviation?

   OR

   Define azeotropes. What type of azeotrope is formed by positive deviation from Raoult's law? Give an example. **[DELHI 2015]**

5. Non-ideal solutions exhibit either positive or negative deviations from Raoult's law. What are these deviations and why are they caused? Explain with one example of each type.

▶ 3 Mark Questions

6. (a) In reference to Freundlich adsorption isotherm, write the expression for adsorption of gases on solids in the form of an equation.
   (b) Write an important characteristic of lyophilic sols.
   (c) Based on type of particles of dispersed phase, give one example each of associated colloid and multi molecular colloid.

[DELHI 2014]

7. A solution prepared by dissolving 1.25 g of oil of wintergreen (methyl salicylate) in 99.0 g of benzene has a boiling point of 80.31°C and K_b for benzene $= 2.53°C\ kg\ mol^{-1}$

▶ 5 Mark Questions

8. (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 $K\ kg\ mol^{-1}$)

[ALL INDIA 2013]

Solutions

1. Azeotropes are mixtures with fixed concentrations of components such that they boil at constant temperatures and distil out unchanged in their composition. e.g. :- A mixture of ethanol and water containing 95.4% of ethanol forms an azeotrope with boiling point 351.15 K. i.e.95% ethanol and 5% water by mass mixture. **[1]**

2. (i) Raoult's law states that for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction. **[1]**
   (ii) Henry's law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas over the solution. i.e. "The partial pressure of a gas in vapour phase (p) is proportional to the mole fraction of the gas (χ) in a solution." **[1]**

$$P \propto x$$

$$P = K_H x$$

where, K_H = Henry's law constant

3. Raoult's law states that the partial pressure of the vapour of a volatile component in a solution is directly proportional to its mole fraction in the solution. **[1]**

   Raoult's law is a special case of Henry's law. Both Henry's law and Raoult's law describe the relationship between a solution and its vapour that is in equilibrium with each other. **[1]**

4. Positive deviation from Raoult's law means that the observed vapour pressure is greater than expected, and it occurs when A — B attractions are weaker than the average of the attractions in the pure component of the mixture. For example: A mixture of ethanol and acetone shows a positive deviation from Raoult's law. **[1]**

   In case of solutions showing positive deviations, absorption of heat takes place;

   i.e., $\Delta_{mix}H$ has a positive (+) sign. **[1]**

OR

Azeotropes are the binary mixtures which have the same composition in liquid and vapour phases and boil at a constant temperature. **[1]**

A minimum-boiling azeotrope is formed by solutions showing a large positive deviation from Raoult's law at a specific composition. Example: $C_2H_5OH + H_2O$ **[1]**

(An ethanol-water mixture)

5. For non-ideal solutions, vapour pressure is either higher or lower than that predicted by Raoult's law. If it is higher the solution exhibits positive deviation and if it is lower it exhibits negative deviation from Raoult's law.

Positive Deviation	**Negative Deviation**
When solute – solvent interactions are weaker than solute – solute or solvent-solvent interactions, vapour pressure increases which result in positive deviation	When solute solvent interactions are stronger than solute – solute or solvent – solvent interactions, vapour pressure decreases which result in negative deviation.
Eg : Ethanol +Acetone. for a solution showing positive deviation $P_A > P^o{}_A\, X_A$ and $P_B > P^\circ{}_B X_B$	Eg: Chloroform + Acetone. for a solution showing negative deviation $P_A < P^o{}_A X_A$ and $P_B < P^0{}_B X_B$
ΔH_{mix} = positive and ΔV_{mix} = positive	ΔH_{mix} = negative and ΔV_{mix} = negative

[2]

6. (a) Expression for Freundlich adsorption isotherm- $\frac{x}{m} = K_p^{\frac{1}{n}}$ (Where n>1) **[1]**

Where, x = mass of the gas adsorbate
m = mass of the adsorbent (solid)
p = pressure of the gas
n and *k* are constants, which depend on the nature of the adsorbate and adsorbent. *n* is greater than 1.

(b) Lyophilic sols are stable and reversible in nature i.e., if two constituents of the sol are separated by any means (such as evaporation), then the sol can be prepared again by simply mixing the dispersion medium with the dispersion phase and shaking the mixture. **[1]**

(c) **Associated colloid**: Soap solution/ detergent solution

Multi molecular colloid: Sulphur sol/ Gold sol. **[1]**

7. Elevation of boiling point,

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1} \qquad \text{... (Eq. 1)}$$ **[1]**

Here solute is methyl salicylate and solvent is benzene, thus
W_2 = 1.25 g
W_1 = 99.0 g
Boiling point of solution (i.e. methyl salicylate in benzene), (T_b) = 80.31°C. Boiling point of pure solvent (benzene), (T_b) = 80.0°C
K_b = 2.53°C *kg mol*$^{-1}$

$$\Delta T = T_b - T_b^o = 80.31°C - 80.10°C = 0.21°C$$ **[1]**

From Eq. 1,

$$M_2 = \frac{K_b \times 1000 \times w_2}{\Delta T_b \times w_1}$$

$$M_2 = \frac{2.53 \times 10^3 °C\, g\, mol^{-1} \times 1000 \times 1.25\, g}{0.21°C \times 99.0\, g}$$

$$M_2 = 152.11 \times 10^3\ g\, mol^{-1}$$ **[1]**

8. (a) According to Raoult's law vapour pressure of a component is directly proportional to its mole fraction at a particular temperature **[1]**

$$P_A \propto x_A$$

$$P_A = P_A^o X_A$$

Similarly, $P_B = P_B^o X_B$

$$\therefore P_T = P_A^o X_A + P_B^o X_B$$

In Henry's law mole fraction of a gas at a particular temp. is proportional to the pressure exerted over gas **[1]**

$$P_{gas} = K_H X_{gas}$$

∴We can says for volatile substance it is a special case of Henry's law.

(b) $\Delta T_f = K_f m$

$$\Delta T_f = K_f \frac{w_B}{M_B} \times \frac{1000}{W_A}$$ **[1]**

$$0.40 = 5.12 \times \frac{1}{M_B} \times \frac{1000}{50}$$ **[1]**

$$M_B = \frac{512}{2} = 256\, g\, /\, mol$$ **[1]**

Topic 3: Colligative Properties, Determination of Molecular Mass and Abnormal Molar Mass

Summary

Colligative properties depend on the number of solute particles but do not depend on its chemical identity. When a non volatile solute is added to volatile solvent, vapour pressure decreases. The properties of such solutions are:

- **Relative lowering of vapour pressure of solvent:** A relation between vapour pressure of solution, mole fraction and vapour pressure of the solvent is as follows:

  $p_i = x_i p_i^o$

  Reduction in vapour pressure of solvent is given by:

  $\Delta p_i = \left(1 - x_i\right) p_i^o = x_j p_i^o$

  $$\frac{\Delta p_i}{p_i^o} = \frac{p_i^o - p_i}{p_i^o} = x_j$$

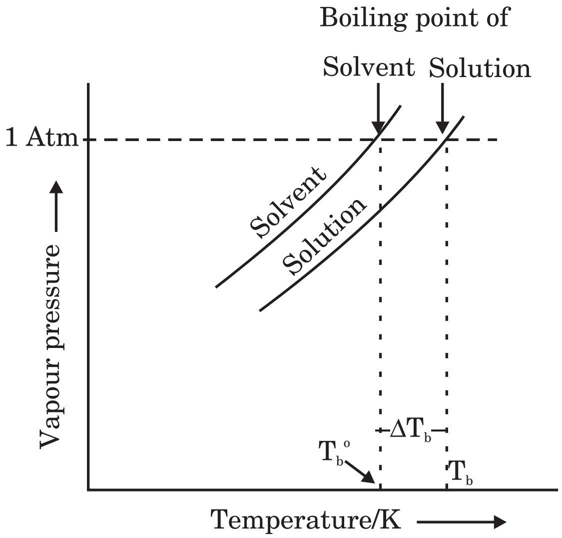
  This expression is called relative lowering of vapour pressure which equals mole fraction of the solute.

- **Elevation of boiling point:** Boiling point of a solution is always higher than the boiling point of the pure solvent. The elevation of boiling point depends on the number of solute molecules.

  The difference between the boiling point of solution and boiling point of pure solvent gives the elevation of boiling point.

  $\Delta T_b = T_b - T_b^o$

  For dilute solutions, $\Delta T_b = K_b m$, where K_b is called Boiling Point Elevation Constant, and m is molality.

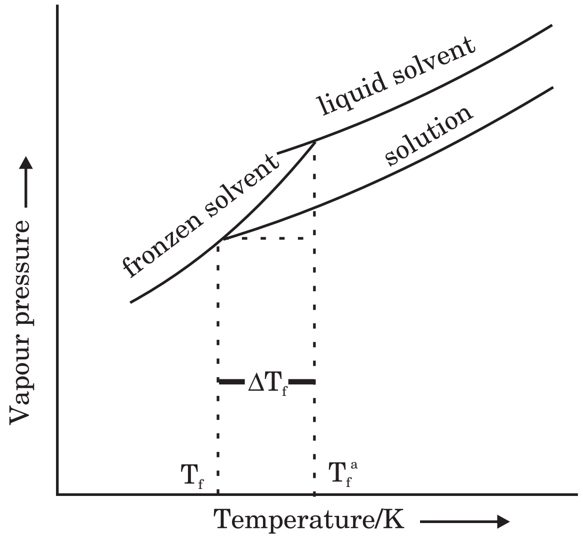


ΔT_b denotes elevation of boiling point of solvent

- **Depression of freezing point:** Lowering of vapour pressure causes depression of freezing point. The difference between the freezing point of pure solvent and freezing point of solvent when non volatile solute is dissolved in it gives the depression in freezing point.

  $\Delta T_f = T_f^o - T_f$

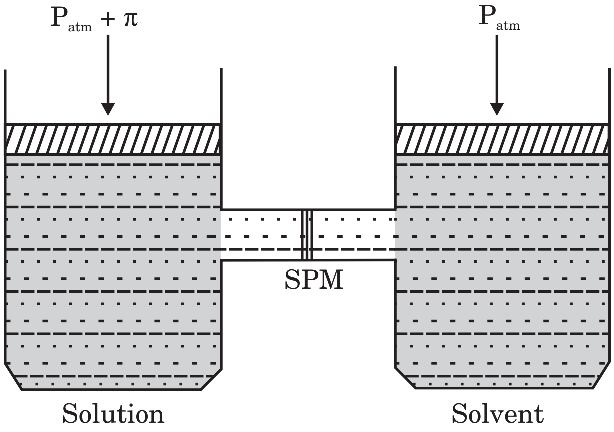
  For dilute solutions, $\Delta T_f = K_f m$, where K_f is the freezing point depression constant



- **Osmosis:** The flow of solvent molecules from pure solvent to solution is called osmosis. Some extra pressure applied which just stops the flow of solvent is called osmotic pressure.

  Osmotic pressure of solution

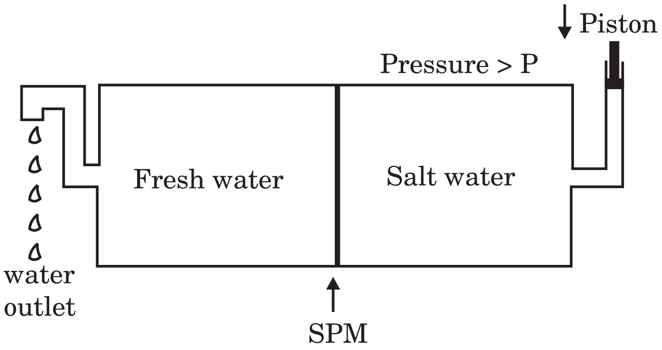
  $\pi = \frac{n}{VRT}$, where $\pi = CRT$ as the osmotic pressure



  Excess pressure is equal to the osmotic pressure

- **Isotonic solutions:** Any two solutions having same osmotic pressure are called isotonic solutions. No osmosis occurs between such solutions which are separated by semi permeable membrane.
- **Hypertonic and hypotonic solutions:** When cells shrink due to water flowing out of the cell due to more salt concentration, then the solution is called hypertonic solution. When water flows into the cell due to less salt concentration, then the solution is called hypotonic solution.

- **Reverse Osmosis:** Pressure larger than the osmotic pressure when applied on the solution side causes reverse osmosis. It is used for water purification.



- **Abnormal Molar Mass:** A molar mass higher or lower than the normal molar mass is called abnormal molar mass.
- **Van't Hoff factor:** The Van't Hoff factor is the ratio between the actual concentration of particles produced when the substance is dissolved, and the concentration of a substance as calculated from its mass.

$$i = \frac{\text{observed (experimental) value of a colligative property}}{\text{Normal (calculated) value of the same colligative property}}$$

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 3

1 Mark Questions

1. What are isotonic solutions? **[DELHI 2014]**
2. Out of $BaCl_2$ and KCl, which one is more effective in causing coagulation of a negatively charged colloidal sol? Give reason. **[DELHI 2015]**

2 Mark Questions

3. 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 trichloroacetic acid. (K_b for water = 0.512 $K\ kg\ mol^{-1}$)

   OR

   Define the following terms:
   1. Mole fraction
   2. Isotonic solutions
   3. Van't Hoff factor
   4. Ideal solution **[ALL INDIA 2012]**

4. Write the dispersed phase and dispersion medium of the following colloidal system?

   (i) Smoke (ii) Milk.

   OR

   What are lyophilic and lyophobic colloids? Which of these, sols can be easily coagulated on addition of small amounts of electrolytes?

   [DELHI 2013]

5. Calculate the mass of compound (molar mass = 256 g mol^{-1}) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K (K_f = 5.12 $K\ kg\ mol^{-1}$)

   [DELHI 2014]

6. Calculate the freezing point of a solution containing 60 g of glucose (Molar mass = 180 g mol^{-1}) in 250g of water. (K_f of water = 1.86 K kg/mol^{-1})

   [ALL INDIA 2018]

3 Mark Questions

7. Calculate the amount of KCl which must be added to 1kg of water so that the freezing point is depressed by 2K.

   [ALL INDIA 2011]

   (K_f for water = 1.86 K kg/mol^{-1})

8. Determine the osmotic pressure of a solution prepared by dissolving 2.5×10^{-2} g of K_2SO_4 in 2 L of water at 25°C, assuming that it is completely dissociated.

(R = 0.0821 $L\ atm\ K^{-1}$ mol^{-1}, Molar mass of K_2SO_4 = 174 g mol^{-1}) **[DELHI 2013]**

9. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the Van't Hoff factor and predict the nature of solute (associated or dissociated). (Given: Molar mass of benzoic acid = 122 g mol^{-1}, K_f for benzene $= 4.9\ K\ kg\ mol^{-1}$)

[DELHI 2015]

10. Vapour pressure of water at 20ºC is 17.5 mm Hg. Calculate the vapour pressure of water at 20ºC when 15 g of glucose (Molar mass = 180 g mol^{-1}) is dissolved in 150 g of water.

[ALL INDIA 2015]

11. Calculate the boiling point of solution when 4g of $MgSO_4$ (M = 120 g mol^{-1}) was dissolved in 100 g of water. Assuming $MgSO_4$ undergoes complete ionization. **[DELHI 2015]**

(K_b for water $= 0.52\ K\ kg\ mo1^{-1}$)

12. Calculate the temperature at which a solution containing 54 g of glucose, $\left(C_6H_{12}O_6\right)$, in 250 g of water will freeze. **[DELHI 2016]**

(K_f for water $=\ 1.86\ K\ mol^{-1}kg$)

13. Give reasons for the following:

(a) Measurement of osmotic pressure method is preferred for the determination of molar masses of macromolecules such as proteins and polymers

(b) Aquatic animals are more comfortable in cold water than warm water

(c) Elevation of boiling point of 1M KCl solution is nearly double than that of 1M sugar solution

[DELHI 2016]

5 Mark Questions

14. (a) Define the terms osmosis and osmotic pressure. Is the osmotic pressure of a solution a colligative property? Explain

(b) Calculate the boiling point of a solution prepared by adding 15.00 g of NaCl to 250.0 g of water. (K_b for water $= 0.512K\ kgmol^{-1}$,

Molar mass of $NaCl = 58.44g$)

[DELHI 2011]

15. (a) 30g of Urea (M = 60 $g\ mol^{-1}$) is dissolved in 846 g of water. Calculate the vapour pressure of water for this solution if vapour pressure of pure water at 298 K is 23.8 mm Hg.

(b) Write two difference between ideal solution and non-ideal solutions.

[All INDIA 2017]

16. (a) Define the following terms:

(i) Mole fraction

(ii) Van't Hoff factor

(b) 100 mg of a protein is dissolved in enough water to make 10.0 mL of a solution. If this solution has an osmotic pressure of 13.3 mmHg at 25°C, what is the molar mass of protein?

(R = 0.0821 $L\ atm\ mol^{-1}\ K^{-1}$ and 760 $mmHg$ = 1 atm)

OR

a. What is meant by:

i. Colligative properties

ii. Molality of a solution

b. What concentration of nitrogen should be present in a glass of water at room temperature? Assume a temperature of 25°C, a total pressure of 1 atmosphere and mole fraction of nitrogen in air of 0.78.

[K_H for nitrogen = 8.42×10^{-7} M/mm Hg]

[DELHI 2017]

Solutions

1. Two or more solutions having same osmotic pressure are called isotonic solutions, e.g. 0.5 M NaCl, 0.5 M KCl and 1M glucose are isotonic.

[1]

2. According to the Hardy-Schulze rule, greater the valency of a flocculating ion, the greater is its power to cause precipitation. Between Ba^{2+} (from $BaCl_2$) and K^+ (from KCl), Ba^{2+} has greater valency. Therefore, $BaCl_2$ will be more effective in causing the coagulation of a negatively charged colloidal sol. **[1]**

3. Given:

$$\Delta T_b = 373.18 - 373 = 0.18K$$

$$K_b = 0.512\,K\,kg\,mol^{-1}$$

$$m = 1$$

$$\Delta T_b = iK_bm$$ **[1]**

$$i = \frac{\Delta T_b}{K_b m} = \frac{0.18}{0.512 \times 1}$$

$i = 0.35$ **[1]**

OR

1. Ratio of the number of moles of a component in a mixture to the total number of moles in the mixture is called the mole fraction of that component. It is denoted by *x*. **[½]**
2. Two solutions having the same molar concentration are said to be isotonic solutions, eg: All intravenous injections must be isotonic with body fluids. **[½]**
3. The ratio of observed colligative property to the calculated colligative property is called the Van't Hoff factor. It is denoted by Y. **[½]**
4. Solutions that follow Raoult's law at all temperatures and concentrations are called ideal solutions. **[½]**

4. *(i)* Dispersed phase in smoke: Solid, dispersion medium in smoke: Gas **[1]**

(ii) Dispersed phase in milk: Fats (liquid), dispersion medium in milk: Water (liquid) **[1]**

OR

Lyophilic colloids (Liquid Loving): These are the colloidal solutions in which dispersed phase has great affinity for dispersion medium. Such solutions are quite stable and are reversible in nature. E.g. starch, proteins, etc. **[1]**

Lyophobic Colloids (Liquid Hating): These are the colloidal solutions in which dispersed phase has very little affinity for the dispersion medium. Such solutions are unstable and are irreversible in nature. **[1]**

Eg. (As_2S_3 Sol).

Lyophobic colloids can be easily coagulated because on addition of small amount of electrolyte, the charge on colloidal particles is removed, as a result the particles will come closer to each other and then aggregate to form a cluster which settle down under the force of gravity.

5. Given,

$M_B = 256 g\, mol^{-1}, W_A = 75 g,$

$K_f = 5.12 kg\, mol^{-1}, \Delta T_f = 0.48K$

From the formula, $\Delta T_f = K_f \times \frac{W_B}{M_B} \times \frac{1000}{W_A}$ **[1]**

Mass of solute, $W_B = \frac{\Delta T_f \times M_B \times W_A}{K_f \times 1000}$

$$= \frac{0.48 \times 256 \times 75}{5.12 \times 1000}$$

$$= \frac{(0.48K)(256\, g\, mol^{-1})(0.075\, Kg)}{(5.12\, K\, Kg\, mol^{-1})} = 1.8\, g$$ **[1]**

6. We know $\Delta T_f = k_f \times m$

$m = \frac{60/180\, mol}{0.25\, kg} = 1.33\, mol\, kg^{-1}$ **[1]**

$\Delta T_f = 1.86 \times 1.33K$

$\Rightarrow \Delta T_f = 2.4738K$

$\Rightarrow T_f^o - T_f = 2.4738K$

$\Rightarrow T_f = T_f^o - 2.4738K$

$= 273 - 2.4738K$

$= 270.5262K$ **[1]**

7. Given, $K_f = 1.86\, K\, mol^{-1}$

$i = 2, \Delta T_f = 2K$

$M = 74.5$

$\Delta T_f = iK_f M$ **[1]**

$2 = \frac{2 \times 1.86 \times \text{Mass of KCl}}{74.5}$ **[1]**

Mass of KCl $= \frac{74.5}{1.86} = 40.05\, gm$ **[1]**

8. We know

$\pi = iCRT \Rightarrow \pi = \frac{inRT}{V} \Rightarrow \pi = i \times \frac{w}{M} \times \frac{1}{V} RT$ **[1]**

Given, $w = 2.5 \times 10^{-2}, g = 0.025g$

$V = 2L, T = 25°C = 298K$

$M = K_2SO_4 = 2 \times 39 + 32 + 4 \times 16 = 174\, g\, mol^{-1}$

[1]

K_2SO_4 dissociates completely as

$$K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$$

Ions produced $= 3$ i.e., $i = 3$

Hence, $\pi = \frac{3 \times 0.025 g}{174 g\, mol^{-1}} \times \frac{1}{2L} \times 0.0821 \times 298K$

$\pi = 5.27 \times 10^{-3}$ **atm** **[1]**

9. Given: Mass of solute (W_B)
i.e., $C_6H_5COOH = 3.9\, g$

Mass of solvent $(W_A) = 49\, g = \frac{49}{1000} Kg$

Molar mass of $C_6H_5COOH (M_S) = 122\, g/mol$

$K_f = 4.9\, K\, Kg\ mol^{-1}$

$\Delta T_f = 1.62K$

To find: Vant Hoff factor $(i = ?)$

We know that the depression in freezing point is given by: **[1]**

$\Delta T_f = i \times K_f \times m$

$$\Delta T_f = i \times K_f \times \frac{W_B}{M_S} \times \frac{1}{W_A (Kg)}$$

$$i = \frac{\Delta T_f \times M_S \times W_A (Kg)}{K_f \times W_B}$$

$$i = \frac{1.62 \times 122 \times 49}{4.9 \times 3.9 \times 1000}$$ **[1]**

$i = 0.5067$

Since, $i < 1$, hence solute benzoic acid (C_6H_5COOH) will undergo association in benzene **[1]**

10. $\frac{p^o - p}{p^o} = \frac{w_b \times M_A}{M_b \times w_A}$ **[1]**

Here $w_b = 15\, g$(glucose)

$M_A = 15g(water)$

$M_b = 150$(glucose)

$w_A = 150(water)$

$$\frac{17.5 - p}{17.5} = \frac{15 \times 18}{180 \times 150}$$ **[1]**

$17.5P = 17.5 \times 0.01$

$P = 17.325\, mmHg$ **[1]**

11. Given:

$K_b = 0.52K\ kg\ mol^{-1}$

Mass of solute, $MgSO_4 = 4\, g$

Mass of solvent, water $= 100\, g$

So, Molarity of solution, $m = \frac{4}{120} \times \frac{1000}{100}$ **[1]**

$m = 0.33\, mol / L$

Also, $MgSO_4$ undergoes complete isolation, thereby yielding 2 moles of constituent ions for every mole of $MgSO_4$ **[1]**

Therefore, $i = 2$

Now, **elevation in boiling point** is given as,

$\Delta T_b = iK_b m$

$= 2 \times 0.52 \times 0.33 = 0.34$

$T_b = 373.15 + 0.34 = 373.49K$

Therefore, the **new boiling point of the solution is** $373.49\, K$. **[1]**

12. $\Delta T_f = K_f m$

No. of moles of glucose $= \frac{54 g}{180\, g\, mol^{-1}}$ **[1]**

Molarity of Glucose solution

$= \frac{54}{180} mol^{-1} \times \frac{1000}{250\, kg} = 1.20\, mol\, kg^{-1}$

$\Delta T_f = K_f m$

$= 1.86\, K\, kgmol^{-1} \times 1.20\, mol\, kg^{-1} = 2.23\, K$ **[1]**

Temperature at which solutions freezes

$= 273.15 - 223\, K$

$= 270.77$ K or $2.23°C$

or $(273.000 - 2.23)\, K$

$= 270.7$ K **[1]**

13. (a) Measurement of osmotic pressure method is preferred for the determination of molar masses of macromolecules such as proteins and polymers because: **[1]**

1. Osmotic pressure can be measured at room temperature whereas other colligative properties need either high temp or low temp conditions.
2. Most of the macromolecules get denatured in high temp so this can be avoided.
3. Values of other colligative properties are so small that a small error can account to large difference.

(b) Aquatic animals are more comfortable in cold water than warm water because the amount of dissolved oxygen in water decreases with rise in the water's temperature. Cold water has more dissolved oxygen per unit area than warm water **[1]**

(c) Elevation of boiling point of 1M KCl solution is nearly double than that of 1M sugar solution because KCl gets dissociated completely into K^+ and Cl^- ions and as the number of particles get doubled, the colligative properties get doubled. Therefore KCl have double the boiling point of that of sugar solution **[1]**

14. (a) Osmosis is the phenomenon of flow of solvent through a semi-permeable membrane from the region of higher concentration to the region of lower concentration.

The osmotic pressure of a solution is the excess pressure that must be applied to the solution to prevent the passage of solvent molecule through a semi-permeable membrane into the solution.

Yes, osmotic pressure is a colligative property as it depends only on the amount of solute present in the solution.

(b) Initial moles after dissociation we know that,

$$\begin{array}{ccc} NaCl \longrightarrow & Na^+ & + Cl^- \\ 1 & 0 & 0 \\ 0 & 1 & 1 \end{array}$$

(Total no. of moles 1 + 2 = 2)

$$\therefore\ i = \frac{2}{1} = 2$$

Initial moles after dissociation we know that,

$$\Delta T_b = iK_b m$$

$$T_b - T_b{}^\circ = 2 \times 0.512 \times \frac{15 \times 1000}{58.44 \times 250}$$

$$T_b - 373K = \frac{15360}{14610} = 1.05K$$

$$T_b = 1.05K + 373K$$

$$\therefore T_b = 374.05K$$

15. (a) Vapour pressure of water,

$p_1 =\ 23.8\ mm\ of\ Hg$

Weight of water = 846 g

Weight of urea = 30 g

Molecular weight of water

(H_2O) $= 1 \times 2 + 16 = 18\ g\ mol^{-1}$

Molecular weight of urea

$(NH_2CONH_2) = 2N + 4H + C + O$

$= 2 \times 14 + 4 \times 1 + 12 + 16$

$= 60\ \text{g mol}^{-1}$

Number of moles of water, $n_1 = \dfrac{846}{18} = 47$

Number of mole of urea, $n_2 = \dfrac{30}{60} = 0.5$

Now, we have to calculate vapour pressure of water in the solution. We take vapour pressure as $p_{1.}$

Use the formula of Raoult's law

$$\frac{\left(P_1{}^0 - P_1\right)}{P_1{}^0} = \frac{n_2}{\left(n_1 - n_2\right)}$$

Plug the values we get

$$\frac{\left(23.8 - P_1\right)}{23.8} = \frac{0.5}{\left(47 + 0.5\right)}$$

$$\frac{\left(23.8 - P_1\right)}{23.8} = 0.5106$$

After cross multiply

$23.8\ -\ p_1 =\ 23.8\ \times\ 0.5106$

Solving it, we get $p_1 =\ 11.6\ mm\ Hg$

So, Vapour pressure of water in the given solution $=\ 11.6\ mm\ of\ Hg$

(b) **Ideal Solution**: Obey Raoult's law at every range of concentration. Non-ideal Solution: Do not obey Raoult's law. $\Delta H_{\textbf{mixing}} < 0$

Neither heat is evolved nor absorbed during dissolution.

$\Delta H_{\text{mixing}} > 0$

Endothermic dissolution; heat is absorbed.

16. (a)

(i) Mole fraction of a component is the ratio of number of moles of the component to the total number of moles of all the components. **[1]**

(ii) Van't Hoff factor is the ratio of normal molar mass to the abnormal molar mass. Van't Hoff factor is the ratio of observed value of colligative property to calculated value of colligative property assuming no association or dissociation. **[1]**

(b) Mass of protein = 100 mg = 0.1 g **[1]**

$V = 10\ ml$

$$\pi = 13.3\,mm = \frac{13.3}{760}\ \text{atm}$$

$$\pi V = nRT$$

Number of moles, $n = \frac{0.1}{M}$ **[1]**

$$\frac{13.3}{760} \times 0.01 = \frac{0.1}{M} \times 0.0821 \times 298$$

$M = 13980\ g = 13.98\ kg$

Molar mass of protein = 13.98 kg **[1]**

OR

(a) (i) All the properties which depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution are known as colligative properties. **[1]**

(ii) Molality of solution is the number of moles of solute present in 1 kilogram of solvent. **[1]**

(b) $\rho_{N_2} = \chi_{N_2} \times \rho_{total}$

$= 0.78 \times 760\ mm\ Hg$ **[1]**

$= 592.8\ mm\ Hg$

$K_H = 8.42 \times 10^{-7}\ M/mmHg$

$\chi_{N_2} = ?$

$\chi_{N_2} = K_H \times \rho_{N_2}$ **[1]**

[Since K_H is given in M/mmHg therefore this formula is used]

$\chi_{N_2} = 8.42 \times 10^{-7} \times 592.8$

$\chi_{N_2} = 4.991 \times 10^{-10}$ **[1]**

Smart Notes ....

Smart Notes ....

CHAPTER 3

Electrochemistry

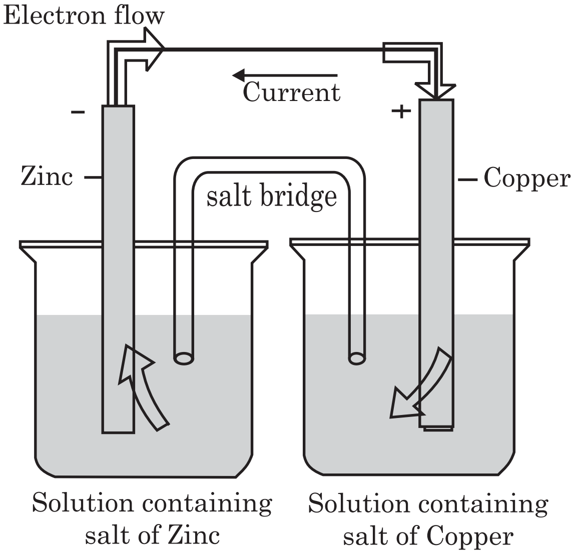
Chapter Analysis with respect to Last 3 Years' Board Exams

List of Topics	**2016**		**2017**		**2018**	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Redox reactions, conductance in electrolytic solutions			(2 marks)	(2 marks)		
Specific and molar conductivity, variations of conductivity with concentration	(3 marks)	(3 marks)				
Kohlrausch's Law, electrolysis and law of electrolysis (elementary idea)	(2 marks)					
Dry cell -electrolytic cells and Galvanic cells, lead accumulator						
EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells	(3 marks)	(2 marks)	(3 marks)	(3 marks)	(5 marks)	(5 marks)
Relation between Gibbs energy change and emf of a cell						
Fuel cells, corrosion						

Topic 1: Electrochemical Cells, Galvanic cells and Nernst Equation

Summary

- Electrolytic conduction: The conduction of an electrical current by the movement of ions.
- Electrolyte: A substance that dissociates into ions in solution and hence conducts electricity.
- Degree of ionization: The ratio of the number of ions of a solute to the total number of molecules of that solute in a solution.
- Specific resistivity: It is the resistance offered by a material or solution occupying one cm^3 volume.
- Specific conductance or conductivity (κ): It is the conductance of a material between two electrodes of cross sectional area 1 cm^2, separated by 1 cm distance.
- Electrochemical cell: It is a device that generates a potential difference between electrodes using redox reactions.
- Galvanic cell or voltaic cell: The Galvanic Cell is a device which transforms chemical energy into electric energy.
- Daniel cell: A galvanic cell in which one electrode is Zn plate in $ZnSO_4$ (or Zn^{++} ion) solution and the other is Cu plate in $CuSO_4$ (or Cu^{++} ion) solution. Following diagram shows a Daniel cell:



- Salt Bridge: A salt bridge is a combination of two noncovalent interactions i.e. electrostatic interactions and hydrogen bonding. Since, noncovalent interactions are weak interactions, formation of salt bridges provide an additional level of stabilizing interactions that can add important contribution to the overall stability of a molecule.
- Standard electrode potential (E°): It is defined by measuring the potential relative to a standard hydrogen electrode using 1 mol solution at 25 °C and 1 bar pressure.
- Emf of a cell can also be defined as the work done or required for transforming a unit positive charge from negative to positive terminal within the cell.

$$E_{cell} = E_{cathode} - E_{anode}$$

- The standard reduction potentials of a number of electrodes are measured using standard hydrogen electrode as the reference electrode. These various electrodes can be arranged in increasing order of their reduction potentials which is called electrochemical series.

Application of electrochemical series:

- Calculation of the standard EMF of the cell
- Predicting the feasibility of a redox reaction
- Comparison of the reactivities of metals.

Debye-Huckel-Onsagar equation:

It is for a strong electrolyte

$$\Lambda = \Lambda^0 - AC^{\frac{1}{2}}$$

$\Lambda =$ Equivalent conductivity at given concentration.
$\Lambda^0 =$ Equivalent conductivity at infinite dilution.
$C =$ Concentration
and A is a constant

- Redox reaction: When both reduction and oxidation reactions go side-by-side, it is known as a redox reaction.
- Redox couple: It is defined as having together the oxidized and reduced form of a substance taking part in and oxidation or reduction half reaction.

Nernst Equation:

It is used when the concentration of species in the electrode reaction is not equal to 1M.

$$aA + bB \xrightarrow{ne^-} mM + nN$$

The Nernst equation at 298 K can be written as

$$E_{cell} = E^0{}_{cell} - \frac{0.059}{n} \log \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

- Gibb's Energy:

$$\Delta G^0 = nFE^0{}_{cell}$$

For spontaneous cell reaction, ΔG must be negative.

$$\Delta G^0 = -2.303 RT \log K$$

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 1

2 Mark Questions

1. The chemistry of corrosion of iron is essentially an electro-chemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere. **[DELHI 2011]**

2. Complete the following chemical equations:

(i) $Cr_2O_7{}^{2-} + H^+ + I^- \longrightarrow$

(ii) $MnO_4{}^- + NO_2{}^- + H^+ \longrightarrow$

[DELHI 2012]

3. The standard electrode potential (E^o) for Daniel cell is +1.1V. Calculate the ΔG° for the reaction

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

$\left(1F = 96500 C\, mol^{-1}\right)$ **[ALL INDIA 2013]**

3 Mark Questions

4. Complete the following chemical equations:

(i) $MnO_4{}^- + C_2O_4{}^{2-} + H^+ \rightarrow$

(ii) $KMnO_4 \xrightarrow{heated}$

(iii) $Cr_2O_7{}^{2-} + H_2S + H^+ \rightarrow$

[DELHI 2011]

5. Calculate the emf of the following cell at 298 K:

$$Fe(s) \mid Fe^{2+}(0.001M) \parallel H^+(1M) \mid H_2(g)(1bar),$$

(Given $E^o_{cell} = +0.44V$) **[DELHI 2013]**

6. Calculate the emf of the following cell at 25ºC

$$Ag(s) \mid Ag^+(10^{-3}M) \parallel Cu^{2+}(10^{-1}M) \mid Cu(s)$$

Given $E^o_{cell} = +0.46\ V$ and $\log 10^n = n$

[ALL INDIA 2013]

7. (a) Calculate ΔrG° for the reaction

$$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$$

Given: $E^o_{cell} = +2.71V, 1F = 96500\,mol^{-1}$

(b) Name the type of cell which was used in Apollo space programme for providing electrical power.

[ALL INDIA 2014]

8. Calculate E^o_{cell} cell and $\Delta_r G^0$ for the following reaction at 25°C:

$$A^{2+} + B^+ \longrightarrow A^{3+} + B$$

Given: $K_C = 10^{10}$, $1\ F = 96500C\ mol^{-1}$

[ALL INDIA 2015]

9. Calculate emf of the following cell at 25°C:

$$Fe \mid Fe^{2+}(0.001M) \mid H^+(0.01M) \mid \mid H_2(g)(1bar) Pt(s) E^o(Fe^{2+} \mid Fe) = -0.44V\, E^o(H^+ / H_2) = 0.00V$$

[DELHI 2015]

10. A copper- silver cell is set up. The copper ion concentration in it is 0.10 M. The concentration of silver ion is not known. The cell potential measured is 0.422 V. Determine the concentration of silver ion in the cell.

Given: $E^o_{Ag^+/Ag} = +0.80\ V$, $E^o_{Cu^{+2}/Cu} = +0.34\ V$

[DELHI 2017]

11. (a) The cell in which the following reactions occurs:

$$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$$

$E^o_{cell} = 0.236\ V$ at 298 K. Calculate the standard Gibbs energy of the cell reaction. (Given: $1F = 96{,}500\ C\ mol^{-1}$)

(b) How many electrons flow through a metallic wire if a current of 0.5 A is passed for 2 hours? (Given: $1F = 96{,}500\ C\ mol^{-1}$)

[ALL INDIA 2017]

5 Mark Questions

12. (a) Calculate E°_{cell} for the following reaction at 298 K:

$$2A1(s) + 3Cu^{2+}(0.01\ M) \longrightarrow 2Al^{3+}(0.01M) + 3Cu(s)$$

Given: $E_{\text{cell}} = 1.98\ V$

(b) Using the E° values of A and B, predict which is better for coating the surface of iron $\left[E^o_{(Fe^{2+}/Fe)} = -0.44V\right]$ to prevent corrosion and why?

Given:

$E^o_{(A^{2+}/A)} = -2.37V : E^o_{(B^{2+}/B)} = -0.14V$

13. (a) Write the cell reaction and calculate the e.m.f. of the following cell at 298K.

$$Sn(s) \mid Sn^{2+}(0.004M) \parallel H^+(0.020M) \mid H(g)(1bar) \mid Pt(s)$$

(Given: $E^o_{Sn^{2+}/Sn} = -0.14V$)

(b) Give reasons:

(i) On the basis of E^o values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl.

(ii) Conductivity of CH_3COOH decreases on dilution.

OR

(a) For the reaction

$$2AgCl(s) + H_2(g)(1atm) \longrightarrow 2Ag(s) + 2H^+(0.1M) + 2Cl^-(0.1M)$$

$\Delta G^o = -43600J$ at 25^oC. Calculate the e.m.f. of the cell. $\left[\log 10^{-n} = -n\right]$

(b) Define fuel cell and write its two advantages.

[ALL INDIA 2018]

Solutions

1. According to Electrochemical theory of rusting, the impure iron surface behaves like small electrochemical cell in the presence of water containing dissolved oxygen or carbon dioxide. In this cell pure iron acts as an anode and impure iron surface acts as cathode. Moisture having dissolved CO_2 or O_2 acts as an **electrolyte**. Electrons released at the anodic spot move through the metallic object and go to another spot of object. There, in the presence of H^+ ions, the electrons reduce molecular oxygen. This spot behaves as the cathode. There H+ ions come either from H_2CO_3 , which are formed due to the dissolution of carbon dioxide from air into water or from the dissolution of other acidic oxides from the atmosphere in water. The reactions at cathode and anode are as follows: **[1]**

At anode: $Fe(s) \to Fe^{2+}(aq) + 2e^-$ **[½]**

At cathode:

$O_{2(g)} + 4H^{+1} + 4e^- \to 2\,H_2O$

$H_2O + CO_2 \to H_2CO_3$ **[½]**

Net Reaction:

$$2Fe(s) + O_2(g) + 4H^+ \to 2Fe^{2+} + 2H_2O$$

2. (i) $Cr_2O_7^{\ 2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$

[1]

(ii) $2MnO_4^{\ -} + 5NO_2^{\ -} + 6H^+ \longrightarrow$ **[1]**

$2Mn^{2+} + 3H_2O + 5NO_3^{\ -}$

3. $\Delta G = -nFE^o_{cell}$ **[1]**

$= -2 \times 96500 \times 1.1$

$= -212300$ J $= -212.3\ kJ$ **[1]**

4. (i) $2MnO_4^{\ -} + 5C_2O_4^{\ 2-} + 16H^+ \to$ **[1]**

$2Mn^{2+} + 8H_2O + 10CO_2$

(ii) $2KMnO_4 \xrightarrow{heated} K_2MnO_4 + MnO_2 + O_2$

[1]

(iii) $Cr_2O_7^{\ 2-} + 3H_2S + 8H^+ \to 2Cr^{3+} + 3S + 7H_2O$

[1]

5. At **anode**: $Fe \longrightarrow Fe^{2+} + 2e^-$

At **cathode**: $2H^+ + 2e^- \longrightarrow H_2$ **[1]**

So, total number of electrons (n) transferred = 2

Given that: $E^o_{cell} = +0.44V$

Temperature (T) = 298K

We know,

$$E_{cell} = E^o_{cell} - \left(\frac{2.303RT}{nF}\right)\log\frac{a_{oxi}}{a_{red}}$$

$$E_{cell} = E^o_{cell} - \left(\frac{0.05916V}{n}\right)\log\frac{\left[Fe^{2+}\right]}{\left[H^+\right]^2}$$ **[1]**

$$= 0.44 - \frac{0.5916}{2}\log\frac{0.001}{1}$$

$= 0.44 - 0.02955 \times (-3)$

$= 0.44 + 0.08865$

$\therefore E_{cell} = 0.53\ V$ **[1]**

6. Cell reaction:

$2Ag(s) + Cu^{2+}(aq) 2Ag^+(aq) + Cu(s)$ **[1]**

$$E_{cell} = E^o_{cell} - \frac{0.059}{n}\log\frac{\left[Ag^+\right]^2}{\left[Cu^{2+}\right]}$$ **[1]**

$$= 0.46 - \frac{0.059}{n}\log\frac{\left(10^{-3}\right)^2}{\left(10^{-1}\right)}$$

$$= 0.46 - \frac{0.059}{n}\log\left(10^{-5}\right)$$

$$= 0.46 - \frac{0.059}{2}\times(-5)$$

$= 0.46 + 0.14775 = 0.60775$ V **[1]**

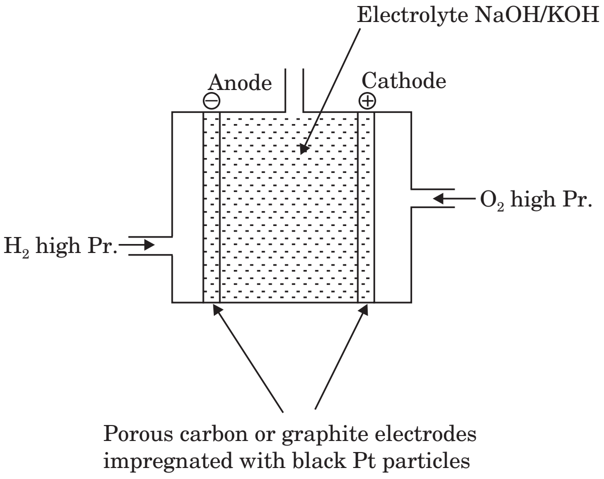
7. (a) $\Delta G^\circ = -nFE^o_{cell}$ **[1]**

$= -2 \times 96500 \times 2.71$

$= -523030$

$= -523.03\ kJ$

(b) Fuel cell



[1]

- * In fuel cell porous carbon electrodes impregnated with *Pt* particles are used.
- * *NaOH* or *KOH* are used as electrolyte
- * Reaction at anode :

$$H_2O + OH^- \rightarrow 2H_2O + 2e^-$$

At **cathode**: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$ s **[1]**

Overall cell reaction

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$

Advantage of fuel cell

(i) High efficiency

(ii) No harmful products are formed

(iii) No part of the cell creates environmental hazards

8. $A^{2+} + B^+ \longrightarrow A^{3+} + B$

$K_c = 10^{10}$; $E^o_{cell} = ?$

$n = 1$, $\Delta G^\circ = ?$

$$E^o_{cell} = \frac{0.059}{1}\log K_c \left[\log 10^{10} = 10\right]$$ **[1]**

$$E^o_{cell} = 0.059 \times 10 = 0.59\ V$$

$= \Delta G^\circ = -nFE_{\text{cell}}$ **[1]**

$= -1 \times 96500 \times 0.59$

$= -56935$ J/mol or -56.935 kJ/mol **[1]**

9. For the given cell representation, the cell reaction will be

$$Fe(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2(g)$$

The standard emf of the cell will be

$$E^o_{cell} = E^o_{H^+/H_2} - E^o_{Fe^{2+}/Fe}$$

$$E^o_{cell} = 0 - (-0.44) = 0.44V$$ **[1]**

The Nernst equation for the cell reactionat 25°C will be

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{\left[Fe^{2+}\right]}{\left[H^+\right]^2}$$ **[1]**

$$= 0.44 - \frac{0.0591}{2}\log\frac{0.001}{(0.01)^2}$$

$$= 0.44 - \frac{0.0591}{2}\log 10$$

$$= 0.44 - \frac{0.0591}{2}$$

$$E_{cell} = 0.4105V^2 \approx 0.41V$$ **[1]**

10. $E_{\text{cell}} = 0.422\ V$

Since $E^o_{Ag^+/Ag} > E^o_{Cu^{+2}/Cu}$

So, Ag$^+$/Ag is cathode and Cu^{2+}/Cu is the anode

$E^o{}_{cell} = E_{reduction} - E_{oxidation}$ s

$$E^o_{cell} = 0.80 - 0.34$$

$$E^o_{cell} = 0.46\ V$$ **[1]**

Cell Reaction: $2Ag^+ + Cu \longrightarrow Cu^{2+} + 2Ag$ x

$$E_{cell} = E^o{}_{cell} - \frac{0.059}{n}\log\frac{\left[Cu^{+2}\right]\left[Ag\right]^2}{\left[Ag^+\right]^2\left[Cu\right]}$$ **[1]**

$$E_{cell} = 0.46 - \frac{0.059}{2}\log\frac{[0.1]}{\left[Ag^+\right]^2}$$

$$0.422 = 0.46 - 0.029\left\{log[0.1] - log\left[Ag^+\right]^2\right\}$$

$$log\ [0.1] - 2\ log\left[Ag^+\right] = 1.310$$

$$\left(log\ 10^{-1}\right) - 2\ log\left[Ag^+\right] = 1.310$$

$$-1 - 2\,log\left[Ag^+\right] = 1.310$$

$$-2\,log\left[Ag^+\right] = 2.310$$

$$log\left[Ag^+\right] = -1.155$$

$$\left[Ag^+\right] = Antilog(-1.155)$$

$$\left[Ag^+\right] = 0.0699M$$ **[1]**

11. (a) $E^o_{cell} = 0.236\ V$

$\Delta G° = -NFE°$

$n = 2,\ F = 96500C$

$\Delta G^0 = 2 \times (96500C) \times (0.236\ V)$

= –45548 J **[1]**

Or

$\Delta G° = -2303\ RT\ log\ KC$

$$logK_c = \frac{\Delta G^0}{2.303\ RT}$$

$$= \frac{-45.55}{\left(2.303 \times 8.314 \times 10^{-3} \times 298\right)}$$

= 7.983 **[1]**

$K_c = antilog(7.983) = 9.62 \times 10^7$

(b) Current, $I = 0.5\,A$

Time, t = 2 hours $t = 2\ hours$

In sec we get Time,

$t = 2 \times 60 \times 60\ s = 7200\ s$

Charge: $Q = I \times t$

= $0.5\,A \times 7200\,s$

= 3600 Coulombs

Number of electrons = total charge / charge on 1 electrons

$$= \frac{3600}{1.6 \times 10^{-19}}$$

= 2.25×10^{22} electrons **[1]**

12. (a) $E_{cell} = E^o_{cell} - \dfrac{RT}{nF}\ln Q$ **[1]**

$$E_{cell} = E^o_{cell} - \frac{2.303RT}{nF}\log Q$$

$$E^o_{cell} = E_{cell} + \frac{2.303}{nF}\log Q$$ **[1]**

$$E^o_{cell} = 1.98 + \frac{0.0591}{6}$$

$= 1.99V$ **[1]**

(b) For electroplating of iron, we need cathode couple which gives $(+)E^0{}_{cell}$ value. When we compare the value of given options, we find

$E^0{}_{cell} = E^0{}_{cathode} - E^0{}_{anode}$

Case 1:

$E^0{}_{cell} = E°\left(A^{2+}/A\right) - E°\left(Fe^{2+}/Fe\right)$

$= (-2.37 + 0.44) = -1.93V$ **[1]**

Case 2:

$E°{}_{cell} = E°\left(B^{2+}/B\right) - E°\left(Fe^{2+}/Fe\right)$

$= (-0.14 + 0.44) = 0.3V$ **[1]**

Due to **B's (+)ve value**, it is **correct choice for coating** the surface of iron.

13. (a) Cell reaction:

At anode:

$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$ (Oxidation) **[1]**

At cathode:

$2H^+(aq) + 2e^- \longrightarrow H_2(g)$ (Reduction)

$Sn + 2H^+ \longrightarrow Sn^{2+} + H_2$ (Redox)

$E^o_{cell} = E^o{}_{H^+/H_2} - E^o{}_{sn^{2+}/sn}$

= 0.0 – (–0.14) = 0.14 V **[1]**

$$E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{\left[Sn^{2+}\right]\left(P_{H_2}\right)}{\left[H^+\right]^2}$$

$$= 0.14 - \frac{0.0591}{2}\log\frac{0.004 \times 1}{(0.02)^2}$$

$$= 0.14 - 0.029 \log \frac{4 \times 10^{-3}}{2 \times 2 \times 10^{-4}}$$

$$= 0.14 - 0.029 \log 10$$

$$E_{cell} = 0.111V$$ **[1]**

(b)

(i) The standard reduction potential of water is slightly less and therefore it has slightly more chance of getting oxidized. However in concentrated solution of NaCl, oxidation of chloride ions is preferred than water at anode. The unexpected result is due to over voltage. **[1]**

(ii) The number of ions furnished by an electrolyte depends upon degree of dissociation with increase in dilution. The degree of dissociation increases as a result molar conduction of acetic acid increases with dilution. **[1]**

OR

(a) $\Delta G^\circ = -nFE^\circ$

$$-43600 = -2 \times 96500 \times E^\circ$$ **[1]**

$$E^\circ = \frac{43600}{2 \times 96500} = 0.23V$$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{2} \log \frac{\left[H^+\right]^2 \left[Cl^-\right]^2}{\left(P_{H_2}\right)}$$ **[1]**

$$= 0.23 - \frac{0.0591}{2} \log (0.1)^2 (0.1)^2$$

$$E_{cell} = 0.23 - 0.029 \log \left(10^{-4}\right)$$

$$E_{cell} = 0.23 + (0.029 \times 4)$$

$$E_{cell} = 0.3482V$$ **[1]**

(b) These are voltaic cells in which the reactants are continuously supplied to the electrodes. They are designed to convert the energy from the combustion of fuel directly into electrical energy. **[1]**

Advantage:

(1) Fuel cell works with an efficiency of 60 to 70%. **[½]**

(2) There are no objectionable by products and therefore, it's a pollution free source of energy **[½]**

Topic 2: Conductance of Electrolytic Solutions or Ionic Solution and its Measurement

Summary

Conductance

- The electrical resistance of an object is given by $R = \rho\frac{l}{A}$ where l is the length and the area of cross section is A. ρ is called as resistivity.
- Conductance (G): It is the tendency of a material to allow current through it. It is the reciprocal of resistance. It depends on the following factors
  - ➢ Temperature
  - ➢ Nature an structure of the metal
  - ➢ Number of valence electrons per atom
- The conductance of electricity by ions present in thesolutions is called electrolytic or ionic conductance. The conductivity of electrolytic (ionic) solutions depends on following factors
  - ➢ Temperature
  - ➢ Concentration of electrolyte
  - ➢ The nature of electrolyte added
  - ➢ The nature of solvent and its viscosity
  - ➢ Size of ions produced and their solvation

Measurement of conductivity of Ionic Solutions

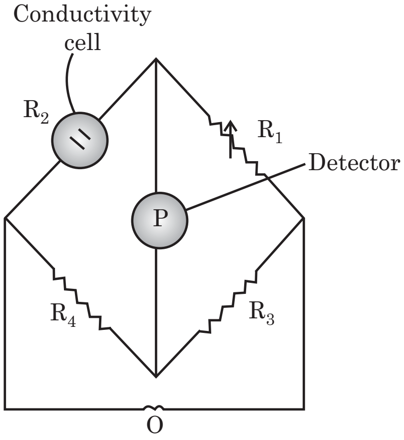
Measuring resistance of ionic solution using Wheatstone bridge faces two problems

- A solution cannot be connected to the bridge like a metallic wire. This problem is solved by using a specially designed vessel which is called conductivity cell.
- The composition of the solution is changed by passing direct current. This problem is solved by using alternating current source of power.

Cell constant (G*): The ratio of the distance between the electrodes to the cross sectional area of the electrodes is known as cell constant.

$$G = \frac{l}{A} = R\kappa$$

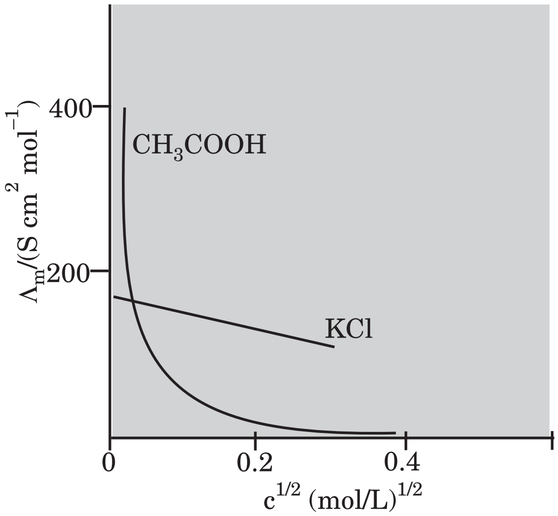
After determining the cell constant, it is used for measurement of resistance or conductivity of the solution using the circuit shown below:



Unknown Resistance $R_2 = \frac{R_1R_4}{R_3}$

Variation of conductivity and molar conductivity with concentration

- **Strong Electrolytes**
  - ➢ On dilution, the number of ions per unit volume that carry the current in a solution decreases. Hence, conductivity and molar conductivity decreases with decrease in concentration for strong and weak electrolytes.
  - ➢ Molar conductivity increases with decrease in concentration as the total volume of solution containing one mole ofelectrolyte also increases.
  - ➢ Λ increases with dilution and is shown as $\Lambda_m = E_m{}^o - Ac^{\frac{1}{2}}$ where $E_m{}^o$ is limiting molar conductivity.



- **Kohlrausch's law of independent migration of ions.**

  Limiting molar conductivity of an electrolyte at infinite dilution is expressed as the sum of contributions from the individual ions.
  $\Lambda_m{}^\infty = v_+\lambda_+{}^\infty + v_-\lambda^\infty$ where v_+, v_- are the number of cations and anions per formula of electrolyte.

Application of Kohlrausch's law

- ➢ Calculation of limiting conductivities of weak electrolytes
- ➢ Determination of degree of ionization (α) of weak electrolyte

- **Weak Electrolytes**
  - ➢ Weak electrolytes have lower degree of dissociation at higher concentrations and hence for such electrolytes, the change in Λ_m with dilution is due to increase in the degree of dissociation and consequently the number of ions in total volume of solution that contains 1 mol of electrolyte. For weak electrolyte is obtained using Kohlrausch's Law.
  - ➢ $E_m{}^o$
  - ➢ $K_a = \dfrac{c\Lambda_m{}^2}{\Lambda_m{}^o\left(\Lambda_m{}^o - \Lambda_m\right)}$

PREVIOUS YEARS'
EXAMINATION QUESTIONS
TOPIC 2

1 Mark Questions

1. Express the relation between conductivity and molar conductivity of a solution held in a cell. **[DELHI 2011]**

2 Mark Questions

2. The conductivity of 0.20 M solution of KCl at 298 K is 0.025 $S\ cm^{-1}$. Calculate its molar conductivity. **[DELHI 2014]**

3. Define the following terms:

(i) Molar conductivity $\left(\Lambda_m\right)$

(ii) Secondary batteries **[DELHI 2013]**

5 Mark Questions

4. (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 a 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 KCl solution at 298 K is $0.146 \times 10^{-3} S\ cm^{-1}$?

5. (a) Define the following terms:

(i) Limiting molar conductivity

(ii) Fuel cell

(b) Resistance of a conductivity cell filled with 0.1 $mol\ L^{-1}$ KCl solution is 100 Ω. If resistance of the same cell when filled with 0.02 $mol\ L^{-1}\ KCl$ solution is 540 Ω, calculate the conductivity and molar conductivity of $0.02 mol\ L^{-1}\ KCl$ solution. The conductivity of 0.1 $mol\ L^{-1}$ KCl solution is $1.29 \times 10^{-2}\ \Omega^{-1}$ $cm^{-1} 1.29 \times 10^{-2} \Omega^{-1}\ cm^{-1}$.

6. Conductivity of 0.00241 M acetic acid solution is $7.896 \times 10^{-5}\ S\ cm^{-1}$. Calculate its molar conductivity in this solution. If Δ^o_m for acetic acid be 390.5 $S\ cm^2\ mol^{-1}$, what would be its dissociation constant?

7. (a) The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is $3.905 \times 10^{-5} S\ cm^{-1}$. Calculate its molar conductivity and degree of dissociation (α).

Given: $E^o_{(H+)} = 349.6\ S\ cm^2 mol^{-1}$ and

$\lambda^o_{\left(CH_3C00^-\right)} = 40.9\ S\ cm^2 mol^{-1}$

(b) Define electrochemical cell. What happens if external potential applied becomes greater than E^o_{cell} of electrochemical cell? **[ALL INDIA 2016]**

8. **(a)** State Kohlrausch's law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch's law.

(b) Calculate $\Lambda^0{}_m$ for acetic acid.

Given that $\Lambda^0{}_m\left(HCl\right) = 426\ S\ cm^2 mol^{-1}$

$\Lambda^0{}_m\left(NaCl\right) = 126\ S\ cm^2 mol^{-1}$

$\Lambda^0{}_m\left(CH_3COONa\right) = 91\ S\ cm^2 mol^{-1}$

Solutions

1. The molar conductivity of a solution is related to conductivity of that solution as:

$$\Lambda_m = \frac{K}{C} = \frac{\text{Conduvtivity}}{\text{Concentration}}.$$ **[1]**

2. Given: $k = 0.025\ S\ cm^{-1}$

Molarity, $M = 0.20M$

Molar conductivity, $\left(\Lambda_m\right) = \frac{\kappa \times 1000}{M}$ **[1]**

$= \frac{0.025 \times 1000}{0.20}$

$\therefore \Lambda_m = 125\,S\,cm^2 mol^{-1}$ **[1]**

3. (i) **Molar Conductivity** $\left(\Lambda_m\right)$: Molar conductivity can be defined as conductance of all the ions present in a certain volume (V cm^3), if solution is kept between electrodes present 1 cm apart and area of electrode is such that whole solution is confined them. **[1]**

(ii) Secondary batteries: The batteries which can be recharged again and again are called as secondary batteries. Eg. Lead storage battery. **[1]**

4. (a) Molar conductivity of a solution at a given concentration is the conductance of volume V ml of a solution containing 1 g mole of the electrolyte kept between two electrodes with the area of cross-section A and distance of unit length. **[1]**

$$\Lambda_m = K\frac{A}{l}$$

Now, $l = 1$ and $A = V$ (volume containing 1 g mole of the electrolyte).

$$\Lambda_m = kV$$

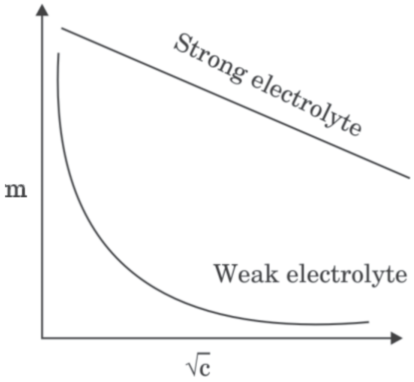
Molar conductivity increases with a decrease in concentration. This is because the total volume V of the solution containing one mole of the electrolyte increases on dilution. **[1]**

Variation of molar conductivities with dilution:

For strong electrolytes, molar conductivity slowly increases with dilution.

For weak electrolytes, molar conductivity increases steeply on dilution, especially near lower concentrations. **[1]**

The variation of Λ_m with $\sqrt{c}$ for strong and weak electrolytes is shown in the following plot:



(b) $\kappa = 0.146 \times 10^{-3} cm^{-1}\Omega^{-1}$ **[1]**

$R = 1500\Omega$

Specific Conductance

$$= \frac{\text{Cell constant}}{\text{Resistance}}$$

Cell constant

$= \kappa R = 0.146 \times 10^{-3} \times 1500 = 0.219\ cm^{-1}$ **[1]**

5. (a)

(i) Limiting molar conductivity is the molar conductivity of a solution when the concentration approaches zero (infinite dilution, $C \to 0$). It is also defined as molar conductivity at infinite dilution and is denoted by Λ_m^o. On the plot, molar conductivity against $\sqrt{C}$, we can obtain Λ_m^o by extrapolating the graph to $\sqrt{C} = 0$. **[1]**

(ii) A fuel cell is a galvanic cell in which the heat energy is directly converted into electrical energy. Most important fuel cell is $H_2 - O_2$ fuel cell and is used as a source of electric power in space vehicles. **[1]**

(b) Given, $R_1 = 100\ \Omega$

$C_1(\text{Concentration of KCl solution}) = 0.1 mol\, L^{-1}$

$K_1 = 1.29 \times 10^{-2}\Omega^{-1}cm^{-1}$ **[1]**

$R_2 = 520\ \Omega$

$C_2(\text{Concentration of KCl solution}) = 0.02 mol\, L^{-1}$

Cell constant (G) = conductivity × resistance

$= 1.29 \times 10^{-2}\ \Omega^{-1}cm^{-1} \times 100\Omega = 1.29cm^{-1}$

$\therefore Conductivity(K_2) = \frac{\text{Cell constant}}{\text{Resistance}}$ **[1]**

$= \frac{1.29cm^{-1}}{520\Omega} = 2.48 \times 10^{-3}\Omega^{-1}cm^{-1}$

Molar Conductivity $(\Lambda_m) = \frac{K_2 \times 1000}{C_2}$

$= \frac{2.48 \times 10^{-3} \times 1000\, Scm^{-1}}{0.02\, mol\, cm^{-3}}$

$= 1.24 \times 10^2$ or $124\, Scm^2\, mol^{-1}$ **[1]**

6. $\Lambda_m = \frac{\kappa}{C}$

$= \frac{7.896 \times 10^{-5}\, Scm^{-1} \times 1000\, cm^3 L^{-1}}{0.00241\, mol\, L^{-1}}$ **[1]**

$= 32.90\, S\, cm^2\, mol^{-1}$

$= \frac{\Lambda_m}{\Lambda_m^o}$ **[1]**

$= \frac{32.90\, S\, cm^2\, mol^{-1}}{390.5\, S\, cm^2\, mol^{-1}}$

$= 0.084\, S\, cm^2\, mol^{-1}$ **[1]**

$k = \frac{Ca^2}{(1-a)} = Ca^2$ **[1]**

$= 0.00241 \times (0.084)^2$

$= 1.7 \times 10^{-5}$ *or* 1.856×10^{-5} (if α is not neglected)

[1]

7. (a) $\Delta_m = \frac{K}{c}, \Delta_m = \frac{K}{c} \times 1000$ **[1]**

$\Delta_m = 39.05 S\, mol^{-1}$

Here, K = Measured conductivity

c = Electrolyte concentration

Degree of dissociation

$= \frac{\text{Molar coductance particular concentration}}{\text{Molar conductance at infinite dilution}}$

[1]

Degree of dissociation $= \frac{39.05}{390.5 \times 0.1}$ =1 **[1]**

(b) An electrochemical cell is a device capable of generating electrical energy from chemical reactions. If external potential is higher than E°$_{\text{cell}}$ potential of the cell, the flow of current is reversed and recharging of cell takes place. **[2]**

8. (a) Kohlrausch's law of independent migration of ions: The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. **[1]**

$\Lambda_m^o(CH_3COOH) = \Lambda^o_{CH_3COO^-} + \Lambda^o_{H^+}$ **[1]**

(b) $\Lambda_m^o(CH_3COOH) = ?$

$\Lambda_m^o(HCl) = 426\, S\, cm^2\, mol^{-1}$

$\Lambda_m^o(NaCl) = 126\, S\, cm^2\, mol^{-1}$

$\Lambda_m^o(CH_3COONa) = 91 S\, cm^2\, mol^{-1}$ **[1]**

$\Lambda_m^o(CH_3COOH) = \Lambda_m^o(HCl) +$

$\Lambda_m^o(CH_3COONa) - \Lambda_m^o(NaCl)$ **[1]**

$\Lambda_m^o(CH_3COOH) = 426 + 91 - 126$

$= 391 S\, cm^2\, mol^{-1}$ **[1]**

Topic 3: Electrolysis, Batteries, Fuel Cells and Corrosion

Summary

- Electrolysis is the passage of electricity through an electrolyte, in which cations move to the cathode to get reduced, and anions move towards the anode to get oxidized.
- Faraday's Laws of Electrolysis
  - ➢ Faraday's First Law of Electrolysis

  The mass of the substance (m) which occurs at any electrode is directly proportional to the quantity of electricity or charge (Q) passed.

  $m = ZIt$, where Z= Electrochemical equivalent

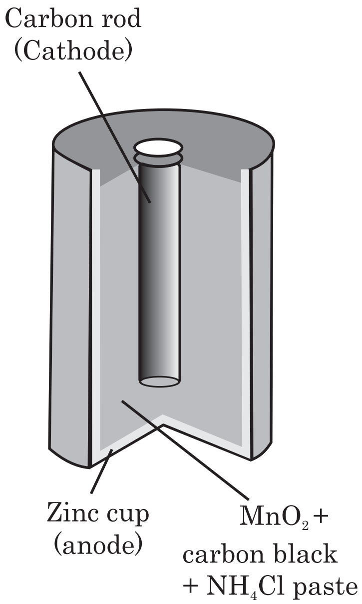
  - ➢ Faraday's second Law of Electrolysis

  When the same quantity of electricity is passed through different electrolytes, the masses of different ions liberated at the electrodes are directly proportional to their chemical equivalents (Equivalent weights)

  $$\frac{w}{E_1} = \frac{w}{E_2}$$

- The product of electrolysis depends on the types of electrode used and the physical state of the material.
- Batteries: It is a source of electrical energy where one or more cells are connected in series.
  - ➢ Primary Battery: They are non-chargeable batteries like Dry cell and Lechlanche Cell.

Dry cell



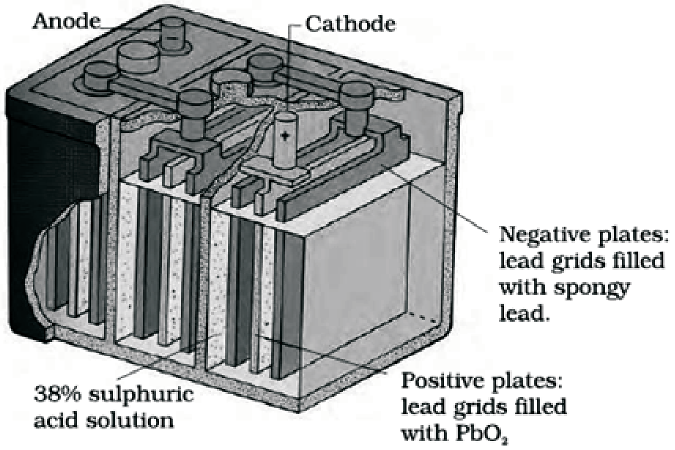
At anode: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

At cathode: $MnO_{2(s)} + NH_{4(aq)}^{\ +} + 2e^- \rightarrow MnO(OH) + NH_3$

The net reaction: $Zn + MnO_{2(s)} + NH_{4(aq)}^{\ +} \rightarrow Zn^{2+} + MnO(OH) + NH_3$

- ➢ Secondary Battery: These are the chargeable cells like lead storage battery and nickel-cadmium cells.

Lead storage battery:



Anode: Spongy lead

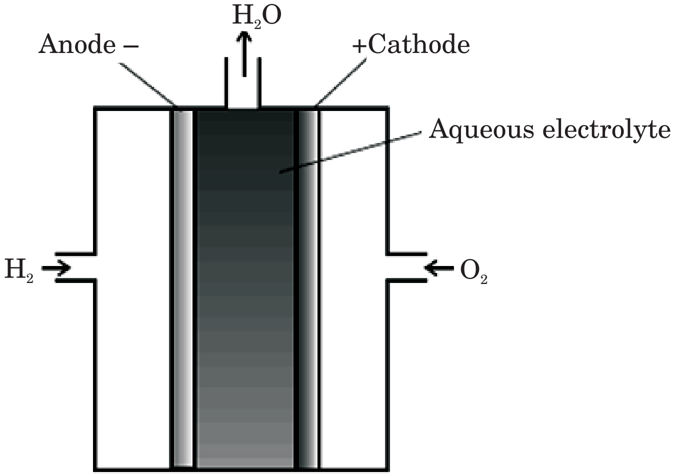
Cathode: Lead packed with lead dioxide

Electrolyte: Aqueous solution of S_2SO_4

At anode: $Pb_{(S)} + SO_4{}^{2-}{}_{(aq)} \rightarrow PbSO_{4(S)} + 2e^-$

At cathode: $PbSO_{4(S)} + 2e^- \rightarrow Pb_{(S)} + SO_4{}^{2-}{}_{(aq)}$

- Fuel cell: These are the cells which convert energy from fuels like methane, hydrogen into electrical energy. Following diagram shows a fuel cell.



Anode: $\left[H_{2(g)} + 2OH_{(aq)}{}^- \rightarrow 2H_2O_{(l)} + 2e^-\right] \times 2$

Cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-{}_{(aq)}$

Net reaction: $O_{2(g)} + 2H_{2(g)} \rightarrow 2H_2O_{(l)}$

- Corrosion: The conversion of metals into undesirable compounds (usually oxides) on reaction with moisture and other gases.

Rusting of Iron:

$$Fe_{(S)} + 2H^{+}{}_{(aq)} + \frac{1}{2}O_{2(g)} \rightarrow Fe^{2+}{}_{(aq)} \,{}_{-}\!+ H_2O_{(l)}$$

$$\underline{2Fe^{2+}{}_{(S)} + \frac{1}{2}O_{2(g)} + 2H_2O_{(l)} \rightarrow Fe_2O_{3(S)} + 4H^{+}}$$

$$Fe_2O_{3(S)} + xH_2O_{(l)} \rightarrow Fe_2O_3{\bullet}xH_2O$$

Corrosion can be prevented using following measures

- Alloying
- Barrier protection by covering the surface with paint.
- Sacrificial protection by galvanization

PREVIOUS YEARS'
EXAMINATION QUESTIONS
TOPIC 3

2 Mark Questions

1. What type of a battery is lead storage battery? Write the anode and the cathode reactions and the overall reactions occurring in a lead storage battery. **[ALL INDIA 2011]**

2. (*a*) Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution:

$$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s); E^{\circ} = +0.80V$$

$$H^{+}(aq) + e^{-} \longrightarrow \frac{1}{2}H_2(g); E^{\circ} = 0.00V$$

On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why?

(*b*) Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with decrease in concentration? **[DELHI 2015]**

3. Calculate the time to deposit 1.5 g of silver at cathode when a current of 1.5 was passed through the solution of $AgNO_3$. (Molar mass of Ag = 108 $g\ mol^{-1}$, 1F = 96500 $C\ mol^{-1}$) **[ALL INDIA 2015]**

4. What type of cell is a lead storage battery? Write the anode and the cathode reactions and the overall cell reaction occurring in the use of a lead storage battery?

OR

Construct the redox equation from the two half cell reactions and predict if this reaction favours formation of reactants or product shown in the equation. **[DELHI 2017]**

5. Write the name of the cell which is generally used in transistors. Write the reactions taking place at the anode and cathode of this cell. **[ALL INDIA 2017]**

5 Mark Questions

6. (a) What type of a battery is lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery.

(b) Calculate the potential for half-cell containing

$0.10\ M\ K_2Cr_2O_7(aq),\ 0.20\ M\ Cr^{3+}(aq)$

and $1.0 \times 10^{-4}\ M\ H^{+}(aq)$

The half-cell reaction is

$$Cr_2O_7{}^{2-}(aq) + 14\ H^{+}(aq) + 6\ e^{-} \longrightarrow 2\ Cr^{3+}(aq) + 7\ H_2O\ (l)$$

and the standard electrode potential is given as E_o = 1.33 V

OR

(a) How many moles of mercury will be produced by electrolyzing 1.0 $M\ Hg\ (NO_3)_2$ solution with a current of 2.00A for 3 hours? $\left[Hg(NO_3)_2 = 200.6\ g\ mol^{-1}\right]$

(b) A voltaic cell is set up at 25°C with the following half-cells Al^{3+} (0.001 M) and Ni^{2+} (0.50 M). Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

(Given: $E^o_{Ni^{2+}/Ni} = -0.25V,$ $E^o_{Al^{3+}/Al} = -1.66V$)

[ALL INDIA 2011]

7. (a) What type of a battery is the lead storage battery? Write the anode and the cathode reactions and the overall reactions 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.

$$Zn(s) + Ag_2O(s) + H_2O(l) \longrightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$$

Determine E° and ΔG° for the reaction.

(Given: $E^\circ_{Ag^+/Ag} = +0.80V,$)
$E^\circ_{Zn^+/Zn} = -0.76V$

8. (a) State Faraday's first law of electrolysis. How much charge in terms of Faraday is required for the reduction of 1 mol of Cu^{2+} to Cu.

(b) Calculate emf of the following cell at 298 K:

$$Mg(s)|Mg^{2+}(0.1M)||Cu^{2+}(0.01M)|Cu(s)$$

[Given: $E^o_{cell} = +2.71V, 1F = 96500\,Cmol^{-1}$]

[DELHI 2016]

9. Three electrolytic cells A, B and C containing solutions of zinc sulphate, silver nitrate and copper sulphate, respectively are connected in series. A steady current of 1.5 ampere was passed through them until 1.45 g of silver were deposited at the cathode of cell B. How long did the current flow? What mass of copper and what mass of zinc were deposited in the concerned cells? (Atomic masses of Ag = 108, Zn = 65.4, Cu = 63.5) **[DELHI 2016]**

10. (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.

(Given : $E^0_{Ag+/Ag} = +0.80\ V,$).
$E^0_{Cu^{2+}/Cu} = +0.34\ V$

Solutions

1. The lead storage battery is a secondary cell which is rechargeable. During discharging, the electrode reaction occurs as follows :

At anode:

$$Pb(s) + SO_4^{-2}(aq) \longrightarrow PbSO_4(s) + 2e^-$$ **[½]**

At cathode:

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+ + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$

[½]

Net reaction:

$$Pb(s) + PbO_2(s) + 4H^+ + 2SO_4^{-2}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

[1]

2. (a) The relationship between the standard free energy change and emf of a cell reaction is given by : $\Delta G^\circ = -nFE^\circ$

Thus, more positive the standard reduction potential of a reaction, the more negative is the standard free energy change associated with the process and, consequently, the higher is the feasibility of the reaction. **[½]**

Since $E^o_{Ag^+/Ag}$ has a greater positive value than $E^o_{H^+/H}$, the reaction which is feasible at the cathode is given by

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$ **[½]**

(b) The limiting molar conductivity of an electrolyte is defined as its molar conductivity when the concentration of the electrolyte in the solution approaches zero. **[1]**

The conductivity of an electrolyte solution is the conductance of ions present in a unit volume of the solution. The number of ions (responsible for carrying current) decreases when the solution is diluted or the concentration is decreased. As a result, the conductivity of an electrolyte solution decreases with the decrease in concentration.

3. $Ag^+ + e^- \longrightarrow Ag$

108 g of Ag are deposited by 96500 C

1.5g of Ag will be deposited by **[1]**

$$t = \frac{Q}{I} = \frac{1340.27}{1.5} = 893.5s$$ **[1]**

OR

$$W = \frac{E}{F}It$$ **[1]**

$$1.5 = \frac{108}{96500} \times 1.5 \times t$$

T = 893.5 s **[1]**

4. Lead storage battery is a secondary cell.

Anode: **[1]**

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$ **[½]**

Cathode:

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$

[½]

Overall cell reaction:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

OR

The half cell reactions of an electrochemical cell are given below: **[1]**

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l),\ E^o = 1.51\ V$$

$$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq),\ E^o = +0.15\ V$$

Cathode-reduction reaction:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$$

Anode-Oxidation reaction:

$$Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2e^-$$

Redox equation:

$$2MnO_4^-(aq) + 16H^+(aq) + 5Sn^{2+}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Sn^{4+}(aq)$$

Cell potential $= E^o_{\text{reduction}} - E^o_{\text{oxidation}}$

$= 1.51 - (-0.15) = 1.66\ V$ **[1]**

5. Zinc–carbon batteries were the first commercial dry batteries, developed from the technology of the wet Leclanche cell. They made flash lights and other portable devices possible, because the battery can function in any orientation. They are still useful in low drain or intermittent use devices such as remote controls, flashlights, clocks or transistor radios.

Reaction **at Anode**: **[1]**

$$Zn(s) \longrightarrow Zn^{2+(}aq) + 2\ e^-$$ **[½]**

Reaction **at Cathode**: **[½]**

$$2MnO_2(s) + 2\ e^- + 2\ NH_4Cl(aq) \longrightarrow Mn_2O_3(s) + 2\ NH_3(aq) + H_2O(l) + 2\ Cl^-$$

6. (a) It is **secondary cell** **[1]**

Anode Reaction:

$$Pb + SO_4^{2-} \longrightarrow PbSO_4(s) + 2e^-$$

Cathode Reaction:

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$$

Net Reaction:

$$Pb + PbO_2 + 2SO_4^{2-} + 4H^+ \longrightarrow 2PbSO_4 + 2H_2O$$

[1]

(b) $$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log\frac{\left[Cr^{+3}\right]^{2}}{\left[Cr_{2}O_{7}\right]^{-2}\left[H^{+}\right]^{14}}$$

[1]

$$E_{cell} = 1.33V - \frac{0.0591}{6}\log\frac{\left[0.20\right]^{2}}{\left[0.10\right]^{-2}\left[10^{-4}\right]^{14}}$$

$E_{\text{cell}} = 1.33V - 0.55V$

$E_{\text{cell}} = 0.78V$ **[1]**

OR

(a) $m = ZIt$

$$m = \frac{M \times I \times t}{nF}$$ **[1]**

$$m = \frac{M}{2 \times 96500\,C\,mol^{-1}} \times 2A \times 3 \times 60 \times 60\,s$$

$m = 0.112 mol \times M$

no. of moles of mercury $= \frac{0.112\,mol \times M}{M}$

no. of moles of mercury = **0.112 mol** **[1]**

(b) $2Al + 3Ni^{2+} \longrightarrow 2Al^{3+} + 3Ni$

$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$

$= \left[-0.25V - \left(-1.66V\right)\right] = 1.41V$ **[1]**

$E^{o}_{cell} = 1.41V$

Nernst Equation:

$2Al + 3Ni^{2+} \longrightarrow 2Al^{3+} + 3Ni$

n = 6 electrons

$$E_{cell} = E^{o}_{cell} - \frac{0.059}{n}\log\frac{\left[Al^{+3}\right]^{2}}{\left[Ni^{2+}\right]^{3}}$$ **[1]**

$$E_{cell} = 1.41V - \frac{0.059}{6}\log\frac{\left[0.001M\right]^{2}}{\left[0.50M\right]^{3}}$$

$$E_{cell} = 1.41V - \frac{0.059}{6}\left[-5.097\right]\log\left(10^{4}\right)$$

$E_{cell} = 1.41V + 0.050V = 1.46V$ **[1]**

7. (a) lead storage battery is secondary cell and can be recharged by passing current through it. **[1]**

At anode: $Pb + SO_{4}^{2-} \longrightarrow PbSO_{4} + 2e^{-}$

[½]

At cathode:

$PbO_{2} + SO_{4}^{2-} + 4H^{+} + 2e^{-} \longrightarrow PbSO_{4} + 2H_{2}O$ **[½]**

Overall cell reaction:

$Pb + PbO_{2} + 4H^{+} + 2SO_{4} \longrightarrow 2PbSO_{4} + 2H_{2}O$

[1]

(b) $E^{\circ}_{cell} = 0.8 - \left(-0.76\right) = 1.56V$

$\Delta G^{\circ} = -nFE^{\circ}_{cell}$ **[1]**

$= -2 \times 96500 \times 1.56 = -301\,kJ\,mol^{-1}$ **[1]**

8. (a) The mass of substance deposited or liberated at any electrode is proportional to the quantity of electric charge passed through an electrolysis cell. **[1]**

Reduction of 1 mol of Cu^{2+} to 2 moles Cu

$Cu^{2+} + 2e^{-} \longrightarrow Cu$

One mole of electron carries 1F charge. Since 2 moles of electrons are required for reduction of 1 molof Cu^{2+}. So charge required is 2F. **[1]**

(b) $Mg + Cu^{2+} \longrightarrow Mg^{2+} + Cu$ **[1]**

$$E_{cell} = E^{o}_{cell} - \frac{0.059}{n}\log\frac{\left[Mg^{2+}\right]}{\left[Cu^{2+}\right]}$$

$$= 2.71 - \frac{0.059}{2}\log\frac{\left[Mg^{2+}\right]}{\left[Cu^{2+}\right]}$$ **[1]**

= 2.71 – 0.02595 log 10

= 2.71 – 0.0295

= 2.6805 V **[1]**

9. $Ag^{+1} + e^{-} \longrightarrow Ag$ **[1]**

108 g is deposited by 96500C electric charge

So, 1.45g of silver is deposited by $\frac{96500C \times 1.45\,g}{108\,g} = 1295.6C$ **[1]**

Quantity of electricity passed = Current × t

$t = \frac{1295.6C}{1.5amp} = 863.7s$ **[1]**

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

2×96500 C deposits 63.5 g of Cu **[1]**

So, 1295.6 C deposits $\dfrac{63.5g \times 1295.6C}{2 \times 96500C}$ of Zn

= 0.44 g of Zn **[1]**

10. (a) Lead storage battery:

Anode:

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

[½]

Cathode:

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O\ (l)$$

[½]

Overall reaction:

$$Pb\ (s) + PbO_2(s) + H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O\ (l)$$

[1]

(b)

$$\begin{array}{l} Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^- \\ \underline{2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)} \\ Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s) \end{array}$$

[1]

$$E^o_{cell} = E^o_{Ag^+/Ag} - E^o_{Cu^{2+}/Cu}$$

$= +0.80\ V - 0.34\ V$

$= 0.46\ V$

$n = 2$

$$E_{cell} = E^o_{cell} - \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$\therefore 0.422V = 0.46V - \frac{0.059}{2}\log\frac{0.1}{[Ag^+]^2}$$

$$-0.038 = -\frac{0.059}{2}\log\frac{0.1}{[Ag^+]^2}$$

$$0.038 = \frac{0.059}{2}\log\frac{0.1}{[Ag^+]^2}$$ **[1]**

$$\Rightarrow \log\frac{0.1}{[Ag^+]^2} = \frac{0.038V \times 2}{0.059} = 1.2881$$

$$\Rightarrow \frac{0.1}{[Ag^+]^2} = anti\log(1.2881) = 1.941 \times 10^1$$

$$[Ag^+]^2 = \frac{0.1}{1.947 \times 10^1}$$

$$[Ag^+]^2 = 0.00515$$

$$[Ag^+] = 0.071\,mol\,L^{-1}$$ **[1]**

Smart Notes ……………………

Smart Notes ....

CHAPTER 4

Chemical Kinetics

Chapter Analysis with respect to Last 3 Years' Board Exams

List of Topics	2016		2017		2018	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Rate of a reaction (Average and instantaneous)	(2 marks)		(2 marks)			
Factors affecting rate of reaction: concentration, temperature, catalyst				3 marks		
Order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half life (only for zero and first order reactions)	(2, 3 marks)	(2, 3 marks)		(3 marks)	(2 ,3 marks)	(2 ,3 marks)
Concept of collision theory (elementary idea, no mathematical treatment)						
Activation energy, Arrhenious equation				(1 mark)		

Topic 1: Rate of a Chemical Reaction and Factors Influencing Rate of a Reaction

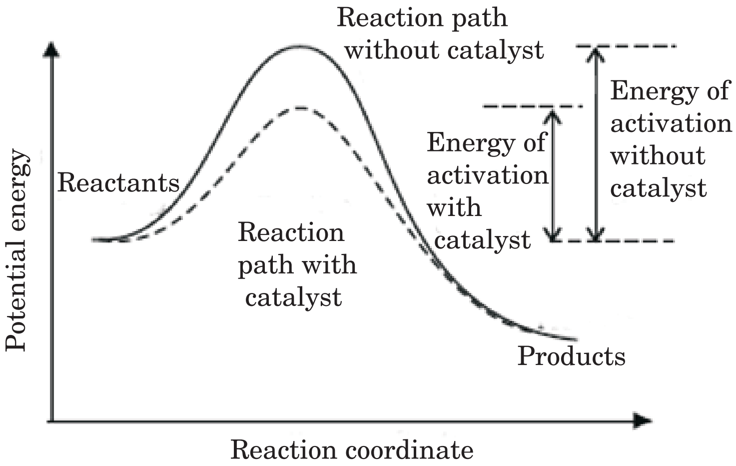
Summary

- **Chemical Kinetics**: The study of chemical reactions, their rates, effect of various factors on rate of reaction is considered under chemical kinetics.
- **Rate of Reaction:** The change in concentration of reactant or product with respect to time is called the rate of reaction.

  For the reaction, R → P

  Rate of disappearance of R $= -\frac{\Delta[R]}{\Delta t}$; Rate of appearance of P $= \frac{\Delta[P]}{\Delta t}$

  Units of rate of reaction are concentration × time^{-1}. Unit of concentration varies according to the state of the reactant. For gases, concentration is expressed as partial pressures, for liquids, concentration is in mol L^{-1}.
- Rate of chemical reaction can be instantaneous or average. Rate of reaction at a particular moment of time is instantaneous rate while the rate of reaction over a time interval is average rate.
- **Factors affecting the rate of a chemical reaction:** There are various factors which affect the rate of reaction.
  - **Pressure of the reaction:** Pressure varies directly with the rate of reaction. As the pressure is increased, volume decreases and concentration increases. Therefore with increase in concentration, rate of reaction increases.
  - **Temperature of the reaction:** Temperature varies directly with the rate of reaction. As the temperature of the reaction increases, rate increases and vice versa.
  - **Concentration of the reaction:** As the concentration of the reactants increases, rate of reaction increases and if the concentration of the reactants is less then rate of reaction decreases.
  - **Surface area of the reactants:** For reactions which takes place on the surface of the reactant, the rate of reaction increases with increase in surface.
  - **Presence of catalyst:** Rate of reaction increases on adding catalyst. It is because the catalyst decreases the activation energy of the reaction.



  - **Nature of reactants:** Simpler molecules separate easily and take part in chemical reaction while molecules which are complex take time to separate the bonds and the rate of reaction thus decreases.

- **Rate Law:** It is an expression where rate of chemical reaction is written in terms of concentration of the reactants with each term raised to some power which may or may not be same as the stoichiometric coefficients of the reacting species.

  For example: For the reaction, $2NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$

  Rate = $k\ [NO]^2\ [O_2]$

  Here k is the rate constant.
- **Molecularity:** It is defined as the number of reacting species (molecules, atoms or ions) in an elementary reaction. It cannot be a non integer or zero.
- **Elementary or complex reactions:** If a reaction takes place in a single step, it is an elementary reaction while a reaction involving series of elementary reactions is called complex reaction.
- **Rate determining step:** The step which takes place slowly is called the rate determining step.

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 1

1 Mark Question

1. Define 'order of a reaction'. **[ALL INDIA 2011]**

2 Mark Questions

2. What do you understand by the rate law and rate constant of a reaction? Identify the order of a reaction if the units of its rate constant are:

- *(i)* $L^{-1}\ mol\ s^{-1}$
- *(ii)* $L\ mol^{-1}\ s^{-1}$ **[ALL INDIA 2011]**

3. What do you understand by the 'order of a reaction'? Identify the reaction order from each of the following units of reaction rate constant:

- *(i)* $L^{-1}\ mol\ s^{-1}$
- *(ii)* $L\ mol^{-1}\ s^{-1}$ **[ALL INDIA 2012]**

4. For a reaction:

$$H_2 + Cl_2 \longrightarrow 2HCl$$

Rate = k

- *(i)* Write the order and molecularity of this reaction.
- *(ii)* Write the unit of 'k'.

[ALL INDIA 2016]

5. For the reaction

$$2N_2O_5\left(g\right) \longrightarrow 4NO_2\left(g\right) + O_2\left(g\right),$$

the rate of formation of NO_2 (g) is 2.8×10^{-3} Ms^{-1}. Calculate the rate of disappearance of N_2O_5 (g). **[ALL INDIA 2018]**

6. Distinguish between 'rate expression' and 'rate constant' of a reaction. **[DELHI 2011]**

7. Write two differences between 'order of reaction' and 'molecularity of reaction'. **[DELHI 2014]**

8. What is meant by the 'rate constant, k' of a reaction? If the concentration be expressed in mol L^{-1} units and time in seconds, what would be the units for k

- *(i)* for a zero order reaction and
- *(ii)* for a first order reaction? **[DELHI 2016]**

9. Define the following:

- *(i)* Elementary step in a reaction
- *(ii)* Rate of a reaction **[DELHI 2017]**

3 Mark Questions

10. For the first order thermal decomposition reaction, the following data were obtained

$$C_2H_5CI\left(g\right) \longrightarrow C_2H_4\left(g\right) + HCl\left(g\right)$$

Time/sec	Total pressure/atm
0	0.30
300	0.50

Calculate the rate constant. (Given: $log2 = 0.301$, $log3 = 0.4771$, $log4 = 0.6021$)

[ALL INDIA 2016]

11. For the reaction:

$$2NO\left(g\right) + Cl_2\left(g\right) \longrightarrow 2\ NOCl\left(g\right)$$

Experiment no.	Initial $[NO]$ (M)	Initial $[Cl_2]$ (M)	Initial rate of disappearance of Cl_2 (M/min)
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	1.20
4	0.25	0.25	?

(a) Write the expression for rate law.

(b) Calculate the value of rate constant and specify its units.

(c) What is the initial rate of disappearance of Cl_2 in exp. 4? **[ALL INDIA 2012]**

12. Nitrogen pentoxide decomposes according to equation:

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

The 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

(i) Calculate the rate constant. Include units with your answer.

(ii) What will be the concentration of N_2O_5 after 100 minutes?

(iii) Calculate the initial rate of reaction.

[DELHI 2011]

13. For the reaction

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

the following data were collected. All the measurements were taken at 263 K:

Experiment No.	Initial [NO] (M)	Initial $[Cl_2]$ M)	Initial rate of disappearance of Cl_2 (M/min)
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

(a) Write the expression for rate law.

(b) Calculate the value of rate constant and specify its units.

(b) What is the initial rate of disappearance of Cl_2 in exp. 4?

[ALL INDIA 2012]

14. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	Time/s^{-1}	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.

(Given: $log 4 = 0.6021, log 2 = 0.3010$)

[ALL INDIA 2014]

15. A first order reaction has a rate constant of 0.0051 min^{-1}. If we begin with 0.10 M concentration of the reactant, what concentration of the reactant will be left after 3 hours? **[DELHI 2017]**

16. The rate constant for a reaction of zero order in A is 0.0030 molL^{-1} s^{-1}. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M?

Solutions

1. The sum of powers of the concentration terms of the reactants in the rate law expression is called the order of that chemical reaction.

Mathematically, $rate = k[A]^P [B]^q$ **[1]**

Order of reaction = $p + q$

2. The representation of rate of reaction in terms of concentration of the reactants is known as rate law. The rate constant is defined as the rate of reaction when the concentration of reactants is unity. **[1]**

(i) zero order **[1/2]**

(ii) second order **[1/2]**

3. The sum of the powers of the concentrations of the reactants of a chemical reaction in the rate law expression is called the order of that chemical reaction. **[1]**

Rate = $k[A]^x [13]^Y$

Order of reaction = $x + y$

The orders of reaction for the following units are:

(i) $L^{-1} mol\ s^{-1}$: Zero order **[½]**

(ii) $L\ mol^{-1} s^{-1}$: Second order **[½]**

4. (i) As per given information that rate = k. It can be inferred that the given reaction is a zero-order reaction. The molecularity of the reaction based on the stoichiometry is 2. **[1]**

(ii) Since it is a zero-order reaction, the unit of rate constant is $mole\ L^{-1} sec^{-1}$ **[1]**

5. $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

Rate of reaction

$$= -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$ **[1]**

According to the question

$$\frac{d[NO_2]}{dt} = 2.8 \times 10^{-3}\, Ms^{-1}$$

$$-\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{1}{2} \times 2.8 \times 10^{-3}\, Ms^{-1}$$

$$-\frac{d[N_2O_5]}{dt} = 1.4 \times 10^{-3}\, Ms^{-1}$$ **[1]**

6. Rate constant is the rate of reaction when the concentration of each reactant is taken as unity. **[1]**

Rate expression expresses the rate of reaction in terms of molar concentrations of the reactants with each term raised to their power, which may or may not be same as the stoichiometric coefficient of that reactant in the balanced chemical equation. **[1]**

7.

Molecularity	Order of reaction
1. It is the number of reacting species taking part in an elementary reaction.	It is equal to the sum of all the exponents of all the reactants present in the rate law expression.
2. It is a theoretical concept and cannot be zero or fractional.	It is determined experimentally and can be equal to zero or can have fractional value.

[2]

8. Rate constant 'k' of a reaction is defined as the rate of reaction when the concentration of the reactant(s) is unity. Or Rate constant is the proportionality factor in the rate law. **[1]**

(i) Unit for 'k' for a zero order reaction $= mol\ L^{-1}\ s^{-1}$ **[1/2]**

(ii) Unit for 'k' for a first order reaction $= s^{-1}$ **[1/2]**

9. *(i)* An elementary step in a reaction is a chemical reaction in which one or more of the reactants react directly to form products in a single reaction step. **[1]**

(ii) Rate of a reaction is defined as the **rate** of decrease in concentration of any one of the reactants or the rate of increase in concentration of any one of the products. **[1]**

10. Given:

$P_i = 0.30\ atm \quad P_t = 0.50\ atm$

$$\begin{array}{llll} C_2H_5CI(g) \longrightarrow & C_2H_4(g) & + HCl(g) & \\ P_i & 0 & 0 & (\text{At } t = 0\text{ s}) \\ P_i - x & x & x & (\text{At } t = 300\text{ s}) \end{array}$$

$\therefore P_i - x + x + x = P_t \quad 0.30 + x = 0.50 \quad x = 0.20$

$P_i - x = 0.30 - 0.20 = 0.10\ atm$ **[1]**

For a first order decomposition reaction,

$$k = \frac{2.303}{t}\log\left(\frac{P_i}{P_i - x}\right)$$ **[1]**

$$= \frac{2.303}{300}\log\left(\frac{0.30}{0.10}\right)$$

$$= \frac{2.303 \times \log 3}{300}$$

$$= \frac{2.303 \times 0.4771}{300}$$

$k = 0.0037\, s^{-1}$ **[1]**

11. (a) Rate law may be written as

$$\text{Rate} = k\,[NO]^p[Cl_2]^q$$

The initial rate becomes

$$(\text{Rate})_0 = k\,[NO]^p[Cl_2]^q$$

Comparing experiment 1 and 2

$$(Rate)_1 = k(0.15)^p(0.15)^q = 0.60 \ldots \text{(i)}$$

$$(Rate)_2 = k\,(0.15)^p(0.30)^q = 1.20 \ldots \text{(ii)}$$

Dividing equation (ii) by (i)

$$\frac{(Rate)_2}{(Rate)_1} = \frac{k(0.15)^p(0.30)^q}{k(0.15)^p(0.15)^q} = \frac{1.20}{0.60}$$

Or $2^q = 2^1$

$q = 1$

order with respect to $Cl_2 = 1$

Comparing experiment 1 and 3

$$(Rate)_1 = k(0.15)^p(0.15)^q = 0.60 \ldots \text{(i)}$$

$$(Rate)_3 = k(0.30)^p(0.15)^q = 2.40 \ldots \text{(ii)}$$

Dividing equation (ii) by (i)

$$\frac{(Rate)_3}{(Rate)_1} = \frac{k(0.30)^p(0.15)^q}{k(0.15)^p(0.15)^q} = \frac{2.40}{0.60}$$

Or $2^p = 4$

$2^p = 2^2$

$p = 2$

Thus order with respect to NO is 2.

Rate law $= k[NO]^2(Cl_2)^1$ **[1]**

(b) The rate law for the reaction

Rate $= k\ [N0]^2[Cl_2]$

Rate constant can be calculated by substituting the value of rate [NO] and [Cl_2] for any experiment

$$k = \frac{\text{Rate}}{[NO]^2[Cl_2]} = \frac{0.60}{(0.15)^2(0.15)}$$

$$= \frac{0.60}{0.003375}$$

$$= 177.77\,mol^{-2}L^2\min^{-1}$$ **[1]**

(c) Let initial rate of disappearance of Cl_2 in exp 4 is r_4.

$\therefore r_4 = k[N0]^2[C1_2]$

$= 177.77 \times (0.25)^2(0.25) = 2.78$ M/min **[1]**

12. (i) We know that

$$k = \frac{2.303}{t}\log\frac{[A_o]}{[A]}$$

Substituting the values we get,

$$k = \frac{2.303}{20}\log\frac{0.400}{0.289}$$

$$k = \frac{2.303}{20}\log 1.3840$$

Or $k = 0.11515\ \log 1.3840$

$\therefore k = 0.0163\min^{-1}$ **[1]**

(ii) Using the formula, $k = \dfrac{2.303}{t}\log\dfrac{[A_o]}{[A]}$

$$\log\frac{0.400}{[A]} = \frac{0.0163 \times 100}{2.303}$$

$$\log\frac{0.400}{[A]} = 7.0777$$

$\therefore [A] = 0.078\text{M}$ **[1]**

(iii)Initial rate, $R = k[N_2O_5]$

$= 0.0163 \times 0.400 = 0.00652\text{M}\min^{-1}$ **[1]**

13. (a) Rate law $= k[NO]^2[Cl_2]^1$ **[1]**

(b) $R = k[NO]^2[Cl_2]^1$

$$k = \frac{R}{[NO]^2[Cl_2]^1} = \frac{0.60}{(0.15)^2(0.15)^1}$$

$$= \frac{0.60}{(0.15)^3} = 177.75\,mol^{-2}\,L^2\min^{-1}$$ **[1]**

(c) $R_4 = k[NO]^2[Cl_2]^1$

$= 177.75 \times (0.25)^2(0.25)$

$= 2.78\,M/\min$ **[1]**

14.

$$\begin{array}{llll} & SO_2Cl_2 & \longrightarrow SO_2 & + Cl_2 \\ At\ t = 0 & 0.4 & 0 & 0 \\ At\ t = 100 & 0.4 - x & x & x \end{array}$$ **[1]**

$P_t = 0.4 - x + x + x$

$0.7 = 0.4 + x$

$x = 0.3$

$$K = \frac{2.303}{t}\log\frac{P_o}{2P_o - P_t}$$ **[1]**

$$= \frac{2.303}{100}\log\frac{0.4}{2 \times 0.4 - 0.7}$$

$$= \frac{2.303}{1000}\log\frac{0.4}{0.1}$$

$$K = \frac{2.303 \times 0.602}{100} = 1.38 \times 10^{-2}s^{-1}$$ **[1]**

15. $k = 0.0051\, min^{-1}$

$\left[A_o\right] = 0.10\, M$

$T = 3 \text{ hours} = 3 \times 60 \text{ min}$

$$k = \frac{2.303}{t}\log\frac{\left[A_o\right]}{\left[A\right]}$$ **[1]**

$$0.0051 = \frac{2.303}{3\times 60}\log\frac{0.1}{\left[A\right]}$$ **[1]**

$$\log\frac{0.1}{\left[A\right]} = 0.3986 \quad \frac{0.1}{\left[A\right]} = 2.504$$

So, $\left[A\right] = 4.0\times 10^{-2} M$ **[1]**

16. Given: Rate constant,
$k = 0.0030\, molL^{-1}s^{-1}$

Initial concentration,
$\left[R_2\right] = 0.10M$ **[1]**

Concentration after time t,
$\left[R\right] = 0.075M$

For zero order reaction,

$$k = \frac{\left[R_o\right]-\left[R\right]}{t}$$ **[1]**

$$t = \frac{\left[R_o\right]-\left[R\right]}{k}$$

$$t = \frac{0.10M - 0.75M}{0.003\, mol\, L^{-1}s^{-1}}$$

$t = 8.33s$ **[1]**

Topic 2: Integrated Rate Equation, Pseudo First Order Reaction

Summary

- Order of reaction: It is defined as the sum of powers of the concentration of reactants in the rate law expression. It can be zero and even fraction.

  Units of rate constant are different for reactions of different order.

Reaction	Order	Units of rate constant
Zero order reaction	0	mol L^{-1} s^{-1}
First order reaction	1	s^{-1}
Second order reaction	2	mol^{-1} Ls^{-1}

- **Integrated rate equations:** A relation between directly measured experimental data and rate constant is given by integrated rate equation. There are different rate equations for different order of reactions.
  - **Zero order reaction:** Rate of reaction is independent of the concentration of the reactants.

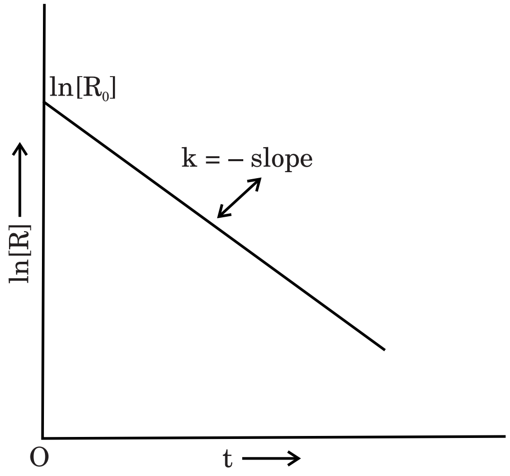
    For the reaction, $2NH_3(g)\xrightarrow[Pt\ catalyst]{1130K}N_2(g)+3H_2(g)$

    Rate = $k\ [NH_3]^0 = k$
  - **First order reaction:** Rate of reaction is directly proportional to the first power of the concentration of the reactants.

    For the reaction, $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

    Rate = $k\ [C_2H_4]$

    $$k = \frac{2.303}{t}\log\frac{[A_o]}{[A]}$$



Graph showing the relation between *ln* [*R*] and t for first order reaction

  - **Second order reaction:** In this rate law the sum of powers of concentration terms in rate law is equal to 2.

    For example: $A + B \rightarrow C + D$

    $$\frac{dx}{dt} = k[A]'[B]'$$

- Pseudo first order reaction: The reaction is not of first order but certain conditions makes the reaction of first order.

  For example: Reaction of ethyl acetate with water.

  $$CH_3COOHC_2H_5 + H_2O \xrightleftharpoons{H^+} CH_3COOH + C_2H_5OH$$

  It should be of second order but water is in very less quantity so it is pseudo first order reaction.

- **Half life of a reaction:** The time in which concentration of the reactant reduces to half of the initial concentration is called half-life of a reaction. It is represented as $t_{½}$.

  For a zero order reaction, the rate constant at $t_{½}$,

  $$k = \frac{[R]_o}{2t_{1/2}}$$

  For a first order reaction, the rate constant at $t_{½}$

  $$t_{1/2} = \frac{0.693}{k}$$

PREVIOUS YEARS'

EXAMINATION QUESTIONS

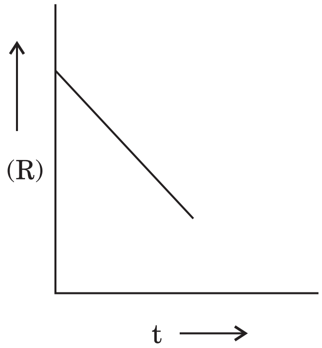
TOPIC 2

2 Mark Questions

1. The thermal decomposition of HCO_2H is a first order reaction with a rate constant of $2.4 \times 10^{-3}\, s^{-1}$ at a certain temperature. Calculate how long will it take for three-fourths of initial quantity of HCO_2H to decompose.
   ($log0.25 = -0.6021$) **[ALL INDIA 2011]**

2. For a reaction $A + B \rightarrow P$, the rate law is given by $r = k[A]^{1/2}[B]^2$
   (a) 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. **[ALL INDIA 2013]**

3. For a chemical reaction $R \rightarrow P$, the variation in the concentration (R) vs. time (t) plot is given as



   (i) Predict the order of the reaction.
   (ii) What is the slope of the curve?
   [ALL INDIA 2014]

4. Define the following terms:
   (i) Pseudo first-order reaction
   (ii) Half-life period of reaction ($t_{1/2}$).
   [DELHI 2014]

5. Explain the following terms:
   (i) Rate constant (k)
   (ii) Half life period of reaction ($t_{1/2}$)
   [DELHI 2014]

6. A reaction is of first order in reactant A and of second order in reactant B. How is the rate of this reaction affected when
   (i) the concentration of B alone is increased to three times
   (ii) the concentrations of A as well as B are doubled? **[DELHI 2018]**

3 Mark Questions

7. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time taken when 75% of the reaction will be completed?
   (Given: $log2 = 0.3010$, $log3 = 0.4771$, $log4 = 0.6021$)
   [ALL INDIA 2017]

8. A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its $t_{1/2}$ value. **[DELHI 2016]**

5 Mark Questions

9. (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 concentrations 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)

OR

(a) For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

(b) Rate constant 'If 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. ($R = 8.314 \, J^{-1} \, mol^{-1}$) **[DELHI 2013]**

10. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:

t/s	0	30	60
$[CH_3COOCH_3]/mol\ L^{-1}$	0.60	0.30	0.15

(i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.

(ii) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

(Given log 2 = 0.3010, log 4 = 0.6021)

OR

(a) For a reaction $A + B \rightarrow P$, the rate is given by

Rate = $k[A][B]^2$

(i) How is the rate of reaction affected if the concentration of B is doubled?

(ii) What is the overall order of reaction if A is present in large excess?

(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction.

(log 2 = 0.3010) **[DELHI 2015]**

Solutions

1. $t = \frac{2.303}{k} \log \frac{[A_o]}{[A_t]}$ **[1]**

$[A_t] = [A_0] - \quad [A_0] = \quad [A_t]$

$$t = \frac{2.303}{2.4 \times 10^{-3}\, s^{-1}} \log \frac{[A_o]}{[A_o]/4}$$

$$t = \frac{2.303}{2.4 \times 10^{-3}\, s^{-1}} \log 4$$

$$t = \frac{2.303}{2.4 \times 10^{-3}\, s^{-1}} \times 0.60212$$

$t = 578\, s$ **[1]**

2. (a) order of reaction is $= 2 + \frac{1}{2} = 2\frac{1}{2}$ **[1]**

(b) $t_{\frac{1}{2}} = \frac{0.693}{K} = \frac{0.693}{5.5 \times 10^{-14}} = 0.126 \times 10^{14}$ **[1]**

$t_{\frac{1}{2}} = 1.26 \times 10^{13}$ sec

3. (i) Order of reaction = 0 **[1]**

As integrated rate law is $(a_0 - x) = -kt + a_0$

(ii) And slope of curve = $-k$ **[1]**

4. (i) Reactions which are actually first order but behave as second order under certain conditions like excess of one of the reactants, are psuedo first order reaction, e.g. Acid hydrolysis of ethyl acetate. **[1]**

(ii) The time taken for the concentration of reactants to be reduced to half of its initial value is called the half life of a reaction. **[1]**

5. (i) Rate constant (k) is the rate of reaction when the concentration of reactants is unity. **[1]**

(ii) Half life period ($t_{1/2}$) of reaction is the time in which the concentration of reactant is reduced to half of its initial concentration. **[1]**

6. (*i*) It is given that a reaction is first order in reactant A and second order in reactant B$r = k[A][B]^2$ Where r is the rate of reaction and k is the rate constant of the reaction

When concentration of B alone is increased three times, let the new rate be r_1. **[1]**

$$\therefore \quad r_1 = k[A]\,[3B]^2 = 9k\,[A]\,[B]^2 \text{(Eq-2)}$$

Divide (Eq-2) by (Eq-1)

$\therefore\ r_1 = 9r$

Thus, when the concentration of B alone is increased to three times, rate of reaction increases by 9 times

(*ii*) When concentration of A and B are doubled, let the new rate be r_2, **[1]**

$$\therefore \quad r_2 = k[2A]\,[2B]^2 = 8k[A]\,[B]^2$$

$\therefore\ r_2 = 8r$

Thus, when the concentration of A and B are doubled, the rate of reaction increases by 8 times.

7. For the first order reaction

$$k = \frac{2.303}{t}\log\frac{a}{a-x} \qquad \textbf{[1]}$$

When $x = \frac{25}{100}a = 0.25\,a$

$t = 20$ minutes (given)

Therefore, $k = \frac{2.303}{20}\log\frac{a}{a-0.25a}$

$$k = \frac{2.303}{20}\log\frac{1}{0.75a} = 0.013120\ min^{-1} \qquad \textbf{[1]}$$

Hence the value of the rate constant is 0.013120 min^{-1}

Now we need to find Time for rest 75% reaction t= ?, when x = 0.75 a

From above,

k = 0.013120 min^{-1}

Therefore,

t = (2.303 / 0.013120) log (a / a – 0.75 a)

= (2.303 / 0.013120) log (1 / 0.25)

= 105.6 min.

The time at which the reaction will be 75% complete is 105.6 min. **[1]**

8. $$k = \frac{2.303}{t}\log\frac{[A_o]}{[A]} \qquad \textbf{[1]}$$

$$k = \frac{2.303}{40}\log\frac{[100]}{[70]}$$

$$k = \frac{2.303}{40}\times 0.155 = 0.00892\,\text{min}^{-1} \qquad \textbf{[1]}$$

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$t_{\frac{1}{2}} = \frac{0.693}{0.00892}\text{min}$$

$t_{1/2} = 77.7$ min **[1]**

9. (a)

(*i*) A reaction is second order in A and first order in B.

$$\text{Rate} = \frac{-d[R]}{dt} = K[A]^2[B] \qquad \textbf{[1]}$$

(*ii*) On increasing the concentration of 'A' three times i.e. 3A; the rate of reaction becomes 9 times of the initial rate.

$$\text{Rate} = K[3A]^2[B] = 9K[A]^2[B] =$$

= 9 times rate **[1]**

(*iii*) On increasing the concentration of A and B as 2A and 2B. The rate of reaction becomes 8 times of the initial rate. Rate $= K[2A]^2[2B] = 8K[A]^2[B] =$

= 8 times rate **[1]**

(b)

$$\begin{array}{lcc} & A \longrightarrow & P \\ t = 0 & a & 0 \\ t = t & (a-x) & x \end{array}$$

Now, it takes 40 min for 30% decomposition

i.e. reactant left after 40 min is 70% of its

initial concentration.

So, $(a-x) = \frac{70}{100}a = \frac{7}{10}a$

Using the formula,

$$k = \frac{2.303}{t}\log\frac{a}{a-x} \qquad \textbf{[1]}$$

$$= \frac{2.303}{40} \log \frac{a}{(7/10)a}$$

$$= 0.00891\,\text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.008913}$$

$$\therefore t_{1/2} = 77.78\,\text{min}$$ **[1]**

OR

(a) For a first order reaction,

$$\begin{array}{lll} & A \longrightarrow & P \\ t=0 & a & 0 \\ t=t & (a-x) & x \end{array}$$

Case 1: If t is the time required for 99% completion then x = 99% of a and $(a - x)$ = 1% of $a = \frac{1}{100} \times a = \frac{a}{100}$

$$\therefore t_{99\%} = \frac{2.303}{K} \log \frac{a}{a-x}$$

$$= \frac{2.303}{K} \log \frac{a \times 100}{a} = \frac{2.303}{K} \log 10^2$$ **[1]**

$$t_{99\%} = 2\left[\frac{2.303}{K}\right]$$

Case 2: If t is the time required for 90% of completion then x = 90% of a and

$a - x$ = 10% of a

$$= \frac{10}{100} a = \frac{a}{10}$$

$$t_{90\%} = \frac{2.303}{K} \log \frac{a}{a-x}$$

$$= \frac{2.303}{K} \log \frac{a \times 10}{a}$$

$$t_{90\%} = \frac{2.303}{K}$$

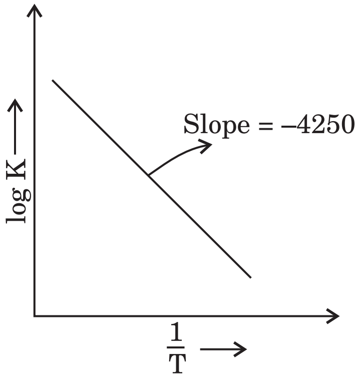
$$\therefore \frac{t_{99\%}}{t_{90\%}} = \frac{\left(\frac{2 \times 2.303}{k}\right)}{\left(\frac{2.303}{k}\right)} = 2$$

$$\therefore t_{99\%} = 2 \times t_{90\%}$$ **[1]**

So, the time required for 99% completion of 1st order reaction is twice the time required for 90% completion.

(b) We know that, $\log k = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$ **[1]**

The above equation is like $y = mx + c$, where if we plot 'y' vs 'x' we get a straight line with slope 'm' and intercept 'c'.



Hence, slope is equal to $\frac{-E_a}{2.303R}$ **[1]**

$$\frac{-E_a}{2.303R} = -4250K$$

$$\therefore E_a = 4250 \times 2.303 \times 8.314 \left(JK^{-1}mol^{-1}\right)$$

$$= 81{,}375.3535\,Jmol^{-1}$$

$$E_a = 81.3733\,kJ\,mol^{-1}$$ **[1]**

10. For the hydrolysis of methyl acetate in aqueous solution:

(i) $K = \frac{2.303}{t} \log \frac{[A]_o}{[A]}$ **[1]**

Where $[A]_0$ = Initial concentration of reactant

$[A]$ = Final concentration of reactant

At $t_1 = 30\,\text{sec}$,

$$K = \frac{2.303}{30} \log \frac{0.60}{0.30}$$ **[1]**

$$K = 0.07677 \log 2$$

$$K = 0.0231 s^{-1}$$

For t = 60 sec

$$K = \frac{2.303}{60} \log \frac{0.60}{0.15}$$

$$K = 0.07677 \log 2$$

$$K = 0.0231 s^{-1}$$

$\therefore$K is same for both the cases hence it is pseudo first order reaction. **[1]**

(ii) Average rate of reaction between the time interval of 30 – 60 seconds is given by

$$K = \frac{-\Delta\left[CH_3COOCH_3\right]}{\Delta t}$$ **[1]**

$$K = -\left(\frac{0.15 - 0.30}{60 - 30}\right)$$

$$= \frac{0.15}{30} = 0.005 \, mol \, L^{-1} s^{-1}$$ **[1]**

OR

(a)

(i) Since the given reaction has order two with respect to reactant B, thus if the concentration of B is doubled in the given reaction, then the rate of reaction will become four times. **[1]**

(ii) It the concentration of B is doubled i.e., $[B]^2$ the overall reaction will be two, because if A is present in large excess, then the reaction will be independent of the concentration of A and will be dependent only on the concentration of B. Order of reaction = 2. **[1]**

(b) $t_{1/2} = 30 \min$

$$\left[R\right] = \left[R\right]_o - 90\% \text{ of } \left[R\right]_o$$

$$= \left[R\right]_o - \frac{90\left[R\right]_o}{100}$$ **[1]**

$$\left[R\right] = \frac{\left[R\right]_o}{10}$$

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 0.0231 \min^{-1}$$

$$t = \frac{2.303}{K} \log \frac{\left[R\right]_o}{\left[R\right]}$$ **[1]**

$$t = \frac{2.303}{0.0231} \log \frac{\left[R\right]_o}{\frac{\left[R\right]_o}{10}} = \frac{2.303}{0.0231} \log 10$$

$$t = 99.7 \min$$ **[1]**

Topic 3: Temperature Dependence of the Rate of a Reaction, Collision Theory of Chemical Reactions

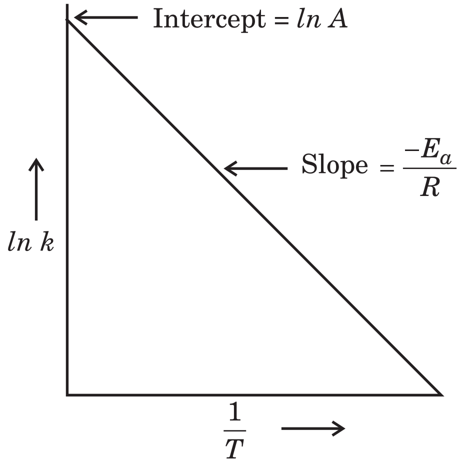
Summary

Electrostatic potential:

- The rate of a reaction depends on temperature. As the temperature increases, rate of reaction increases.
- **Activation Energy:** It is the energy of reactant molecules so that collision of molecules leads to formation of products. It cannot be negative.
- **Threshold energy:** It is the minimum energy required by the reactants to form products.
- **Arrhenius equation:** The relation between rate of reaction and temperature is given in the Arrhenius equation.

  $$k = Ae^{\frac{-E_a}{RT}}$$

  $$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$



- **Collision Theory:** According to this theory, It is assumed that reactant molecules are hard spheres and reaction occurs when reactant molecules collide with each other.

  Number of collisions per second per unit volume gives collision frequency.

  Rate $= Z_{AB}e^{\frac{-E_a}{RT}}$

  Where Z_{AB} is the collision frequency

  When molecules collide with sufficient kinetic energy to facilitate breaking of bonds to form products, it is called effective collisions.

  Rate of reaction $= f \times z$

  Where f is the frequency of effective collisions.
- Collision theory ignores the structural aspect and considers molecules as hard spheres which is a drawback of collision theory.

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 3

1 Mark Questions

1. What is the effect of adding a catalyst on:

   (a) Activation energy (E_a) and

   (b) Gibbs energy (ΔG) of a reaction?

   [ALL INDIA 2017]

2 Mark Questions

2. Determine the values of equilibrium constant (Kc) and **Δ**G° and for the following reaction:

$$Ni(s) + 2Ag^{+}(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$$

$$E^{o} = 1.05V\left(1F = 96500C\,mol^{-1}\right)$$

[DELHI 2011]

3 Mark Questions

3. The rate of a reaction becomes four times when the temperature changes from 293 K to 313 K. Calculate the energy of activation (E_a) of the reaction assuming that it does not change with temperature. [$R = 8.314\ J\ K^{-1}\ mole^{-1}$, $log4 = 0.6021$] **[ALL INDIA 2013]**

4. A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320K. Calculate the activation energy of the reaction. (Given: $log2 = 0.3010$, $log4 = 0.6021$, $R = 8.314\ JK^{-1}\ mol^{-1}$) **[ALL INDIA 2018]**

Solutions

1. (a) Catalyst provides a new reaction pathway in which a lower activation is offered. Hence, catalyst increases the rate of reaction by lowering the activation energy. **[1/2]**

   (b) Gibbs free energy will remain same as for catalyzed & uncatalyzed reaction, as the equilibrium constant is not affected which is a function of Gibbs free energy.

   [1/2]

2. According to the formula

$$\Delta G^{\circ} = -nFE^{\circ} = -2 \times 96500 \times 1.05$$

Or $\Delta G^{\circ} = -202650J\,mol^{-1} = -202.65KJ\,mol^{-1}$

[1]

Now $\Delta G^{\circ} = -202650\,J\,mol^{-1}$

$R = 8.314\,J/mol,\ T = 298K$

$$\log K = \frac{\Delta G^{\circ}}{2.303RT}$$

$$\Rightarrow \log K = \frac{-202650}{2.303 \times 8.314 \times 298}$$

$$\log K = \frac{-202650}{5705.8431} = 35.52$$

$K = Anti\log\ of\ 35.52$

$\therefore K = 0.35 \times 10^{7}$ **[1]**

3. $$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$ **[1]**

$$\log 4 = \frac{E_a}{2.303 \times 8.314}\left(\frac{1}{293} - \frac{1}{313}\right)$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314}\left(\frac{313 - 293}{313 \times 293}\right)$$ **[1]**

$$E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20}$$

$= 52863.33J = 52.863KJ$ **[1]**

4. $$T_2 = 320K,\ K_2 = \frac{0.693}{20}$$

$$T_1 = 300K,\ K_1 = \frac{0.693}{40}$$

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$ **[1]**

$$\log\frac{\frac{0.693}{20}}{\frac{0.693}{40}} = \frac{E_a}{2.303 \times 8.314}\left(\frac{320 - 300}{320 \times 300}\right)$$

$$\log\left(\frac{40}{20}\right) = \frac{E_a}{2.303 \times 8.314}\left(\frac{20}{320 \times 300}\right)$$ **[1]**

$$1.6021 - 1.3010 = \frac{E_a}{2.303 \times 8.314}\left(\frac{20}{320 \times 300}\right)$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 320 \times 300}{20}$$

$= 27764\ J$

$= 27.76\ KJ$ **[1]**

Smart Notes ....

CHAPTER 5

Surface Chemistry

Chapter Analysis with respect to Last 3 Years' Board Exams

List of Topics	2016		2017		2018	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Adsorption - physisorption and chemisorption, factors affecting adsorption of gases on solids			(3 marks)			
Catalysis, Homogeneous and Heterogenous activity and selectivity; enzyme catalysis					(1 mark)	(1 mark)
Colloidal state distinction between true solutions, colloids and suspension	(1 mark)	(1 mark)	(1 mark)	(1 mark)	(3 marks)	(3 marks)
Lyophilic , lyophobic multimolecular and macromolecular colloids	(3 marks)	(3 marks)				
Properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation, emulsion - types of emulsions.			(3 marks)	(3 marks)		

Topic 1: Adsorption

Summary

- The area of chemistry that deals with the phenomena resulting from combined chemical and electrical effects is called Electrochemistry.
- Surface chemistry: The branch of chemistry which deals with the phenomenon that occur at the surfaces or interfaces. This phenomenon is usually studied with the help of adsorption and colloidal state.

Adsorption

- Adsorption: The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption. The surface that adsorbs is known as adsorbent whereas the one that gets adsorbed is known as adsorbate. For example: Silica and aluminium gels are used to adsorb moisture to reduce humidity.
- Types of adsorption:
  - ➢ Physisorption: It is also known as physical adsorption. When the gas is accumulated on the surface of the solid on account of weak van der Waal's forces, it is known as physical adsorption or physisorption.
  - ➢ Chemisorption: It is also known as chemical adsorption. When the gas molecules or atoms are held to the solid surface by chemical bonds, it is known as chemical adsorption or chemisorptions.
- Desorption: It is a process of removing an adsorbed substance from the surface of an adsorbent.
- In absorption, the substance is uniformly distributed throughout the bulk of the solid. For example: Chalk stick dipped in ink.
- Sorption: When adsorption and absorption takes place simultaneously, it is called sorption. For example: Cotton dipped in ink.
- Enthalpy of adsorption: Adsorption generally occurs with the release of energy and is exothermic in nature. The enthalpy change for the adsorption of one mole of an adsorbate on the surface of adsorbent is called enthalpy or heat of adsorption.
- Difference between Adsorption and Absorption:

Adsorption	Absorption
It is a surface phenomenon	It concerns with the whole mass of the absorbent.
The concentration of the adsorbate at the surface of adsorbent is much more than that in the bulk.	Absorbed material is uniformly distributed throughout the bulk. Thus, concentration is same throughout.
It is rapid in the beginning and slows down near the equilibrium.	It occurs at a uniform rate.
Example: NH_3 is adsorbed by charcoal.	Example: NH_3 is absorbed in water to form NH_4OH.

- Factors affecting adsorption of gases on solids:
  - Nature of gas
  - Nature of adsorbent
  - Specific area of the solid
  - Pressure of the gas
  - Effect of temperature
  - Activation of adsorbent
- Adsorption isobar: A plot of extent of adsorption $\left(\frac{x}{m}\right)$ vs. temperature (T) at constant pressure is called adsorption isobar.
- Adsorption isotherm: A plot of extent of adsorption $\left(\frac{x}{m}\right)$ vs. pressure (P) at constant temperature is called adsorption isotherm, where 'x' is the quantity of the gas adsorbed by unit mass 'm' of the solid adsorbed.
- Freundlich Adsorption Isotherm: It gives the relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a constant temperature. It is represented by a mathematical equation,

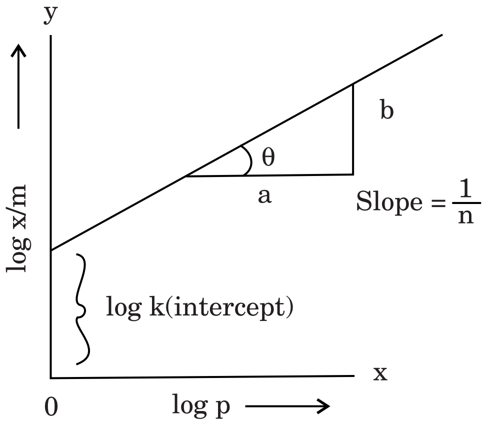
$$\frac{x}{m} = kp^{1/n} \qquad \ldots\ldots (1)$$

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \qquad \ldots\ldots.. (2)$$

A plot of $\log \frac{x}{m}$ vs. $\log p$ gives a straight line with slope $\frac{1}{n}$ and y intercept = $\log k$.

In case of solution, the isotherm takes the form,

$$\frac{x}{m} = k(C)^{1/n} ; \log \frac{x}{m} = logk + \frac{1}{n} \log C$$



Where x is the amount of adsorbate adsorbed on m gram of adsorbent at pressure p or concentration C of the adsorbate, k and n are constants, $n > 1$.

- **Applications of adsorption:**
  - In the preparation of gas masks using activated charcoal.
  - Froth floatation method used for concentration of sulphide ores.
  - Silica gel is used to remove moisture.
  - Ion exchange method used to soften water.
  - Adsorption chromatography is used to purify and separate pigments, hormones etc.
  - Charcoal powder can remove coloured impurities from sugar.
  - Charcoal is used for making high vacuum.
  - The cleaning action of soaps and detergents.
  - In heterogeneous catalysis.
  - In curing diseases.

PREVIOUS YEARS'
EXAMINATION QUESTIONS
TOPIC 1

1 Mark Question

1. Of physisorption or chemisorption, which has a higher enthalpy of adsorption?

[ALL INDIA 2013]

3 Mark Question

2. Define adsorption with an example. Why is adsorption exothermic in nature? Write the types of adsorption based on the nature of forces between adsorbate and adsorbent.

[ALL INDIA 2015]

Solutions

1. Chemisorption has higher enthalpy of adsorption **[1]**

2. The accumulation of molecular species at the surface rather than in the bulk of a solid is termed as adsorption. eg the air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel. During adsorption, there is always bond formation between adsorbate and adsorbent and it results in release of energy. **[2]**

There are two types of adsorption on the basis of nature of forces –

(i) Physisorption which occur due to Vander Waal's force of attraction **[½]**

(ii) Chemisorption which occur due to chemical bond **[½]**

Topic 2: Catalysis

Summary

- Catalysis: Catalyst is a substance that is used to increase the rate of the reaction without changing itself and this process is known as catalysis. For example,

  $$C_6H_6 + Cl_2 \xrightarrow{AlCl_2} C_6H_5Cl + HCl$$

  The catalyst remains unchanged with respect to mass and composition. Catalyst does not affect ΔH, ΔS. ΔG and equilibrium constant k.
- Promoters: Those substances which increase the activity of the catalysts are called promoters. For example, *Mo* is promoter whereas *Fe* is catalyst in Haber's process.

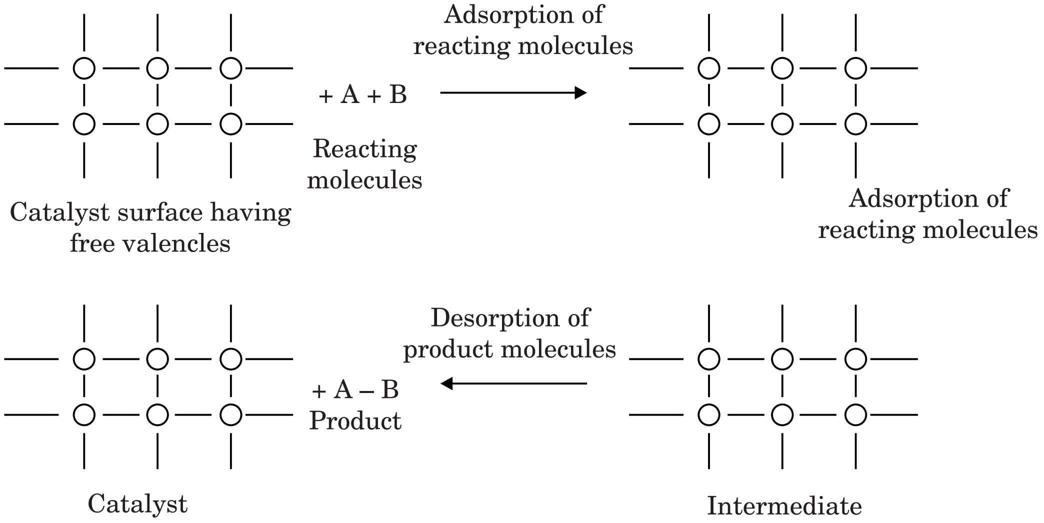
  $$N_2(g) + 3H_2(g) \underset{Mo}{\overset{Fe}{\rightleftharpoons}} 2NH_3(g)$$

- Poisons or Inhibitors: Substances which destroy the activity of the catalyst by their presence are known as poisons or inhibitors. For example,

  Arsenic acts as catalytic poison in the manufacturing of sulphuric acid by contact process.
- Types of catalysis:
  - Homogeneous Catalysis: A catalytic process where the reactants and the catalyst are in the same phase (i.e. liquid or gas). For example,

    Catalytic oxidation of SO_2 to SO_3 in presence of *NO* is an example of Homogeneous catalysis.
  - Heterogeneous Catalysis: A catalytic process where the reactants and the catalyst are in different phase. For example,

    Hydrogenation of vegetable oils in the presence of finely divided nickel as catalyst.
- **Adsorption theory of Heterogeneous Catalysis:** According to modern adsorption theory, there are free valencies on the surface of solid catalyst and mechanism involves following five steps:
  - Diffusion of reactants to the surface of the catalyst.
  - Adsorption of reactant molecules on the surface of the catalyst.
  - Occurrence of a chemical reaction forming an intermediate on the surface.
  - Desorption of the product molecules from the surface.
  - Diffusion of product molecules away from the surface of the catalyst.



- Important features of solid catalysts:
  - Activity: It is the ability of catalyst to increase the rate of reaction.
  - Selectivity: It is the ability of a catalyst to direct the reaction in such a way, that we get a desired product.
- Shape-selective catalysis by zeolites: It is the catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules. Zeolites are shape selective catalyst having honey comb structures. Zeolite catalyst, ZSM-5 is used in petroleum industry to convert alcohols into gasoline by dehydration.
- Enzyme Catalysis: Enzymes are complex nitrogenous organic compounds produced by living plant and animals which are basically protein molecules but with high molecular mass and form colloidal solution in water. In enzyme catalysis, specific biochemical reactions occur. For example, decomposition of urea into ammonia and carbon dioxide. The enzyme urease catalyses this decomposition.

$$\underset{(Urea)}{NH_2CONH_2} + H_2O \xrightarrow{Urease} 2NH \ \ + CO_2$$

- **Characteristics of enzymes:**
  - Enzymes are very active catalysts as they form a colloidal solution in water.
  - Like inorganic catalyst they cannot disturb the final state of equilibrium of a reversible reaction.
  - They are highly specific in nature.
  - They have an optimum temperature range between 25°C–35°C and get deactivated at 70°C. Hence, they are highly specific to temperature.
  - A small quantity of enzyme is sufficient for a large change.
  - They are destroyed by UV rays.
  - Their efficiency is decreased in the presence of electrolytes.
- Mechanism of enzyme catalysed reaction: This type of reaction may proceed in two steps,
  - Binding the enzyme to substrate to form an activated complex.

    $$E + S \longrightarrow ES^{\neq}$$

  - Decomposition of the activated complex to form product.

    $$ES^{\neq} \longrightarrow E + P$$

- Co-enzymes: Certain substances, which can increase the activity of enzymes are known as Co-enzymes.

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 2

▶ 1 Mark Questions

1. What is meant by 'shape selective catalysis? **[ALL INDIA 2011]**

2. $CO(g)$ and $H_2(g)$ react to give different products in the presence of different catalysts,Which ability of the catalyst is shown by these reactions? [**ALL INDIA 2018**]

▶ 2 Marks Question

3. Name the two groups into which phenomenon of catalysis can be divided. Give an example of each group with the chemical equation involved. [**ALL INDIA 2012**]

Solutions

1. The catalytic reaction in which the pore structure of the catalyst and the size of the reactant and product molecules are comparable.

   A catalytic reaction which depends upon the pore structure of the catalyst and on the size of the reactant and the product molecules is called shape-selective catalysis. For example, catalysis by zeolites is a shape-selective catalysis. The pore size present in the zeolites ranges from 260-740 pm. Thus, molecules having a pore size more than this cannot enter the zeolite and undergo the reaction. **[1]**

2. This ability is known as catalytic selectivity which implies that catalyst also can take part in the reaction.

   The characteristic shown by the catalyst is selectivity, i.e, the catalyst determines the products formed.

   If CO and H_2 react in the presence of Ni (nickel) as catalyst the product is methane.

   If CO and H_2 react in the presence of Cu (copper) as catalyst the product formed is methanol. **[1]**

3. The phenomenon of catalysis can be divided into two groups.

   (i) **Homogeneous catalysis**: When the reactant and catalyst are in same phase

   Eg. $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$ **[1]**

   (ii) **Heterogeneous catalysis**: When the reactant and catalyst are in different phase

   $$4NH_3(g) + 5SO_2(g) \xrightarrow{Pt(s)} 4NO + 5S + 6H_2O$$ **[1]**

Topic 3: Colloids

Summary

- Colloids: A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium. The size of colloidal particles is in the range 1-100 nm.
- Colloidal solution: Colloidal solutions, or colloidal suspensions, are nothing but a mixture in which the substances are regularly suspended in a fluid. It is a heterogeneous system in which a very tiny and small material is spread out uniformly all through another substance called dispersion medium. For example, glue, ink, water etc.
- Dispersed phase: It is a component present in small proportion like solute in solution.
- Dispersion medium: The medium in which the colloidal particles are dispersed is called dispersion medium.
- Crystalloids: The substances whose aqueous solution can pass through a semi-permeable membrane are called crystalloids.

Types of colloidal solutions:

Dispersed phase	Dispersion Medium	Name	Examples
Solid	Gas	Aerosol	Smoke, dust particles
Solid	Liquid	Sol	Gold Sol, starch, muddy water
Solid	Solid	Solid Sol	Coloured gem stones, pearls, ruby glass
Liquid	Solid	Gel	Cheese, butter
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog mist, cloud
Gas	Solid	Solid foam	Foam rubber, cork
Gas	Liquid	Foam	Whipped cream, soap lather

Classification based on nature of interaction between:

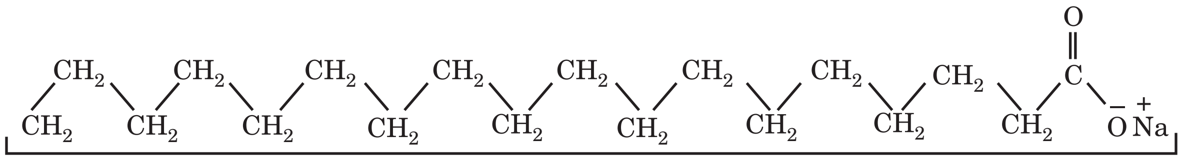
- ➢ Lyophillic Colloids: Lyophillic means "liquid loving", thus, lyophillic colloids are colloids mixed with suitable liquid with high force of attraction between the colloids and the solvent. They are also known as intrinsic colloids. For example, gelatin, starch, etc.
- ➢ Lyophobic Colloids: Lyophobic means "liquid hating", thus, lyophobic colloids consists of the phases which do not interact with each other. Their solution can only be prepared by special methods. They are also known as extrinsic colloids. For example, metals and their sulphides.

Classification based on the type of particles of the dispersal phase:

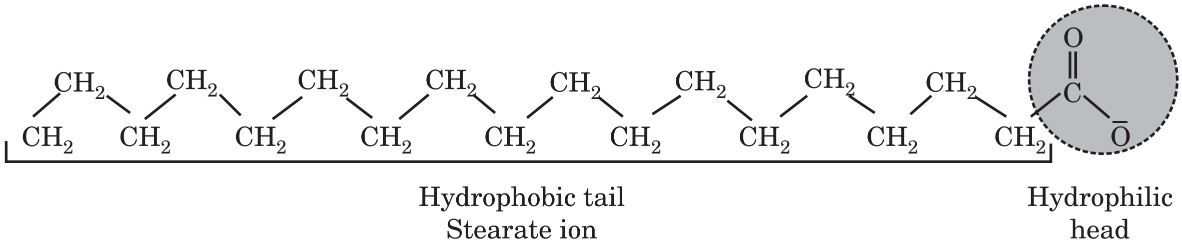
- ➢ Multimolecular Colloids: When a large number of dispersed particles (having diameter less than 1nm) combine together in a dispersion medium to form aggregates of many molecules, it is known as multimolecular colloids. For example, sulphur sol, gold sol etc.
- ➢ Macromolecular Colloids: When certain substances form large molecules whose dimensions are comparable to those of colloidal particles, they are known as macromolecules. When such substances are dispersed in suitable medium, the resulting colloidal solution is known as macromolecular solution. For example, Polythene, nylon etc.
- ➢ Associated Colloids (Micelles):

Micelles: Those colloids which behave as normal strong electrolytes at low concentrations, show colloidal properties at higher concentration due to the formation of aggregated particles of colloidal dimensions. Such compounds are also referred to as associated colloids

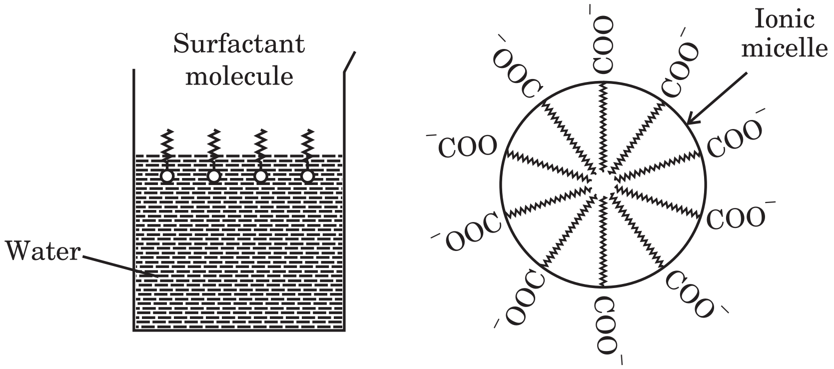
Mechanism of micelles formation: Molecules having lyophillic as well as lyophobic ends generally form micelles. Such types of molecules are known as surface active molecule. Soap is sodium or potassium salt of a higher fatty acid and may be represented as $RCOONA^+$. When dissolved in water, it breaks down into $RCOO^-$ and NA^+ ions. However, it contains two parts – a long hydrocarbon chain R which is hydrophobic and a polar group COO^-, which is hydrophilic.



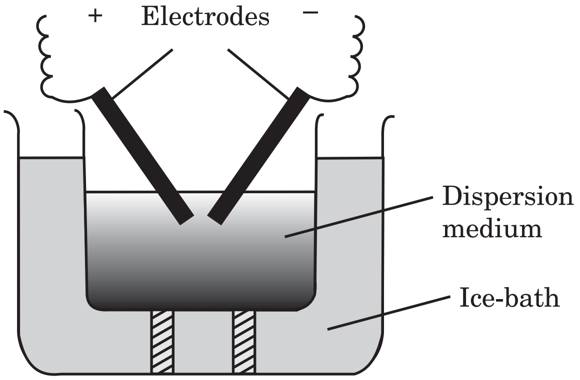
Sodium stearate ($C_{12}H_{33}\,\overset{-}{COO}\,\overset{+}{Na}$)



The $RCOO^-$ ions are present on the surface with their COO^- groups in water and the hydrocarbon chains R staying away from it and remains at the surface. At the critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a spherical shape with their hydrocarbon chains pointing towards the centre of the sphere whereas, the COO^- part remaining outward on the surface of the sphere. The result of this is known as 'ionic micelle'.



- **Preparation of colloidal solution:** Colloidal solutions can be prepared by following methods:
  - **Mechanical dispersion:** A suspension of coarsely ground particles prepared in dispersion medium is fed into a colloidal mill and speed of rotation is adjusted so as to get the particles of colloidal size.
  - **Electrical disintegration or Bredig's Arc method:** This process involves dispersion as well as condensation. In this method, two rods of the metal (Au, Cu, Pt, Ag) are immersed in cold and a direct electric arc is struck between them. This results in the formation of vapours of metal which in turn condense to form particles of colloidal size.



- **Chemical Methods:**

Oxidation: Solutions of non-metals are prepared by this method. For example,

$$2H_2S + 2(O) \xrightarrow{HNO_3(Conc.)} 2S + 2H_2O$$

Reduction: Metal sols can be prepared by this method. For example,

$$2AuCl_3 + 3SnCl_2 \longrightarrow 2Au + 3SnCl_4$$

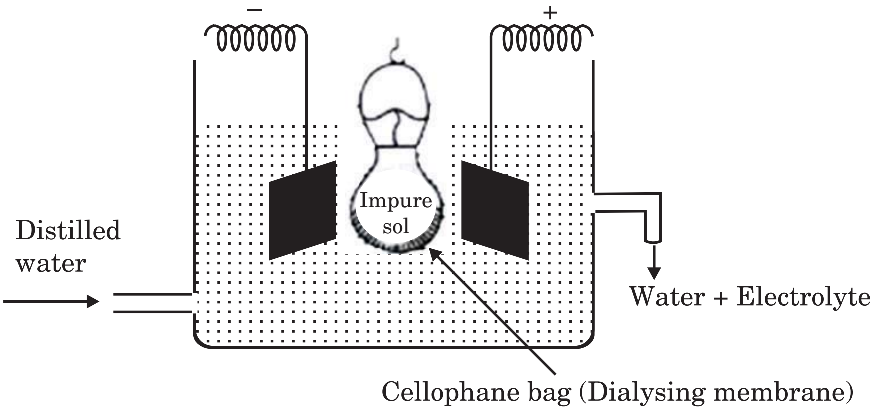
Hydrolysis: Hydroxides sols are prepared by this method.

$$FeCl_3 + 3H_2S \longrightarrow Fe(OH)_3 + 3HCl$$

Double decomposition: This method is used to prepare colloids from inorganic salts.

Exchange of solvent: There are a few substances that form true solution in one solvent but forms colloidal solution in another due to lower solubility. For example, sulphur dissolved in alcohol forms colloidal solution in water.

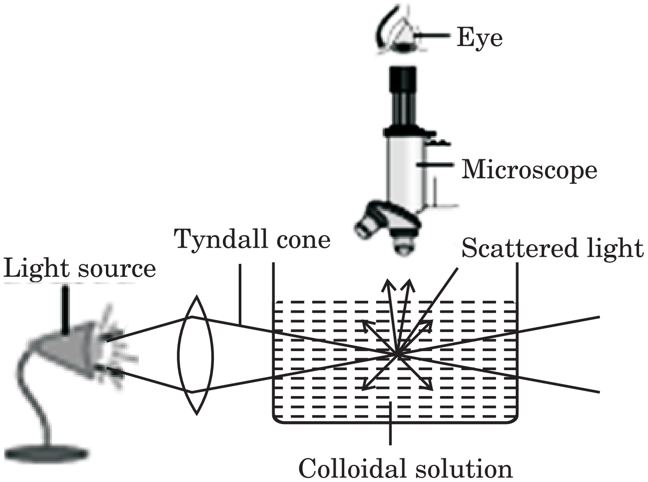
- **Peptization:** When precipitates are passed into a colloidal solution in presence of an electrolyte, it is known as peptization. The electrolyte used is known as peptizing agent.
- **Purification methods of colloidal solutions:** Colloidal solution can be purified by following methods:
  - **Dialysis:** In dialysis, a dissolved substance is removed from a colloidal solution by means of diffusion through a suitable membrane. The membrane used is usually a parchment paper or cellophane membrane.
  - **Electrodialysis:** This method is faster than simple dialysis because in this method, movement of ions across the membrane can be quickened by applying electric potential through two electrodes.



  - **Ultrafiltration:** The process of separating colloidal particles by specially prepared filter papers whose pores is reduced by dipping it in a solution made up of 4% of nitrocellulose in mixture of alcohol and ether.

Properties of colloids:

- **Brownian movement:** The haphazard movement of colloidal particles is known as Brownian movement. The movement of particles is observed under a powerful microscope.
- **Tyndall effect:** Scattering of light by colloidal particles is called Tyndall effect.



Tyndall effect

- **Electrophoresis:** When electricity is passed through a colloidal solution, the colloidal particles move towards one of the electrodes. This phenomenon is called electrophoresis.

Hardy-Schulze rules:

- Opposite charged ions are effective for coagulation.
- The coagulating power of electrolyte increases with increase in charge on the ions used for coagulation. For example, $Al^{3+} > Ba^{2+} > Na^{+}$ for negatively charged colloids.

Coagulation value is the inverse of coagulating power, i.e. lower the coagulation value, higher will be coagulating power.

- **Electrokinetic Potential or Zeta Potential:** The potential difference between the fixed layer and diffused layer of opposite charges is called zeta potential.
- **Coagulation:** It is a process by which a liquid changes into a solid or semi-solid state.
- **Coagulating value:** The minimum concentration of an electrolyte which is required to cause the coagulation is known as coagulating value.

$$Coagulation\,Value \propto \frac{1}{Coagulating\,Power}$$

- **Emulsions:** They are the type of colloidal system where the dispersed phase and the dispersion medium both are liquids. There are two types of emulsions:
  - **Oil in water:** In this type of emulsion, oil is the dispersed phase and water is the dispersion medium. For example, milk.
  - **Water in oil:** In this type of emulsion, water is the dispersed phase and oil is the dispersion medium. For example, butter.
- **Emulsification:** It is a process of preparing an emulsion.
- **Emulsifying agent:** It is a substance used in emulsification, to stabilize the emulsion. For example, soap and detergents.
- **Demulsification:** The process of decomposing an emulsion into it's constituent liquids is called demulsification. It is carried out by centrifugation, freezing, boiling or chemical methods which destroy the emulsifying agent.

Applications of colloids:

- Sewage disposal
- Purification of drinking water
- Smoke precipitation
- Medicines
- Tanning
- Rubber industry

Distinction between true solution, colloids and suspension:

True Solution	Colloids	Suspension
It is homogeneous.	It is heterogeneous, though it appears homogeneous.	It is heterogeneous.
Particle size is less than 1nm.	Particle size ranges from 1nm to 100nm.	Particle size is more than 100nm.
It passes through filter paper.	It passes through ordinary filter paper but not through ultrafilters.	It does not pass through filter paper.
It does not show Tyndall effect.	It shows Tyndall effect.	It does not show Tyndall effect appreciably.
It has higher value of colligative property.	It has low value of colligative property.	It has very low value of colligative property.
Its particles cannot be seen even with powerful microscope.	Its particles can be seen by powerful microscope due to scattering of light.	Its particles can be seen even with naked eyes.

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 3

▶ 1 Mark Questions

1. Define 'Electrophoresis'. **[DELHI 2011]**
2. Which aerosol depletes ozone layer? **[ALL INDIA 2013]**
3. Give one example each of 'oil in water' and 'Water in oil' emulsion. **[DELHI 2014]**
4. Give one example each of sol and gel. [**DELHI 2014**]
5. What are the dispersed phase and dispersion medium in milk? [**ALL INDIA 2014**]
6. Out of $AlCl_3$ and $NaCl$, which is more effective in causing coagulation of a negative sol and why? [**ALL INDIA 2015**]
7. What cause Brownian movement in a colloidal solution? **[DELHI 2016]**
8. What is the reason for the stability of colloidal sols? [**ALL INDIA 2016**]
9. What is the 'coagulation' process? **[DELHI 2017]**
10. What type of colloid is formed when a gas is dispersed in a liquid? Give an example. [**ALL INDIA 2017**]
11. What is an emulsion?

▶ 2 Marks Questions

12. Describe a conspicuous change observed when:
    1. a solution of NaCl is added to a sol of hydrated ferric oxide.
    2. a beam of light is passed through a solution of NaCl and then through a sol. **[DELHI 2011]**
13. Explain the following terms-giving one example for each:
    1. Micelles
    2. Aerosol. **[DELHI 2012]**

14. What is meant by coagulation of a colloidal solution? Describe briefly any three methods by which coagulation of lyophobic sols can be carried out. [**ALL INDIA 2012**]

15. What is the difference between oil/water (O/W) type and water/oil (W/O) type emulsions? Give an example of each type. **[DELHI 2013]**

16. What is the difference between multi-molecular and macromolecular colloids? Give one example of each. **[DELHI 2013]**

3 Marks Questions

17. Define each of the following terms:

1. Micelles
2. Peptization
3. Desorption **[DELHI 2013]**

18. Define the following terms given an example of each

(i) Associated colloids

(ii) Lyophillic solution

(iii) Adsorption [**ALL INDIA 2013**]

19. What are emulsions? What are their different types? Give one example of each type. **[DELHI 2014]**

20. Give reasons for the following observations:

(i) Leather gets hardened after tanning.

(ii) Lyophilic sol is more stable than lyophobic sol.

(iii) It is necessary to remove CO when ammonia is prepared by Haber's process. **[DELHI 2015]**

21. What are lyophilic and lyophobic sols? Give one example of each type. Which one of these two types of sols is easily coagulated and why? **[DELHI 2016]**

22. Define the following term:

(i) Lyophilic colloid

(ii) Zeta potential

(iii) Associated colloids [**ALL INDIA 2016**]

23. Write one difference in each of the following:

(a) Multi-molecular colloid and associated colloid

(b) Coagulation and Peptization

(c) Homogeneous catalysis and Heterogeneous catalysis

OR

(a) Write the dispersed phase and dispersion medium of milk.

(b) Write one similarity between Physisorption and chemisorption.

(c) Write the chemical method by which $Fe(OH)_3$ sol is prepared from $FeCl_3$. [**ALL INDIA 2017**]

24. What happens in the following activities and why?

(i) An electrolyte is added to a hydrated ferric oxide sol in water.

(ii) A beam of light is passed through a colloidal solution.

(iii) An electric current is passed through a colloidal solution. **[DELHI 2017]**

25. What happens when:

(a) a freshly prepared precipitate of $Fe(OH)_3$ is shaken with a small amount of $FeCl_3$ solution?

(b) persistent dialysis of a colloidal solution is carried out?

(c) an emulsion is centrifuged?

26. What is the difference between multimolecular and macromolecular colloids? Give one example of each type. How are associated colloids different from these two types of colloids?

Solutions

1. Electrophoresis is the phenomenon of movement of colloidal particles based on their charge (positive or negative) towards the electrodes (cathode or anode) under applied electric field. **[1]**

2. CFC's and NO **[1]**

3. Oil in water — Milk **[½]**

Water in oil – Butter **[½]**

4. Sol-paint, gel-butter **[1]**

5. Dispersed phase : Oil ; **[½]**

Dispersion medium : Water **[½]**

6. $AlCl_3$, because the greater the valency of the flocculating ion added, the greater is its power to cause precipitation $Al^{3+} > Na^+$ **[1]**

7. Brownian movement is caused due to unbalanced bombardment of the colloidal particles with the molecules of the dispersion medium. **[1]**

8. Main reasons for the stability of colloidal solids are as below:

(a) **Electrostatic stabilisation:** The presence of equal and similar charges on the colloidal particles prevents coagulation of the colloidal sol. **[½]**

(b) **Solvation:** Colloidal particles are covered by a sheath of liquid in which they are extensively solvated and thereby acquiring stability. **[½]**

9. The process of changing the colloidal particles in a sol into the insoluble precipitate by addition of some suitable electrolytes is known as coagulation process. **[1]**

10. Aerosol e.g.: Fog, mist. **[1]**

11. Emulsion is a colloid in which the dispersed phase and dispersion medium are liquids. If a mixture of two immiscible or partially miscible liquids is shaken, a coarse dispersion of one liquid in the other is obtained which is called an emulsion. **[1]**

12. 1. Coagulation of ferric hydroxide sol. would take place. **[1]**

2. NaCl solution is transparent so when beam of light is passed, no tyndall effect is produced. But on passing through ferric Hydroxide solution the path of light becomes visible due to Tyndall effect. **[1]**

13. 1. Micelles are aggregates which exhibit colloidal behavior at higher concentration, with the hydrophilic part outside and the hydrophobic part towards the oil and dirt particle, eg. soap. **[1]**

2. An aerosol is a colloid of fine solid particle or liquid drops in air or another gas. It can be natural or artificial. Example:dust particle and smoke. **[1]**

14. The process of setting of colloidal particles is called coagulation of the sol. It is also known as precipitation. Following are the three methods by which coagulation of lyophobic sols can be carried out. **[1]**

(i) **Electrophoresis**: In this process, the colloidal particles move towards oppositely charged electrodes and get discharged resulting in coagulation.

(ii) **Mixing of two oppositely charged sols**: When equal proportions of oppositely charged sols are mixed, they neutralise each other resulting in coagulation.

(iii) **Dialysis**: By this method, electrolytes present in sol are removed completely and colloid becomes unstable resulting in coagulation. **[1]**

15. Emulsion of oil-in-water has oil as dispersed phase and water as dispersion medium. For example, Milk **[1]**

Emulsion of water-in-oil has water as dispersed phase and oil as dispersion medium. For example, Cod liver oil etc. **[1]**

16. Difference between Multi-molecular and Macromolecular colloids:

Point of Difference	Multi-molecular Colloid	Macromolecular Colloid
Definition	When a large number of atoms or small molecules (having diameters of less than 1 nm) of a substance combine together in a dispersion medium to form aggregates having size in the colloidal range, the colloidal solutions thus formed are called multi molecular colloid.	When substances which have very high molecular masses are dispersed in suitable dispersion medium, the resulting colloidal solutions are known as macromolecular colloids.
Example	Gold sol, sulphur sol	Starch, cellulose

[2]

17. 1. When soaps and detergents are added to water, a cluster of charged particle is formed by the aggregation of variety of molecules which is known as micelle. **[1]**

2. The process of converting a fresh precipitate into colloidal particles by shaking it with the dispersion medium in the presence of a small amount of a suitable electrolyte is called peptization. **[1]**

3. The process of removal of adsorbed substance from the surface of a solid or a liquid by heating or by reducing pressure is called desorption. **[1]**

18. (i) **Associated colloids**: Certain substance form true solution at low concentration but as concentration become greater than critical micelle concentration the particles get associated to form colloidal particle and colloidal solution is obtained. Ex. Soap **[1]**

Soap is sodium or potassium salt of fatty acid, when its concentration become greater than C.M.C., particles get associated to give colloidal solution.

(ii) **Lyophilic solution**: When particles of dispersed phase are solvated by dispersion medium lyophilic colloidal solution is obtained.

This is more stable due to presence of force of attraction between dispersed phase and dispersion medium. Ex. Starch solution in H_2O. **[1]**

(iii) **Adsorption**: When particles of certain substance get associated at the surface of solid, it is called as adsorption. In other words we can say adsorption at the surface is called as adsorption. Ex. Adsorption of gases by activated charcoal. **[1]**

19. Colloidal solution of liquid in liquid is called as emulsion. We have two types of emulsions: **[1]**

1. Oil in water (o/w) **[½]**
2. Water in oil (w/o) **[½]**

(i) **Oil in water:** In this type of emulsion water is medium and oil is dispersed phase, It is soluble in water, Ex. Milk **[½]**

(ii) **Water is oil :** In this type of emulsion oil is medium and water is dispersed into it, it is soluble in oil Ex. Butter **[½]**

20. (i) Animal skin (hide) is colloidal in nature and has positively charged colloidal particles. When a hide is soaked in tanning, mutual coagulation takes place and as a result, leather get hardened. **[1]**

(ii) The stability of lyophilic solution is depends on the result of two factors, the presence of a charge and the solvation of colloid particles. On the other hand, the stability of lyophobic solutions is only because of the presence of a charge. Thus, lyophilic solution is more stable than lyophobic solution due to the extensive solvation. **[1]**

(iii) It is necessary to remove CO when ammonia is prepared by Haber's process because in this process the CO acts as a poison and adversely affects the activity of iron catalyst, used in the process. **[1]**

21. Lyophilic sols are solvent attracting sols. Ex: Gum, gelatin (any one). **[1]**

Lyophobic sols are solvent repelling sols. Ex. Metal sols, metal sulphides (any one) **[1]**

Lyophobic sols are readily coagulated because they are not stable. **[1]**

22. (i) **Lyophilic colloid:** Colloidal sols directly formed by mixing substances like gum, gelatin and starch with a suitable liquid are called lyophilic colloids. An important characteristic of these colloids is that if the dispersion medium is separated from the dispersed phase, the colloid can be reconstituted by simply remixing with the dispersion medium. That is why, these colloids are also called reversible colloids. **[1]**

(ii) **Zeta potential:** For the combination of the two layers of opposite charges around the colloidal particles; the first layer of ions is firmly held and is termed fixed layer, while the second layer is mobile and is termed diffused layer. The charges of opposite sign on the fixed and diffused parts of the double layer results in a difference in potential. This potential difference between the fixed layer and the diffused layer of opposite charges is called the electro-kinetic potential or zeta potential. **[1]**

(iii) **Associated colloids:** There are some substances such as soaps and synthetic detergents that, at low concentrations; behave as normal strong electrolytes; but at higher concentrations, exhibit colloidal behaviour because of the formation of aggregates. The aggregated particles thus formed are called micelles. These are also known as associated colloids. **[1]**

23. (a) In Multimolecular colloid, the atoms or molecules are held by weak Vander waal's forces. In associated colloid, they behave as normal electrolytes at low concentrations and colloidal only at high concentrations. **[1]**

(b) The process of changing the colloid particle in a solution into insoluble precipitate by addition of suitable electrolyte is known as coagulation and conversion of freshly precipitated substance in to colloidal solution by shaking with the suitable electrolyte is called peptization. **[1]**

(c) In Homogeneous catalysis the catalyst and reactant are in the same phase and In Hetrogeneous catalysis the catalyst is in different phase than are the reactant**s**. **[1]**

OR

(a) Milk is an emulsion in which both the dispersed phase and the dispersion medium are in liquid state. In milk, liquid fat is dispersed in water. So fat is the dispersed phase and water is the dispersion medium. **[1]**

(b) Both are surface phenomenon. [1]

(c) A colloidal solution of $Fe[OH]$, is prepared when concentrated solution of ferric chloride is added drop wise to hot water.

$$FeCl_3 + 3H_2O \longrightarrow Fe[OH]_3 + 3HCl \quad \textbf{[1]}$$

24. (i) If an electrolyte is added to a hydrated ferric oxide sol, the colloidal particles get precipitated due to neutralization of charges. **[1]**

(ii) Scattering of light takes place and the path of the beam is illuminated. **[1]**

(iii)The colloidal particles move towards oppositely charged electrodes, get discharged and precipitated. **[1]**

25. (a) Colloidal dispersion of $Fe(OH)_3$ is formed and this process is called peptization. **[1]**

(b) On persistent dialysis a colloidal dispersion gets coagulated. **[1]**

(c) On centrifugation of emulsion, separation of the two liquids will take place. **[1]**

26.

Multimolecular colloids	**Macromolecular colloids**
On dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size in the colloidal range (diameter<1nm). The species thus formed are called multimolecular colloids.	Macromolecules in suitable solvents form solutions in which the size of the macromolecules may be in the colloidal range. Such systems are called macromolecular colloids.
Example: gold sol / sulphur sol (Any one)	Example: starch, cellulose, proteins, enzymes, polythene, nylon, polystyrene, synthetic rubber (Any one)

[1+1]

Some substances at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behavior due to the formation of aggregates. The aggregated particles, thus formed are called associated colloids or micelles. The formation of micelles takes place only above a particular temperature called Kraft temperature and above a particular concentration called critical micelle concentration. On dilution, these colloids revert back to individual ions. **[1]**

Smart Notes ....

Smart Notes ....

CHAPTER 6

General Principles and Processes of Isolation of Elements

Chapter Analysis with respect to Last 3 Years' Board Exams

List of Topics	2016		2017		2018	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Principles and methods of extraction	(3 marks)			(1 mark)		
Concentration, oxidation, reduction - electrolytic method and refining			(1 mark)			
Occurrence and principles of extraction of aluminium, copper, zinc and iron		(2 marks)	(3 marks)	(2 marks)	(3 marks)	(3 marks)

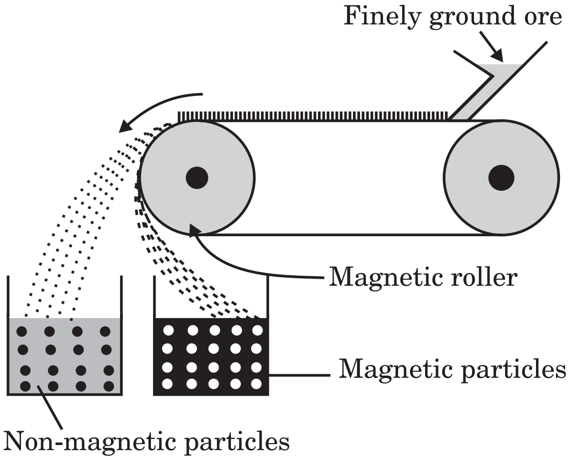
Summary

- **Important terms:**
  - **Minerals:** There are many natural occurring chemical substances present in the earth's crust and mining is needed to obtain them.
  - **Ores:** Out of many minerals, the minerals in which we may find metal are known as ores.
  - **Gangue:** The undesired or earthy materials that contaminate the ore is called gangue.
  - **Metallurgy:** The process that involves isolation of the metal from its ores is known as metallurgy.
  - **Concentration:** Removing the unwanted materials from the ore is called concentration.
  - **Flux:** It is a substance which needs to be added in the ore for the conversion of non-fusible gangue into fusible compound.
  - **Slag:** The fusible compound which is converted by flux from gangue is called slag
- **Concentration of ore:**

  The process to remove the gangue from the ore is carried out by the following methods:
  - **Crushing and Grinding:**

    The process begins with breaking the huge lumps into small pieces in the jaw crushers and then to make the powder, a ball mill or stamp mill is used. This process is alternatively called pulverization.
  - **Magnetic separation method:**

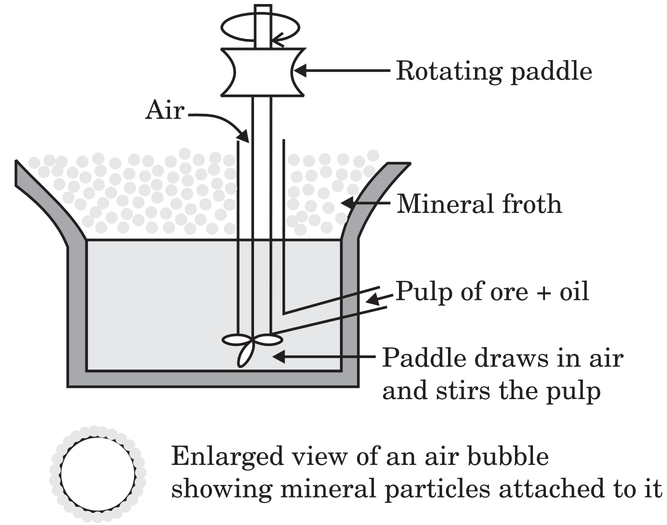
    The process that involves removal of tungsten ore particles from cassiterite (SnO_2) is called magnetic separation.



  - **Froth floatation process:**

    The principal of preferential wetting of solid surfaces is used by this process. This involves the concentration of sulphide ores because the metallic sulphides are more wetted by certain oils and less by water. For example, ores of lead, zinc and copper.

    A blast of air is passed through the mixture to agitate it. The froth which forms in this step then carries the ore particles along with it to the surface and leaves the impurities behind.
    The ore is concentrated by froth floatation process once the froth is scummed off.



- **Hydraulic washing:** It entirely depends on the difference in the densities of the gangue particle and the ore. An upward stream of running water is used to wash away the lighter gangue particles from the powdered ore. After this process only the heavier ore stays behind.
- **Leaching:** If the ore is soluble in a particular reagent then this process is used to make sure that only the ore dissolves in it but not the impurities.

Conversion of ore into oxide:

Conversion of ore into oxides is carried out by the following two methods:

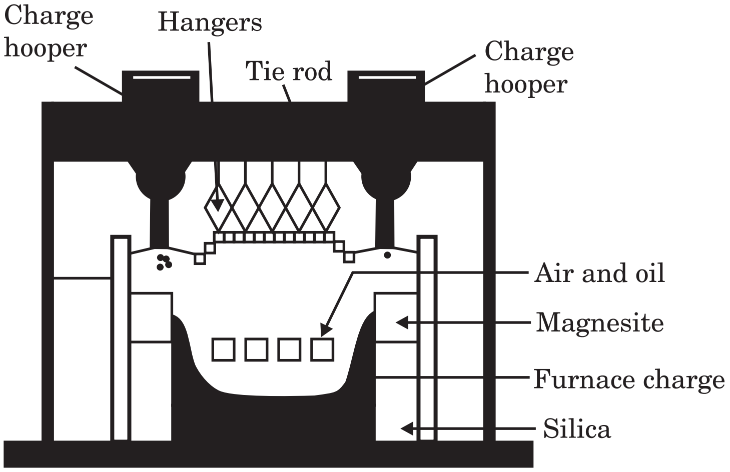
- **Calcination:** This process involves the heating of ore in the absence of air which allows it to convert carbonate ores into oxides.

  $FeCO_3 \xrightarrow{Heat} FeO + CO_2$
  Siderate

  $Fe_2O_3.xH_2O_{(s)} \xrightarrow{Heat} Fe_2O_{3(s)} + xH_2O_{(g)}$

- **Roasting:** This process involves the heating of ore in regular supply of air at a temperature which is below the melting point of the metal which allows the conversion of the given ore into oxides ore. Impurities are removed in this process as volatile oxides. Roasting allows the conversion of sulphide ores into oxides. Reverberatory furnace is used for this process.

  $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$



- **Reduction of oxide to metal:** This process involves the heating of metal oxides with some other substance which acts as reducing agent. Carbon, carbon monoxide or any other metal like AI or Mg are some commonly used reducing agents. This process is carried out by following methods:
  - **Auto reduction:**

    This method involves heating the ore in the air to reduce the inactive metals. This method is used for the extraction of copper, lead, antimony, mercury etc. For example,

    $$2CuS + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \uparrow$$
    $$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2 \uparrow$$
  - **Smelting:**

    This process allows metal oxide to be reduced to metal C or CO. For example,

    $$Fe_2O_3 + 3C \xrightarrow{>1123K} 2Fe + 3CO \uparrow$$
    $$Fe_2O_3 + 3CO \xrightarrow{1123K} 2Fe + 3CO_2 \uparrow$$
    $$ZnO + C \rightarrow Zn + CO \uparrow$$
  - **Aluminothermic reduction:**

    It allows the reduction of metal oxide by aluminium. Thermite process is used to extract metal like manganese and chromium.

    $$3MnO_4 + 8AI \rightarrow 4AI_2O_3 + 3Mn$$
    $$Cr_2O_3 + 2AI \rightarrow AI_2O_3 + 2Cr$$
  - **Reduction with hydrogen:**

    Hydrogen acts as an efficient reducing agent for metal oxides. The ore obtained from roasting is heated in a current of hydrogen and metal oxides and then reduced to metal. Hydrogen is used to reduce oxides of W, Mo etc.

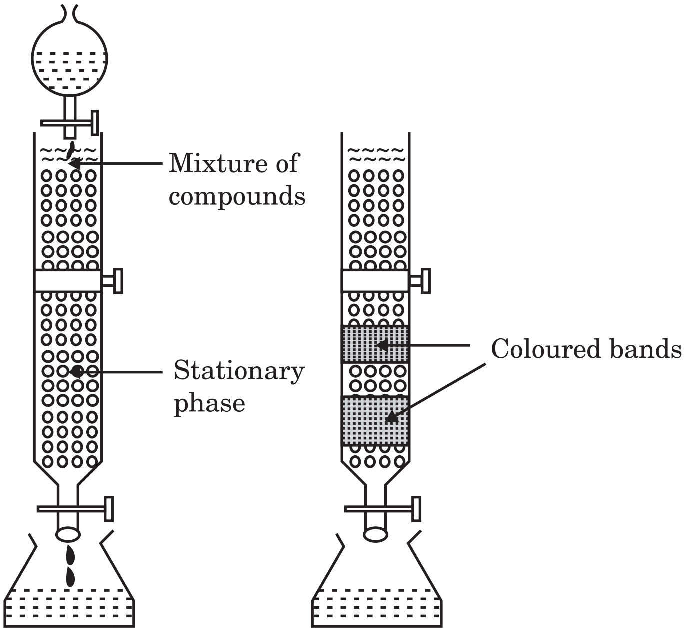
    $$WO_3 + 3H2 \rightarrow W + 3H_2O$$
- **Methods to remove impurities from a metal:**
  - **Distillation:** In this method the impure metal is evaporated to get the pure metal in the form of distillate. This method is used for the purification of metals like zinc and mercury since they have a low boiling point.
  - **Electrolytic refining:** In this method the crude metal is used as anode and the same metal in pure form is used as a cathode. A soluble salt of the same metal is used as an electrolyte.

    Copper is refined using electrolytic refining method. Impure copper is taken as an anode and pure copper strip as cathode.

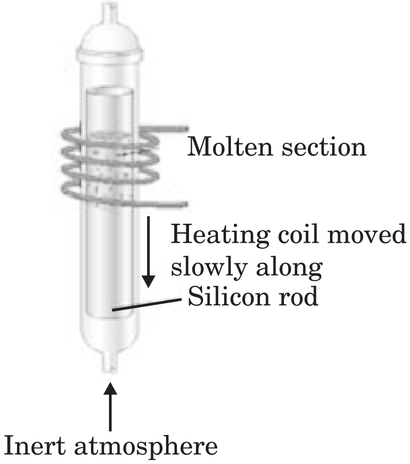
    Anode: $Cu \rightarrow Cu^{2+} + 2^{e-}$

    Cathode: $Cu^{2+} + 2e^{-} \rightarrow Cu$
  - **Liquation:** In this method a metal with low melting point is made to flow on a surface having a certain slope. Hence, the low melting metal can be separated from higher melting impurities.
  - **Chromatographic method:** This method is based on chromatography. Which means that the different components in a mixture are adsorbed differently by an adsorbent. There are several chromatographic techniques such as paper chromatography, column chromatography, gas chromatography, etc.

    In column chromatography method the column of Al_2O_3 is prepared in a glass tube and the moving medium containing a solution of the components is in liquid form.The adsorbed components are removed (eluted) by using suitable solvent (eluant).



- **Zone refining:** In this method a circular mobile heater is moved along the rod. The metal rod is placed inside a small induction furnace. The molten metal moves along with the heater and the pure metal crystallises out of the molten state while the impurities remain in the adjacent molten zone. When the process is repeated several times, the heater is moved in the same direction and impurities gets accumulated at the end. The end is removed or cut off. This method is used for the purification of semiconductors.



- **Vapour phase refining:** In this method, the pure metal is obtained by decomposing the volatile compound formed by the impure metal. It is shown by two methods:

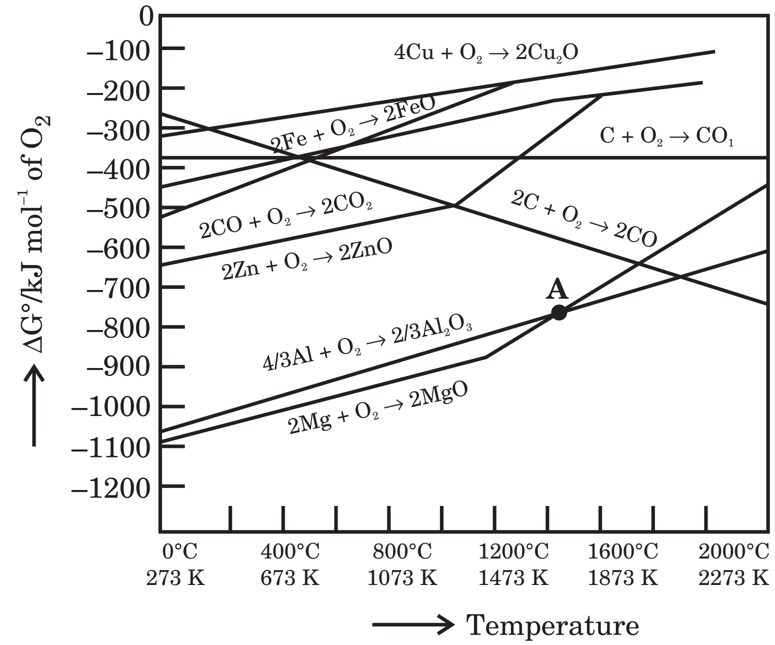
  Mond's process: This process is used for refining nickel. Nickel is heated in a stream of Carbon monoxide and nickel tetracarbonyl is formed as a volatile complex. The carbonyl is heated at a high temperature to obtain pure Nickel.

  $$Ni + 4CO \xrightarrow{330-350K} Ni(CO)_4 \xrightarrow{450-470K} Ni + 4CO$$

  Van Arkel Method: This method is used to refine titanium or zirconium. It removes all nitrogen and oxygen present in the metal as impurities. Heat is imparted to the impure metal in an evacuated vessel in presence of Iodine. The metal iodide is then decomposed on an electrically heated tungsten filament.

  $$\underset{impure}{Zr + 2I_2} \rightarrow ZrI_4 \xrightarrow[\text{Tunsten filament}]{1800K} \underset{\text{Pure}}{Zr + 2I_2}$$

- **Ellingham diagram:** H.J.T. Ellingham first used the graphical representation of Gibbs energy. This diagram helped in selecting the suitable reducing agent for the reduction of oxides



The diagram can be used to predict if the ore can be thermally reduced or not. Ellingham diagram consists of graphs which represent the variation of standard free energy with temperature of the formation of oxides of various elements, i.e. of $\Delta_f G°$ vs T. Similar plots can also be plotted for sulphides and halides.

Consider the formation of a metal oxide (M_xO).

$2xM\,(s) + O_2\,(g) \rightarrow 2M_xO\,(s)$

In this reaction, there is decrease in the value of $\Delta S°$ as (M_xO) is solid and O_2 is a gas, i.e., ΔS is negative. Thus, if temperature is increased, $T\Delta S°$ becomes more negative. As in the equation

$\Delta S° = \Delta H° - T\Delta S°$

$T\Delta S°$ is subtracted, therefore, $\Delta G°$ becomes less negative, i.e., $\Delta G°$ is likely to increase with rise in temperature and this trend is confirmed from the curves.

- The slope of the curves of the formation of metal oxides is +ve because $\Delta G°$ becomes less negative or increases with the rise in temperature.
- Each curve is a straight line except when some change takes place in phase. The temperature at which such a change occurs is indicated by an increase in the slope on the +ve side. For example, in the Zn–ZnO curve, the melting of zinc is indicated by an abrupt increase in the +ve slope at temperature 692 K.
- In the case of less reactive metals like silver and mercury, $\Delta G°$ becomes positive at high temperatures. It indicates that both silver oxide (Ag_2O) and mercury oxide (HgO) are unstable and decompose at high temperature.
- In the curve of CO, $\Delta G°$ decreases as $\Delta S°$ increases. This is indicated by the downward trend.
- Any metal oxide with lower value of $\Delta G°$ is more stable than a metal oxide with higher $\Delta G°$. This implies that the metal oxide placed higher in the diagram can be reduced by the metal involved in the formation of the oxide placed lower in the diagram.

- **Some metal ores and their extractions:**

Aluminium	Bauxite $Al_2O_3.xH_2O$ Cryolite Na_3AlF_6	Electrolysis of Al_2O_3 dissolved in molten Na_3AlF_6	Good source of electricity is required for the extraction.
Iron	Haematite, Fe_2O_3 Magnetite, Fe_3O_4	Oxide is reduced in the Blast furnace with CO and coke.	High temperature is required (2170 K).
Copper	Copper pyrites, $CuFeS_2$ Copper glance, Cu_2S Malachite, $CuCO_3.Cu(OH)_2$ Cuprite, Cu_2O	Sulphides are partially roasted and then reduced.	In a specially designed converter, self-reduction takes place. In hydrometallurgy, H_2SO_4 leaching is also used.
Zinc	Zinc blende or Sphalerite, ZnS Calamine, $ZnCO_3$ Zincite, ZnO	Roasting and reduction with coke.	Purification may be done by fractional distillation.

PREVIOUS YEARS'

EXAMINATION QUESTIONS

1 Mark Questions

1. Differentiate between a mineral and an ore. **[DELHI 2011]**
2. What is the role of graphite in the electro-metallurgy of aluminium? **[DELHI 2012]**
3. Name the method used for refining of Nickel metal. **[DELHI 2013]**
4. Name the method used for refining of copper metal. **[ALL INDIA 2013]**
5. What is the composition of 'Copper matte'? **[DELHI 2013]**
6. Which reducing agent is employed to get copper from the leached low grade copper ore? **[DELHI 2013]**
7. What is meant by the term 'pyrometallurgy'? **[DELHI 2017]**

2 Marks Questions

8. Describe the principle involved in each of the following processes.
   1. Monds process for refining of Nickel.
   2. Column chromatography for purification of rare elements. **[ALL INDIA 2012]**
9. Describe the following:
   1. The role of cryolite in electro-metallurgy of aluminium.
   2. The role of carbon monoxide in the refining of crude nickel. **[DELHI 2012]**
10. (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? [**DELHI 2013**]
11. (a) Give an example of zone refining of metals.

    (b) What is the role of cryolite in the metallurgy of aluminum? **[DELHI 2013]**

12. (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? **[DELHI 2013]**

13. Outline the principles behind the refining of metals by the following methods:

(i) Zone refining method

(ii) Chromatographic method. **[DELHI 2014]**

14. Write the principles of the following methods:

(i) Froth floatation method

(ii) Electrolytic refining **[DELHI 2014]**

15. Write the principle behind the following methods of refining:

(i) Hydraulic washing

(ii) Vapour-phase refining **[DELHI 2014**]

16. Write the principle behind the froth floatation process. What is the role of collectors in this process? **[ALL INDIA 2014]**

17. Describe the underlying principle of each of the following metal refining methods:

(i) Electrolytic refining of metals

(ii) Vapour phase refining of metals

[DELHI 2017]

18. Write the chemical reactions involved in the process of extraction of gold. Explain the role of dilute NaCN and Zn in this process.

[ALL INDIA 2018]

3 Marks Questions

19. (*i*) Name the method of refining of nickel.

(*ii*) What is the role of cryolite in the extraction of aluminium?

(*iii*) What is the role of limestone in the extraction of iron from its oxides?

[DELHI 2016]

20. Describe the principle behind each of the following processes:

1. Vapour phase refining of a metal.
2. Electrolytic refining of a metal
3. Recovery of silver after silver ore was leached with NaCN. **[ALL INDIA 2011]**

21. State briefly the principles which serve as basis for the following operations in metallurgy:

(i) Froth floatation process

(ii) Zone refining

(iii) Refining by liquation **[DELHI 2014]**

22. (*a*) Write the principle of electrolytic refining?

(*b*) Why does copper obtained in the extraction from copper pyrites have a blistered appearance?

(*c*) What is the role of depressants in the froth flotation process? **[ALL INDIA 2017]**

23. Explain the role of each the following in the extraction of metals from their ores:

(i) CO in the extraction of nickel.

(ii) Zinc in the extraction of silver.

(iii) Silica in the extraction of copper.

[DELHI 2017]

24. Describe how the following changes are brought about:

(i) Pig iron into steel.

(ii) Zinc oxide into metallic zinc.

(iii) Impure titanium into pure titanium.

Or

Describe the role of:

(i) $NaCN$ in the extraction of gold from gold ore.

(ii) SiO_2 in the extraction of copper from copper matte.

(iii) Iodine in the refining of zirconium. Write chemical equations for the involved reactions.

Solutions

1. Naturally occurring chemical substances which occur in the earth's crust and are obtainable by mining are called minerals, while the mineral from which the element is extracted economically is called an ore. **[1]**

2. In the metallurgy of aluminium; steel cathode and graphite anode are used. The graphite anode is useful for the reduction of Al_2O_3 into Al. **[1]**

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

3. Method used for refining of nickel metal is Mond's process. **[1]**

4. Electrorefining **[1]**

5. Composition of 'Copper matte' is Cu_2S and FeS. **[1]**

6. Scrap iron is used as reducing agent to obtain copper metal from the solution containing copper.

$$Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$$ **[1]**

7. Pyrometallurgy is the branch of metallurgy which consists of the thermal treatment of minerals and metallurgical ores and their concentrates to bring about physical and chemical transformations in the materials to enable recovery of valuable metals. **[1]**

8. 1. Nickel combined with carbon monoxide to form volatile complex which can further be decomposed to get back pure nickel. **[1]**

2. The basic principle involved in column chromatography is that different elements present in a mixture are adsorbed on adsorbent upto different extents. **[1]**

9. 1. Cryolite lowers the melting point of the mixture from 2050°C to 950°C and brings conductivity. Therefore, it is mixed with alumina during metallurgy of aluminium. **[1]**

2. Carbon monoxide forms a volatile complex with nickel. **[1]**

The volatile complex is then subjected to high temperature to get pure metal through decomposition.

$$Ni + 4CO \xrightarrow{300-350K} \underset{\text{(nickel tetracarbonyl)}}{Ni(CO)_4}$$

$$Ni(CO_4) \xrightarrow{400-450K} Ni + 4CO$$

10. (*a*) **Dilute solution** i.e. 0.5% $NaCN$ and KCN is used for leaching of silver metal in the presence of air.

$$4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow \underset{\text{sod. dicyanoargentate}(I)}{4Na\left[Ag(CN)_2\right]} + 4NaOH$$

[1]

(b) Out of C and CO, CO is a better reducing agent at the lower temperature range in the blast furnace to extract iron from the oxide ore because in Ellingham diagram $\Delta G_{(CO,CO_2)} < \Delta G_{(Fe,FeO)}$. So, CO will reduce

FeO to Fe and will itself be oxidized to CO_2.

$$FeO + CO \xrightarrow{1123K} Fe + CO_2$$ **[1]**

11. (*a*) Zone Refining of metals: This method is used for production of semiconductor and other metals of very high purity like germanium, silicon, boron, gallium and indium. **[1]**

(*b*) Role of cryolite in metallurgy of Aluminium: Cryolite is added to lower the melting point of mixture and to increase the conductivity of electrolyte. **[1]**

12. (*a*) Only sulphide ores are concentrated by this process because pine oil selectively wets the sulphide ore and hence brings it to the froth. **[1]**

(*b*) Silica is added in the reverberatory furnance during the extraction of copper to remove iron oxide present in the ore. * Iron oxide reacts with silica and is removed as slag of iron silicate. **[1]**

13. (*i*) Zone refining Method: This method is employed when impurities are more soluble in the melt than in solid form of the metal. It is used to obtain metals such as Germanium (Ge), Silicon (Si), Gallium (Ga), etc in their purest form. **[1]**

(*ii*) Chromatographic Method: This method is used when the impurities are not very different in chemical properties from the element to be purified. The components of the mixture show different mobility on the stationary phase, i.e., the components are adsorbed differently on the adsorbent. Gas chromatography, liquid chromatography and paper chromatography are various chromatographic methods based on different mobile and stationary phase. **[1]**

14. (i) It is based on the difference in wetting qualities of gangue and the sulphide particles with water and oil. Whereas the ore particles are wetted by oil, the gangue or the earthy particles are wetted by water. **[1]**

(ii) In this process a slab of impure copper is used as anode and a thin sheet of pure copper as cathode. The copper sulphate is used as electrolytic solution. By passing electricity through the cell copper is dissolved from the anode and deposited on cathode. The impurities either remain in solution or collect as an insoluble gangue. **[1]**

15. (i) Hydraulic washing is based on the differences in densities or gravities of the ore and the gangue particles. The lighter gangue particles are washed away and the heavier ores are left behind. **[1]**

(ii) In Vapour phase refining method the metal is converted into its volatile compound and converted elsewhere. It is then thermally decomposed to get the pure metal. E.g. Mond's process. **[1]**

16. Froth floatation process is used when ore has wettability towards oil while impurities have wettability towards water. **[1]**

Collectors are used in froth floatation process to collect ore particles and to remove them with froth. **[1]**

17. (i) In this method, the impure metal acts as anode which undergoes oxidation and pure metal acts as cathode which undergoes reduction. The metal ions deposit on the cathode as metal. **[1]**

(ii) Vapour phase refining is based on the principle that metal is converted to its volatile compound and collected which decomposes to give pure metal. **[1]**

18.
$$4Au(s)+8CN^{-}(aq)+2H_2O(aq)+O_2(g)\longrightarrow 4\left[Au(CN)_2\right]^{-}(aq)+4OH^{-}(aq)$$

[1]

$$2\left[Au(CN)_2\right]^{-}_{aq}+Zn(s)\longrightarrow \left[Zn(CN)_4\right]^{2-}+2Au$$

Gold is leached with a dilute solution of NaCN in the presence of air and Z_n precipitates gold. **[1]**

19. (i) The Mond process is used for refining nickel. **[1]**

(ii) Cryolite is used in the electrolytic reduction of alumina for reducing its melting point and making it a good conductor of electricity. **[1]**

(iii) In the blast furnace, limestone decomposes to form CaO, which reacts with the silicate impurity to form slag.

$$CaCO_3\longrightarrow CaO+CO_2$$ **[1]**

$$CaO+SiO_2\longrightarrow CaSiO_3$$

20. 1. **Vapour Phase refining**: The impure metal is first converted to its unstable volatile compound which is evaporated and then decomposed by heating at higher temperature to give pure metal, leaving behind the impurities. **[1]**

2. In this method impure metal is made anode and a thin sheet of pure metal is made cathode, and are put in a suitable electrolyte containing soluble salt of same metal. On passing current the more basic metal remains in the solution and the less basic one go to the anode and gets deposited as anode mud. **[1]**

3. NaCN acts as a leaching agent or oxidizing agent, thus oxidize Ag to Ag^{+} which then combine with CN^{-} ions to form respective soluble complex. **[1]**

$$4Ag(s)+8CN^{-}(aq)+O_2(g)+2H_2O(l)\rightarrow \left[Ag(CN)_2\right]^{-}(aq)+4OH^{-}(aq)$$

21. (i) **Froth floatation process:** This method is based on the difference in the wettability of the mineral particles (sulphide ores) and the gangue particles. The mineral particles become wet by oils while the gangue particles by water and hence gets separated. **[1]**

(ii) **Zone refining**: This method is based on the principle that the impurities are more soluble in the melt than in the solid state of metal. **[1]**

(iii) **Refining by Liquation**: The method is based on the lower melting point of the metal than the impurities and tendency of the molten metal to flow on the sloping surface. **[1]**

22. (a) **Electrolytic refining**: It is the process of refining impure metals by using electricity. In this process, impure metal is made the anode and a strip of pure metal is made the cathode. A solution of a soluble salt of the same metal is taken as the electrolyte. **[1]**

(b) Copper is extracted from its principal ore copper pyrites ($CuFeS_2$). The ore is concentrated by froth floabtion process. The molten copper is poured out and allowed to cool. The sulphur dioxide escaping from the melt gets trapped in the cooler parts of the surface giving a blistery appearance for copper and hence it is called blister copper. **[1]**

(c) In the froth floatation process, the role of the depressants is to separate two sulphide ores by selectively preventing one ore from forming froth. **[1]**

23. (i) CO is used in the vapour phase refining of nickel.

$$Ni+4CO\xrightarrow{330-350K}Ni(CO)_4$$

$$Ni+(CO)_4\xrightarrow{450-470K}Ni+4CO$$ **[1]**

(ii) Zinc acts as a reducing agent which reduces cyanide complex of silver into pure silver.

$$2\left[Ag(CN)_2\right]^-(aq)+Zn(s)\longrightarrow 2Ag^+(s)+\left[Zn(CN)_4\right]^{2-}(aq)$$

[1]

(iii) Silica is used to remove impurities in the form of metal oxides as slag.

$$FeO+SiO_2\longrightarrow FeSiO_3$$ **[1]**

24. (i) Pig iron into steel. Pig iron is converted to cast iron by heating molten pig iron with scrap iron and coke using hot air blast in specially designed furnaces. Cast iron is used in the manufacture of steel by mixing it with other metals. **[1]**

(ii) Zinc oxide into metallic zinc. Zinc oxide is converted to metallic zinc by reacting it with coke at 673 K.

$$ZnO\ +\ C\xrightarrow{coke,673K}Zn\ +\ CO$$ **[1]**

(iii) Impure titanium into pure titanium. The crude titanium is heated in an evacuated vessel with iodine. The metal iodide being more covalent volatilizes.

$$Ti\ +\ 2I_2\longrightarrow TiI_4$$

Titanium iodide vapours are collected and then decomposed on a tungsten filament by electrically heating to about 1800K. The pure metal is thus deposited on the filament.

$$TiI_4\longrightarrow Ti\ +2I_2$$ **[1]**

Or

(i) Role of NaCN in the extraction of gold from gold ore:-

In the metallurgy of gold, gold metal is leached with a dilute solution of NaCN in the presence of air (for O_2). The gold metal is then obtained from the product by displacement reaction.

$$4Au(s)+8CN(aq)+2H_2O(aq)+O_2(g)\rightarrow 4\left[Au(CN)_2\right](aq)\ +4OH^-(aq)$$

$$2\left[Au(CN)_2\right](aq)\ +\ Zn(s)\longrightarrow 2Au(s)\ +\ \left[Zn(CN)_4\right]^{2-}(aq)$$ **[1]**

(ii) Role of SiO_2 in the extraction of copper from copper matte:-

Copper matte consists of Cu_2S and FeS. In the converter FeS is converted to FeO. Silica helps in removal of FeO impurity as slag.

$$2FeS\ +\ 3O_2\longrightarrow 2FeO\ +\ 2\ SO_2$$

$$FeO\ +\ SiO_2\longrightarrow FeSiO_3(Slag)$$ **[1]**

(iii) Role of Iodine in the refining of zirconium.

Iodine is heated with Zirconium to form a volatile compound which on further heating decomposes to give pure zirconium.

Formation:- $Zr+4l_2\xrightarrow{300-500°C}Zrl_4$

The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal is thus deposited on the filament.

$ZrI_4\rightarrow Zr+2I_2$ **[1]**

Smart Notes ....

CHAPTER 7

p-Block Elements

Chapter Analysis with respect to Last 3 Years' Board Exams

List of Topics	**2016**		**2017**		**2018**	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Group 15 Elements: General introduction, electronic configuration, occurrence, oxidation states	(2 ,3 marks)		(3 marks)	(3 marks)	(1, 2 ,5 marks)	(1, 2 ,5 marks)
Trends in physical and chemical properties; nitrogen preparation properties & uses						
Compounds of nitrogen, preparation and properties of ammonia and nitric acid, oxides of nitrogen (Structure only)	(1 mark)	(1 mark)	(1 mark)			
Phosphorus - allotropic forms, compounds of phosphorus: preparation and properties of phosphine, halides PCl3 , PCl5 and oxoacids			(1 mark)			
Group 16 Elements: General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties		(3 marks)	(2 marks)			
Dioxygen: Preparation, Properties and uses, classification of oxides, Ozone						
Sulphur -allotropic forms; compounds of sulphue: Preparation properties and uses of sulphur-dioxide, oxoacids of sulphur						
Sulphuric acid: industrial process of manufacture, properties and uses;						
Group 17 Elements: General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties						
Compounds of halogens, Preparation properties and uses of chlorine and hydrochloric acid, interhalogen compounds, oxoacids of halogens						
Group 18 Elements: General introduction, electronic configuration, occurrence, trends in physical and chemical properties, uses	(2 marks)	(2 marks)	(2 marks)	(2 marks)		

p – Block Elements

- P-block elements are the elements in the right side of the periodic table with group number 13, 14, 15, 16, 17 and 18.
- They have 3, 4, 5, 6, 7 and 8 electrons in their outermost shell, respectively and subsequently the last electrons of these groups' elements occupies the position in p-sub shell that is why they are named as p-block elements.
- Their general atomic configuration is $ns^2\ np^{1-6}$.
- Elements of p-block:

Group 13	Boron family	B, Al, Ga, In, Tl
Group 14	Carbon family	C, Si, Ge, Sn, Pb
Group 15	Nitrogen family	N, P, As, Sb, Bi
Group 16	Oxygen family	O, S, Se, Te, Po
Group 17	Halogen family	F, Cl, Br, I, At
Group 18	Noble gases	He, Ne, Ar, Kr, Xe, Rn

Topic 1: Group 15 Elements

Summary

- **Electronic configuration:** $ns^2\ np^3$
- **Oxidation state:** They exhibit two important oxidation states, + 3 and + 5 but +3 oxidation is favored by heavier elements due to 'inert pair effect'.
- **Ionization Enthalpy:** Decreases from Nitrogen (N) to Bismuth (Bi) due to increase in atomic size.
- Metallic character increases down the group as the ionization energy decreases.
- Boiling point increases down the group.
- Melting point increases up to As and decreases up to Bi.
- Nitrogen differs from rest of the elements of this group due to its small size, high electronegativity, high ionization energy, and non-availability of d-orbitals and formation of pπ–pπ multiple bonds with itself and with highly electronegative atom like O or C.
- Dinitrogen is a colourless, odourless, tasteless and non-toxic gas
- Dinitrogen can be prepared in laboratory as well as on industrial scale by following reactions.

$$3CuO + 2NH_3 + heat \rightarrow N_2 + Cu + 3H_2O$$

$$CaOCl_2 + 2NH_3 + heat \rightarrow CaCl_2 + 2H_2O + N_2$$

$$NH_4NO_2 + heat \rightarrow Cr_2O_3 + 3H_2O + N_2$$

- The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen, (e.g., calcium cyanamide).
- Nitrogen forms oxides in various oxidation states as $N_2O, NO, N_2O_3, NO_2, N_2O_4 and N_2O_5$. These oxides have resonating structures and have multiple bonds.
- Ammonia is a colourless gas with a pungent odour. Its freezing and boiling points are 198.4 and 239.7 K respectively.
- Ammonia (NH_3) is prepared on large scale by Haber's process.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

- Ammonia is used to produce various nitrogenous fertilisers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate) and in the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid. Liquid ammonia is also used as a refrigerant.
- Nitric acid (HNO_3) is a colorless liquid (f.p. 231.4 K and b.p. 355.6 K) and is a powerful oxidizing agent. Metals and non-metals react with HNO_3 under different conditions to give NO or NO_2.
- The major use of nitric acid is in the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics.
- Phosphorus another important element of group 15 is found in many allotropic forms, the important ones being white, red and black.
- Phosphorus exists as P_4 in elemental form. It forms hydride, PH_3 (phosphine) which is a highly poisonous gas.
- It forms two types of halides as PX_3 and PX_5. PCl_3 is prepared by the reaction of white phosphorus with dry chlorine.
  $P_4 + 6Cl_2 \rightarrow 4PCl_3$
- While PCl_5 is prepared by the reaction of phosphorus with SO_2Cl_2.
  $P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$
- Phosphorus forms a number of oxoacids. Depending upon the number of P–OH groups, their basicity varies. The oxoacids which have P–H bonds are good reducing agents.

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 1

1 Mark Questions

1. Out PH_3 and H_2S which is more acidic and why? **[DELHI 2012]**

2. Which one of PCl_4^+ and PCl_4^- is not likely to exist and why? **[ALL INDIA 2012]**

3. What is the covalency of nitrogen in N_2O_5? **[DELHI 2013]**

4. Why does NH_3 act as a Lewis base? **[ALL INDIA 2014]**

5. Write the formulae of any two oxo-acids of phosphorus. **[ALL INDIA 2015]**

6. What is the basicity of H_3PO_4? **[ALL INDIA 2015]**

7. $Pb(NO_3)_2$ on heating gives a brown gas which undergoes dimerization on cooling? Identify the gas. **[ALL INDIA 2016]**

8. In which one of the two structures, NO_2^+ and NO_2^-, the bond angle has a higher value? **[DELHI 2016]**

9. Why is red phosphorus less reactive than white phosphorus? **[DELHI 2017]**

10. Why does NO_2 dimerise?

2 Marks Questions

11. Give reason for:

1. The N-O bond in NO^-_2 is shorter than the N-O bond in NO^-_3
2. SF_6 is kinetically an inert substance.

OR

State reasons for each of the following:

1. All the $P - Cl$ bonds in PCl_5 molecules are not equivalent.
2. Sulphur has greater tendency for catenation than oxygen. **[DELHI 2011]**

12. Assign a reason for each of the following statements:

(i) Ammonia is a stronger base than phosphine.

(ii) Sulphur in vapour state exhibits a paramagnetic behaviour. **[DELHI 2016]**

13. Draw the structures of white phosphorus and red phosphorus. Which one of these two types of phosphorus is more reactive and why?

14. Among the hydrides of Group-15 elements,which have the

(a) Lowest boiling point?

(b) Maximum basic character?

(c) Highest bond angle?

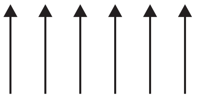
(d) Maximum reducing character?

[ALL INDIA 2018]

3 Marks Questions

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 AgCl is doped with $CdCl_2$? **[DELHI 2013]**

16. Given reasons for the following:

(i) $(CH_3)_3P=O$ exists but $(CH_3)_3N=O$ does not.

(ii) Oxygen has less electron gain enthalpy with negative sign than sulphur.

(iii) H_3PO_2 is a stronger reducing agent than H_3PO_3. **[ALL INDIA 2014]**

17. Give reasons for the following:

(a) Red phosphorus is less reactive than white phosphorus.

(b) Electron gain enthalpies of halogens are largely negative.

(c) N_2O_5 is more acidic than N_2O_3.

[ALL INDIA 2017]

5 Marks Questions

18. (a) Draw the structures of the following molecules:

(i) $(HPO_3)_3$

(ii) BrF_3

(b) Complete the following chemical equations:

(i) $HgCl_2 + PH_3 \longrightarrow$

(ii) $S0_3 + H_2SO_4 \longrightarrow$

(iii) $XeF_4 + H_2O \longrightarrow$

Solutions

1. H_2S is more acidic than PH_3 due to smaller size and higher electronegativity of sulphur, So H_2S has tendency to lose H+.PH_3 is basic in nature because it has lone pair of electron so it has tendency to lose pair of electron. **[1]**

2. PCl_4^- is not likely to exist because the oxidation state of P is +3 here, which is less stable. **[1]**

In PCl_4^-, Oxidation state of P is:

$x - 4 = -1$

$x = +3$

While in PCl_4^+ , oxidation state of P is:

$x - 4 = +1$

$x = +5$

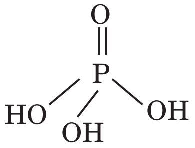
Since the most stable oxidation state of P is +5.Therefore PCl_4^+ exists and PCl_4^- does not exist.

3. In N_2O_5, the covalency of N is restricted to '4' due to sp^2 hybridisation of nitrogen atom involving one 2s and three 2p orbitals. **[1]**

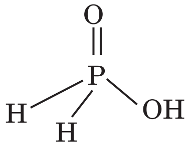
4. NH_3 acts as a Lewis base because N-atom has a lone pair. **[1]**

5. **[1]**

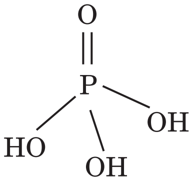
H_3PO_4



H_3PO_2



6. H_3PO_4 has three ionisable hydrogen atoms. Hence, its basicity is **3**. **[1]**



7. On heating, $Pb(NO_3)_2$ undergoes decomposition reaction and gives nitrogen dioxide NO_2. It dimerises to give N_2O_4 gas. **[1]**

$$2\,Pb(NO_3)_2 \longrightarrow 2\,PbO + 4\,NO_2 + O_2$$

$$2NO_2 \longrightarrow N_2O_4$$

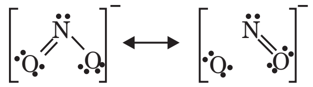
8. NO_2^+ has a higher value of bond angle than NO_2^- because NO_2^- has a lone pair of electron attached to it. Due to the repulsion between them, the Bond angle is reduced. **[1]**

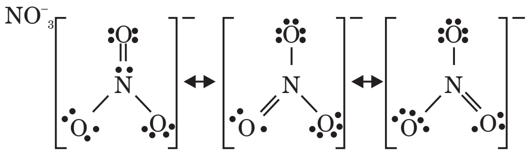
9. Red phosphorus is polymeric which consists of chains of P_4 tetrahedral linked together whereas white phosphorus consists of a single tetrahedron. **[1]**

10. NO_2 contains odd number of valence electrons. It behaves as an odd electron molecule and therefore undergoes dimerisation to form stable N_2O_4 molecule with an even number of electrons. **[1]**

11. 1. The resonating structure of NO^-_2 shows that NO^-_2 two bonds are sharing double bond while in $\mathbf{NO^-_2}$ three bonds are sharing a double bond. Thus, NO^-_2 has shorter bond than that of NO^-_2. **[1]**

Resonating structure of NO^-_2 and NO^-_3

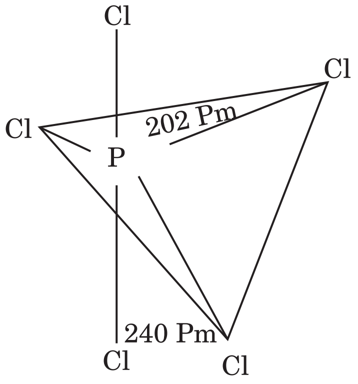




2. SF_6 is kinetically inert due to high oxidizing power and electronegativity of fluorine atom which causes steric hindrance and it is unable to react further with any other atom. **[1]**

OR

1. **[1]**



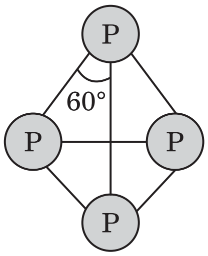
It is because all bonds are not in same plane. Three $P - Cl$ equatorial bonds are in one plane whereas two axial bonds are in vertical plane which are longer than equatorial bonds.

2. Sulphur has a much greater tendency for catenation than oxygen because of its bigger size and low electronegativity due to which the S – S bond is stronger than $O - O$ bond and there is more interelectronic repulsion in $O - O$ than in S – S bond. **[1]**

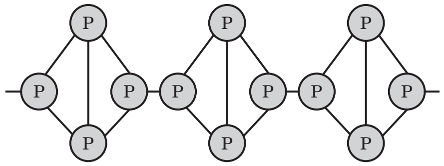
12. (i) The lone pair of electrons on N atom in NH_3 is directed and not diffused/delocalized as it is in PH_3 due to larger size of P/ or due to availability of d-orbitals in P. **[1]**

(ii) S_2 molecule like O_2, has two unpaired electrons in anti-bonding orbitals hence it exhibits a paramagnetic behavior in vapour state. **[1]**

13. **[½]**



White phsophorus



[½]

Red phosphorus

White phosphorus is less stable and therefore, more reactive than the red phosphorus under normal conditions because of angular strain in the P_4 molecule where the angles are 60° only. **[1]**

14. (a) Lowest boiling point = PH_3 **[½]**

(b) Maximum basic character = NH_3 **[½]**

(c) Highest bond angle = NH_3 **[½]**

(d) Maximum reducing character = BiH_3 **[½]**

15. (a) When silicon is doped with boron, p-type semiconductor is obtained. **[1]**

(b) Ferromagnetism is shown in this alignment of magnetic moments. **[1]**

(c) Impurity defect of ionic solids is produced when AgCl is doped with $CdCl_2$. **[1]**

16. (i) Due to absence of vacant d-orbitals N cannot form 5 covalent bonds **[1]**

(ii) O has **e**xceptionally small size. Hence, incoming electron feels more repulsion than expected and its negative electron gain enthalpy becomes less than expected **[1]**

(iii) In H_3PO_2 oxidation state of P is '+1' while in H_3PO_3 oxidation state of P is '+3'. In H_3PO_2 oxidation state of P is lower than that in H_3PO_3 **[1]**

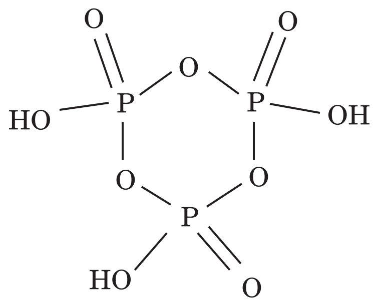
17. (a) Red phosphorus is less reactive than white phosphorus as white phosphorous possess angle strain in the P_4 molecule where the angle are only 60 & also they have low M.P. **[1]**

(b) Electron gain enthalpy of halogen are largely negative. It is due to the fact that they have high effective nuclear charge & smallest size among period. Although they contain 7 electrons in valence shell & required one electron to attain their nearest noble gas configuration. **[1]**

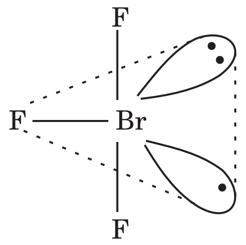
(c) N_2O_5 is more acidic then N_2O_3 as in N_2O_5 the N is in +5 O.S. while in N_2O_3 it is in +3 O.S. So higher the oxidation state of central atom in a given oxide, higher will be acidic character. **[1]**

18. (a)

(i) **[1]**



(ii) **[1]**



(b)

(i) $3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$ **[1]**

(ii) $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$ **[1]**

(iii) $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

[1]

Topic 2: Group 16 Elements

Summary

- **Electronic configuration:** $ns^2\ np^4$
- **Atomic and Ionic radii:** Due to increase in the number of shells, atomic and ionic radii increase from top to bottom in the group. The size of oxygen atom is, however, exceptionally small.
- **Ionization Enthalpy:** Decreases down the group. It is due to increase in size.
- **Electronegativity:** Decreases down the group.
- Oxidation state:They show +2, +4, and +6 oxidation states. Only oxygen shows an oxidation state of -2 (except of OF_2 and H_2O_2).
- Dioxygen is a colourless and odourless gas, it directly reacts with nearly all metals and non-metals except some metals (e.g., Au, Pt) and some noble gases.
- Its combination with other elements is often strongly exothermic which helps in sustaining the reaction.
- In laboratory, dioxygen is prepared by heating $KClO_3$ in presence of MnO_2.
- It forms a number of oxides with metals and they are classified on the basis of chemical nature. For example, Metallic oxides (Na_2O, CaO etc), Non-metallic (CO_2, SO_2 etc), amphoteric oxides (SnO_2, Al_2O_3 etc).
- Allotropic form of oxygen is O_3, which is a highly oxidizing agent.
- Sulphur forms a number of allotropes. Of these, α– and β– forms of sulphur are the most important. Sulphur combines with oxygen to give oxides such as SO_2 and SO_3. SO_2 is prepared by the direct union of sulphur with oxygen.
- SO_2 is used in the manufacture of H_2SO_4.
- Sulphur forms a number of oxoacids. Amongst them, the most important is H_2SO_4.
- It is prepared by contact process. It is a dehydrating and oxidizing agent. It is used in the manufacture of several compounds.

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 2

▶ 1 Mark Questions

1. Analysis shows that FeO has a non-stoichiometric composition with formula $Fe_{0.95}O$.Give reason. **[CBSE 2018]**

▶ 3 Marks Questions

2. How would you account for the following:
   (i) H_2S is more acidic than H_2O.
   (ii) The $N-O$ bond in NO_2^- is shorter than the $N-O$ bond in NO_3^-
   (iii) Both O_2 and F_2 stabilize high oxidation states but the ability of oxygen to stabilize the higher oxidation state exceeds that of fluorine. **[ALL INDIA 2011]**
3. Given reasons for the following:
   (i) Oxygen is a gas but sulphur is a solid
   (ii) O_3 acts as a powerful oxidizing agent
   (iii) BiH_3 is the strongest reducing agent amongst all the hydrides of group 15 elements **[ALL INDIA 2013]**
4. (a) Draw the structures of the following molecules:
   (i) $XeOF_4$
   (ii) H_2SO_4
   (b) Write the structural difference between white phosphorus and red phosphorus **[DELHI 2014]**
5. Account for the following:
   (i) Sulphur in vapour form exhibit paramagnetic behaviour.
   (ii) $SnCl_4$ is more covalent than $SnCl_2$.
   (iii) H_3PO_2 is stronger reducing agent than H_3PO_3. **[DELHI 2014]**

6. Give reasons:

(i) SO_2 is reducing while TeO_2 is an oxidizing agent.

(ii) Nitrogen does not form pentahalide.

(iii) ICl is more reactive than I_2.

[ALL INDIA 2016]

5 Marks Questions

7. (a) Complete the following chemical reactions equations:

(i) $P_4 + SO_2C1_2 \longrightarrow$

(ii) $XeF_6 + H_2O \longrightarrow$

(b) Predict the shape and the asked angle (90° or more or less) in each of the following cases:

(i) SO_3^{2-} and the angle $O-S-O$

(ii) ClF_3 and the angle $F-Cl-F$

(iii) XeF_2 and the angle $F-Xe-F$

OR

(a) Complete the following chemical equations:

(i) $NaOH + Cl_2 \longrightarrow$

(ii) $XeF_4 + O_2F_2 \longrightarrow$

(b) Draw the structures of the following molecules:

(i) H_3PO_2

(ii) $H_2S_2O_7$

(iii) $XeOF_4$ **[DELHI 2012]**

8. (a) Draw the structures of the following:

(i) $H_2S_2O_8$

(ii) $HClO_4$

(b) How would you account for the following:

(i) NH_3 is a stronger base than PH_3.

(ii) Sulphur has a greater tendency for catenation than oxygen.

(iii) F_2 is a stronger oxidising agent than Cl_2.

OR

(a) Draw the structures of the following:

(i) $H_2S_2O_7$

(ii) $HClO_3$

(b) Explain the following observations:

(i) In the structure of HNO_3, the N-O bond (121 pm) is shorter than the N-OH bond (140 pm).

(ii) All the P-Cl bonds in PCl_5 are not equivalent.

(iii) ICl is more reactive than I_2.

[DELHI 2017]

9. (a) Give reasons:

(i) H_3PO_3 undergoes disproportionation reaction but H_3PO_4 does not.

(ii) When Cl_2 reacts with excess of F_2, ClF_3 is formed and not FCl_3.

(iii) Dioxygen is a gas while sulphur is a solid at room temperature.

(b) Draw the structures of the following:

(i) XeF_4

(ii) $HClO_3$

OR

(a) When concentrated sulphuric acid was added to an unknown salt present in a test tube a brown gas (A) was evolved. This gas intensified when copper turnings were added to this test tube. On cooling, the gas (A) changed into a colourless solid (B).

(i) Identify (A) and (B).

(ii) Write the structures of (A) and (B).

(iii) Why does gas (A) change to solid on cooling.

(b) Arrange the following in the decreasing order of their reducing character:

HC, HCl, HBr, HI

(c) Complete the following reaction:

$XeF_4 + SbF_5 \longrightarrow$ **[ALL INDIA 2018]**

Solutions

1. The reason why analysis shows that FeO has a non - stoichiometric composition with formula $Fe_{0.95}O$ is that: The non - stoichiometry reflects the ease of oxidation of Fe^{+} to Fe^{+} effectively replacing a small portion of Fe^{+} with two thirds their number of Fe^{+}. Thus for every "missing" Fe^{+} ions, the crystals contains two Fe^{+} ions to balance the charge. **[1]**

2. (i) Because bond dissociation enthalpy of H-S bond is lower than that of H-O bond and also oxygen is more electronegative than S.

[1]

(ii) In the resonance structure of these two species, in NO_2^-, 2 bonds are sharing a double bond while in NO_3^-, 3 bonds are sharing a double bond which means that bond in NO_2^- will be shorter than in NO_3^-

In NO_2^-, bond order is 1.5 while in NO_3^- and in NO_2^-, bond order is 1.33. **[1]**

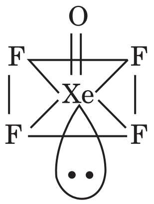
(iii) Because of the tendency of oxygen to form multiple bonds with metal. **[1]**

3. (i) In oxygen discrete O_2 molecules are present while sulphur is polymeric. **[1]**

(ii) O_3 acts as a powerful oxidizing agent because it can produce nascent oxygen [O] **[1]**

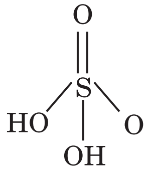
(iii) As we move top to bottom in hydrides of group 15 bonds length increases. Chance of H-removal also increases hence chance of oxidation increases and BiH_3 is the strongest reducing agent amongst all the hydrides of group 15. **[1]**

4. (a) (i) **[1]**



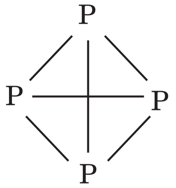
Square pyramidal

(ii) **[1]**



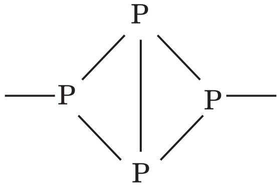
Tetrahedral

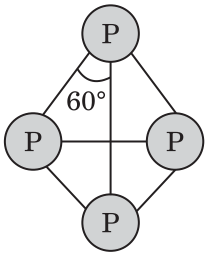
(b) **[1]**



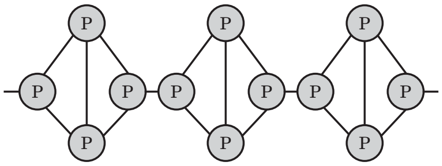
Structural Difference: White Phosphorus: In white phosphorus, P_4 molecules are held by weak Vander Waal's forces and exist as a discrete tetrahedral.

Red Phosphorus — In red phosphorus, P4 molecules are held by covalent bonds in polymeric structure.





White Phosphorus



Red phosphorus

5. (i) In vapour form sulphur partly exists as $\mathbf{S_2}$ molecule which have two unpaired electrons in the antibonding p molecular orbitals like O_2 molecule and hence exhibits paramagnetism. **[1]**

(ii) It is due to higher oxidation state (+4) of Sn is $SnCl_4$, or because of its high polarising power, which in turn increases the covalent character of bond formation between the central atom and the atoms around it. **[1]**

(iii) It is because of two P-H bonds in H_3PO_2 whereas there is only one P-H bond in H_3PO_3. **[1]**

6. (i) SO_2 is a reducing agent because sulphur has empty d-orbitals and it can easily expand its +4 oxidation state to +6 oxidation state. However, as Te **is a heavy element; therefore, due to inert pair effect, its lower oxidation state is more stable**, and TeO_2 acts as oxidising agent. **[1]**

(ii) Due to unavailability of empty d-orbitals in nitrogen, it cannot expand its valency. Hence, nitrogen does not form pentahalide. **[1]**

(iii) In general, interhalogen compounds are more reactive because of lower bond dissociation energy than halogen molecules (except F_2). **[1]**

7. (a)

(i) $P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$ **[1]**

(ii) Equation for complete hydrolysis **[1]**

$$XeF_6 + H_2O \longrightarrow XeO_3 + 6HF$$

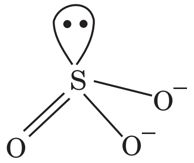
Equations for partial hydrolysis

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

(b)

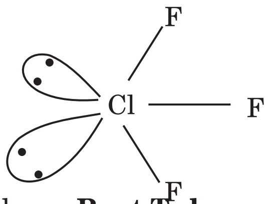
(i) **[1]**



Shape: **Pyramidal**

Angle $O-S-O$ **:** More than $90°$ (ii)

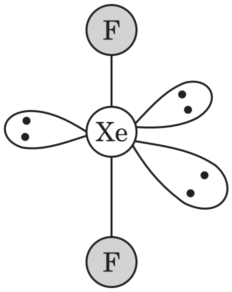
(ii) **[1]**



Shape: **Bent T-shape**

Angle $F-Cl-F$: **Less than** $90°$

(iii) **[1]**



Shape: **Linear**

Angle $F-Xe-F$: $180°$

OR

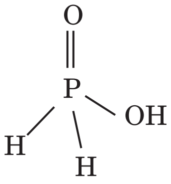
(a)

(i) $6NaOH + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$ **[1]**

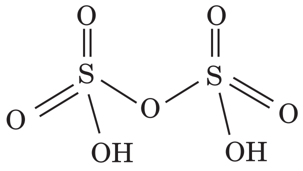
(ii) $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$ **[1]**

(b)

(i) **[1]**

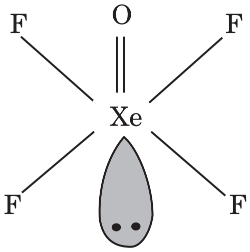


(ii) **[1]**



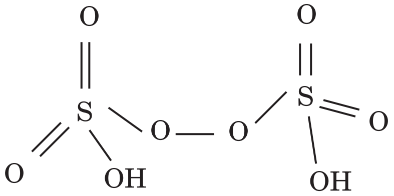
$H_2S_2O_7$

(iii) **[1]**

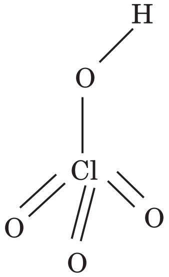


8. (a)

(i) $H_2S_2O_8$ **[1]**



(ii) $HClO_4$ **[1]**



(b)

(i) N is smaller in size and more electronegative than P. So, lone pair of electrons is concentrated more on nitrogen. **[1]**

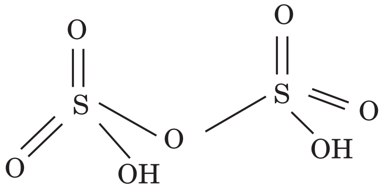
(ii) Oxygen has a small size as compared to sulphur. So, the lone pairs on oxygen repel each other. Thus, the O-O bond is weak whereas in case of sulphur, the lone pair do not repel to the same extent. As a result, S-S bond is stronger than O-O bond. So, S has a greater tendency for catenation than oxygen. **[1]**

(iii) The net energy release for $e^- + \frac{1}{2}X_2(g) \longrightarrow X^-(aq)$ is more negative for fluorine as compared to chlorine i.e. sum of dissociation energy, electron gain enthalpy and hydration energy is more negative for fluorine. So, it is a stronger oxidizing agent than chlorine. **[1]**

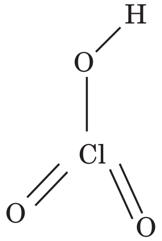
OR

(a)

(i) $H_2S_2O_7$ **[1]**



(ii) $HClO_3$ **[1]**



(b)

(i) Because of partial double bond character of (N-O) bond. **[1]**

(ii) P in PCl_5 is sp^3d hybridized. The axial bonds due to more repulsion are longer than equatorial bonds. **[1]**

(iii) ICl is an interhalogen compound having electronegativity difference. The I-Cl bond is more reactive than I_2. **[1]**

9. (a)

(i) H_3PO_3 : Oxidation number of $P = +3$ **[1]**

H_3PO_4 : Oxidation number of $P = +5$

In H_3PO_4 oxidation number of phosphorus is +5 and H_3PO_3 oxidation number of phosphorus is +3

Therefore H_3PO_4 can undergo only reduction whereas H_3PO_3 can undergo oxidation as well as reduction.

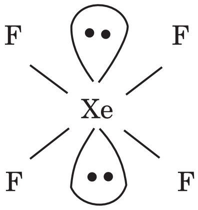
(ii) Fluorine can exist only in – 1 oxidation state whereas chlorine can show positive oxidation states when combined with more electronegative atom. **[1]**

In ClF_3 oxidation number of Cl is + 3 which is possible.

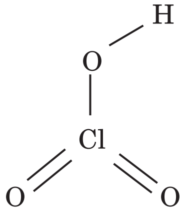
(iii) In oxygen molecule, there is p-p overlap between two oxygen atoms forming double bond. The intermolecular forces in oxygen are weak Vander Waal's forces and therefore oxygen exists as a gas on the other hand, the S are linked by single bonds and form polyatomic complex molecules. Hence sulphur in a solid. **[1]**

(b)

(i) **[1]**



(ii) **[1]**

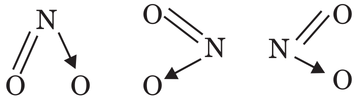


OR

(a)

(i) NO_2 and N_2O_4 **[1]**

(ii) **[1]**



(iii) NO_2 is an odd electron species and hence it dimerises to give N_2O_4 on cooling. **[1]**

(b) $HF > HBr > HCl > HI$ **[1]**

(c) $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]$ **[1]**

Topic 3: Group 17 Elements

Summary

- **Electronic configuration:** $ns^2\ np^5$
- **Atomic and Ionic radii:** They have the smallest radii in their respective periods because of increase in nuclear charge. It increases down the group.
- **Ionization Enthalpy:** Decreases down the group.
- **Electronegativity:** Decreases down the group and they are the most electronegative elements in their respective periods.
- **Oxidation state:** Except fluorine, other elements show oxidation states of +1, +3, +5 and +7. Fluorine shows -1 oxidation state.
- **Melting and boiling point:** It increases as we move down the group due to increase in radii and nuclear charge which causes greater van der Waal's forces of attraction.
- These elements are extremely reactive and as such they are found in the combined state only.
- They form oxides, hydrogen halides, interhalogen compounds and oxoacids.
- **Acidic strength of Hydrogen halides:** $HF < HCl < HBr < HI$.
- Most of the oxides formed by these halogens are unstable and their stability decreases in the order $I > Cl > Br$.
- Acidic strength of oxoacids containing different halogen:

  $HClO > HBrO > HIO$
- Acidic strength of oxoacids containing the same halogen:

  $HClO < HClO_2 < HClO_3 < HClO_4$
- Chlorine is conveniently obtained by the reaction of HCl with $KMnO_4$.

  $MnO_2 4HCl \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$
- **Properties of Chlorine:** Greenish yellow gas with a pungent suffocating smell, soluble in water.
- HCl is prepared by heating NaCl with concentrated H_2SO_4.

  $NaCl + 4H_2SO_4 \xrightarrow{420K} NaHSO_4 + HCl$
- Halogens combines with one another to form a number of compounds known as interhalogen compounds. General formula are XX', XX_3', XX_5', XX_7' where X is a halogen of larger size and higher electro positivity and of smaller size. For example:

  $Cl_2 + F_2 \xrightarrow{470K} 2ClF$

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 3

▶ 1 Mark Questions

1. Draw the structure of BrF_3 molecule.

[DELHI 2011]

2. Write the formula of the compound of Iodine which is obtained when conc. HNO_3 oxidises I_2. **[ALL INDIA 2017]**

▶ 2 Marks Questions

3. Explain the following giving an appropriate reason in each case.

(i) O_2 and F_2 both stabilize higher oxidation states of metals but O_2 exceeds F_2 in doing so.

(ii) Structures of Xenon fluorides cannot be explained by Valence Bond approach.

[ALL INDIA 2012]

4. What happens when

(i) PCl_5 is heated?

(ii) H_3PO_3 is heated?

Write the reaction involved. **[DELHI 2013]**

5. How are inter-halogen compounds formed? What general compositions can be assigned to them? **[ALL INDIA 2013]**

6. Draw the structures of the following molecules:

(i) SF_4

(ii) XeF_4 **[DELHI 2016]**

7. Write the structures of the following:

(i) BrF_3

(ii) XeF_4

OR

What happens when?

(i) SO_2 gas is passed through an aqueous solution Fe^{3+} salt?

(ii) XeF_4 reacts with SbF_5? **[ALL INDIA 2016]**

8. Complete the following chemical reaction equations:

(i) $XeF_2 + H_2O \longrightarrow$

(ii) $PH_3 + HgCl_2 \longrightarrow$ **[DELHI 2017]**

9. Draw the structure of the following:

(a) XeF_4

(b) BrF_5 **[ALL INDIA 2017]**

▶ 3 Marks Questions

10. (a) Draw the structures of the following:

(i) XeF_2

(ii) BrF_3

(b) Write the structural difference between white phosphorus and red phosphorus.

[DELHI 2014]

11. Account for the following:

(i) PCl_5 is more covalent than PCl_3.

(ii) Iron on reaction with HCl forms $FeCl_2$ and not $FeCl_3$.

(iii) The two O-O bond lengths in the ozone molecule are equal. **[DELHI 2014]**

12. Write chemical equations for the following processes:

(i) Chlorine reacts with a hot concentrated solution of sodium hydroxide.

(ii) Ortho phosphorous acid is heated

(iii) PtF_6 and xenon are mixed together

OR

Complete the following chemical equations:

(i) $Ca_3P_2(g) + H_2O(l) \longrightarrow$

(ii) $Cu_2 + (aq) + \underset{\text{(excess)}}{NH_3(aq)} \longrightarrow$

(iii) $F_2(g) + H_2O\ (l) \longrightarrow$

[DELHI 2016]

▶ 5 Marks Questions

13. (a) Explain the following:

(i) NF_3 is an exothermic compound whereas NCl_3 is not.

(ii) F_2 is most reactive of all the four common halogens,

(b) Complete the following chemical equations:

(i) $C + H_2SO_4(\text{conc}) \longrightarrow$

(ii) $P_4 + NaOH + H_2O \longrightarrow$

(iii) $Cl_2 + F_2 \longrightarrow$

OR

(a) Account for the following:

(i) The acidic strength decreases in the order $HCl > H_2S > PH_3$

(ii) Tendency to form pentahalides decreases down the group in group 15 of the periodic table.

(b) Complete the following chemical equation:

(i) $P_4 + SO_2Cl_2 \longrightarrow$

(ii) $XeF_2 + H_2O \longrightarrow$

(iii) $\mathrm{I_2 + HNO_3(conc)} \longrightarrow$ **[DELHI 2011]**

14. (a) What happens when

(i) chlorine gas is passed through a hot concentrated solution of $NaOH$?

(ii) sulphur dioxide gas is passed through an aqueous solution of a Fe (III) salt?

(b) Answer the following:

(i) What is the basicity of H_3PO_3 and why?

(ii) Why does fluorine not play the role of a central atom in inter halogen compounds?

(iii) Why do noble gases have very low boiling points? **[ALL INDIA 2011]**

15. (a) Give reasons for the following:

(i) Bond enthalpy of F_2 is lower than that of Cl_2.

(ii) PH_3 has lower boiling point than NH_3.

(b) Draw the structures of the following molecules:

(i) BrF_3

(ii) $(HPO_3)_3$

(iii) XeF_4

OR

(a) Account for the following:

(i) Helium is used in diving apparatus.

(ii) Flourine does not exhibit positive oxidation state.

(iii) Oxygen shows catenation behaviour less than sulphur.

(b) Draw the structures of the following molecules.

(i) XeF_2

(ii) $H_2S_2O_8$ **[DELHI 2013]**

16. (a) Account for the the following:

(i) Acidic character increases from HF to HI.

(ii) There is large difference between melting and boiling points of oxygen and sulphur.

(iii) Nitrogen does not form pentahalide.

(b) Draw the structures of the following:

(i) ClF_3

(ii) XeF_4,

OR

(i) Which allotrope of phosphorus is more reactive and why?

(ii) How the supersonic jet aeroplanes are responsible for the depletion of ozone layers?

(iii) F_2 has lower bond dissociation enthalpy than Cl_2. Why?

(iv) Which noble gas is used in filling balloons for meteorological observations?

(v) Complete the equation:

$XeF_2 + PF_5$ **[DELHI 2015]**

17. (a) Account for the following :

(i) Bond angle in NH_4^+ is greater than that in NH_3

(ii) Reducing character decreases from SO_2 to TeO_2.

(iii) $\mathrm{HClO_4}$ is a stronger acid than $HClO$.

(b) Draw the structures of the following:

(i) $H_2S_2O_8$

(ii) $XeOF_4$

OR

(a) Which poisonous gas is evolved when white phosphorus is heated with conc. $NaOH$ solution? Write the chemical equation.

(b) Write the formula of first noble gas compound prepared by N. Bartlett. What inspired N. Bartlett to prepare this compound?

(c) Fluorine is a stronger oxidizing agent than chlorine. Why?

(d) Write one use of chlorine gas.

(e) Complete the following equation:

$CaF_2 + H_2SO_4 \longrightarrow$ **[ALL INDIA 2015]**

18. (a) Complete the following chemical equations:

(i) $\mathrm{NaOH + Cl_2}$

(ii) $XeF_6(s) + H_2O(l) \longrightarrow$

(b) How would you account for the following?

(i) The value of electron gain enthalpy with negative sign for sulphur is higher than that for oxygen.

(ii) NF_3 is an exothermic compound but NCl_3 is endothermic compound.

(iii) ClF_3 molecule has a T-shaped structure and not a trigonal planar one.

OR

(a) Complete the following chemical reaction equations:

(i) $XeF_4 + H_2O \longrightarrow$

(b) Explain the following observations giving appropriate reasons:

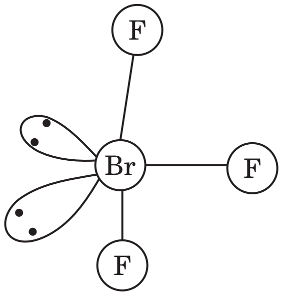
(i) The stability of +5 oxidation state decreases down the group in group 15 of the periodic table.

(ii) Solid phosphorus pentachloride behaves as an ionic compound.

(iii) Halogens are strong oxidizing agents.

Solutions

1. **[1]**



2. HIO_3 (Iodic Acid) is obtained when conc. HNO_3 oxidises I_2. **[1]**

3. *(i)* O_2 and F_2 both stabilize higher oxidation states of metals but O_2 exceeds F_2 in doing so due to ability of oxygen to form multiple bonds to metals. **[1]**

(ii) According to the valence bond approach, covalent bonds are formed by the overlapping of half filled atomic orbital. But xenon has fully filled electronic configuration. Hence the structure of xenon fluorides cannot be explained by VBT. **[1]**

4. (i) PCl_5 on heating gives PCl_3 and Cl_2.

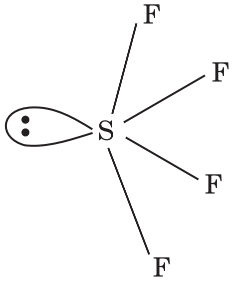
$PCl_5 \rightleftharpoons PCl_3 + Cl_2$ **[1]**

(ii) H_3PO_3 on heating gives orthophosphoric acid and phosphine. **[1]**

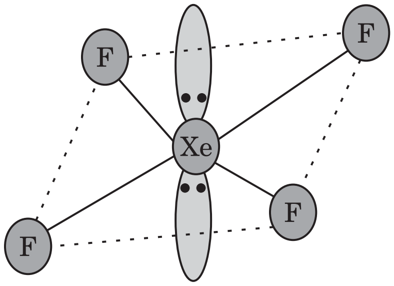
$$4H_3PO_3 \xrightarrow{\Delta} \underset{\text{orthophosphoric acid}}{3H_3PO_4} + \underset{\text{Phosphine}}{PH_3}$$

5. An interhalogen compound is a molecule that contains two or more different halogens. General formula they can be assigned is XYn where n = 1, 3, 5 or 7 and X is the less electronegative of two halogens. **[1] + [1]**

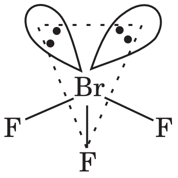
6. SF_4 **[1]**



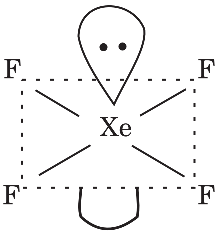
XeF_4 **[1]**

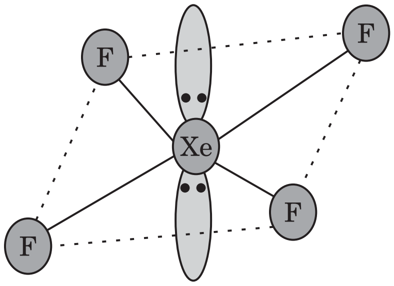


7. (i) Structure BrF_3 will bend in T-shape **[1]**



(ii) Structure of XeF_4 will be square planar in shape. **[1]**





OR

(i) When SO_2 gas is passed through an aqueous solution of Fe^{3+} salt, SO_2 acts as a reducing agent, forming Fe^{2+} i.e. reducing ferric ions to ferrous ions and turning the brown - coloured solution green. **[1]**

$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

(ii) When XeF_4 reacts with SbF_5, the following reaction takes place: **[1]**

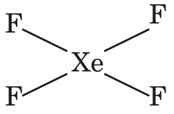
$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$$

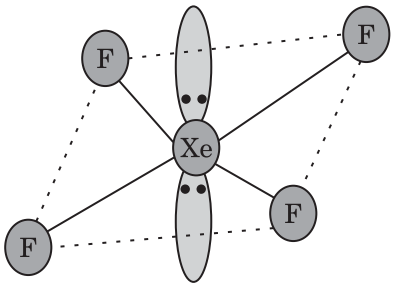
8. i. $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$

ii. $2PH_3 + 3HgCl_2 \longrightarrow Hg_3P_2 + 6HCl$

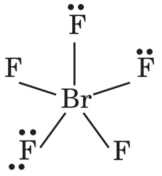
[1] + [1]

9. (a) **[1]**

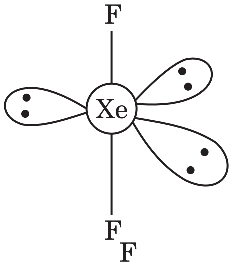




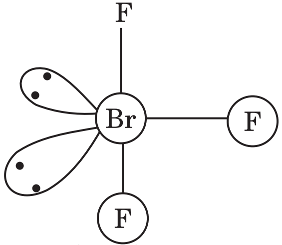
(b) **[1]**



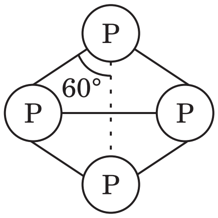
10. (a) (i) **[1]**



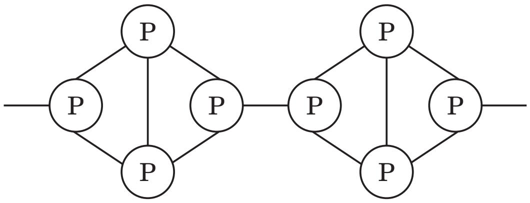
(ii) **[1]**



(b) White phosphorus consists of discrete tetrahedral P_4 molecule with six P-P covalent bonds. **[1]**



Red Phosphorus has polymeric structure in which P4 tetrahedral are linked together through P-P covalent bond to form chain.



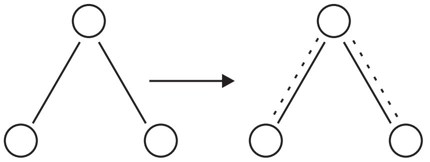
11. (i) According to Fajan's rule higher the oxidation state of the central atom, more is its polarising power, thus more is the covalent character of the bond formed. In the PCl_5 molecule the oxidation state of P is +5 while in PCl_3 it is +3. Thus, PCl_5 is more covalent in nature than PCl_3.

[1]

(ii) The hydrogen gas produced prevents further oxidation of Fe^{2+} to Fe^{3+} **[1]**

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

(iii)An ozone molecule a is resonance hybrid of the molecule in which there is single bond with one terminal oxygen and double bond with other terminal oxygen of the central oxygen atom. **[1]**



So, neither single or double bond is pure. Thus both O — O bond length are equal.

12. (i) $3Cl_2 + 6NaOH \longrightarrow$ **[1]**
$5NaCl + NaClO_3 + 3H_2O$

(ii) $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$ **[1]**

(iii) $Xe + PtF_6 \longrightarrow Xe + [PtF_6]^-$ **[1]**

OR

(i) $Ca_3P_2(s) + 6H_2O\ (l) \longrightarrow$ **[1]**
$3Ca(OH)_2(aq) + 2PH_3(g)$

(ii) $Cu^{2+}(aq) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}(aq)$ **[1]**

(iii) $2F_2(g) + 2H_2O\ (l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$ **[1]**

13. (a)

(i) Due to smaller size of F as compared to Cl, the N-F bond is much stronger than N-Cl bond while bond dissociation energy of F_2 is much lower than that of Cl_2. Therefore, energy related during the formation of NF_3 molecule is more than the energy needed to break N_2 and F_2 molecules into individual atoms. In other words, formation of NF_3 is an exothermic reaction. **[1]**

The energy released during the formation of NCl_3 molecule is less than the energy needed to break N_2 and Cl_2 molecule into individual atoms. Thus, formation of NCl_3 is an endothermic reaction.

(ii) Fluorine is most reactive of all the four common halogens because of its low bond dissociation energy due to which it readily dissociates into atoms and reacts with other substances readily **[1]**

(b) (i) $C + 2H_2SO_4 \longrightarrow CO_2 + 2H_2O + 2SO_2$ **[1]**

(ii) $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$ **[1]**

(iii) $Cl_2 + 3F_2 \xrightarrow{473K} 2ClF_3$ **[1]**

OR

(a)

(i) Because of decrease in electronegativity from chlorine to phosphorus, the dissociation enthalpy from HCl to H-P increases, and their tendency to release H^+ ion decreases and thus acidic strength decreases. **[1]**

(ii) This is due to inert pair effect. The stability of +5 oxidation state decreases down the group in group 15. **[1]**

(b) (i) $P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$ **[1]**

(ii) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$ **[1]**

(iii) $I_2 + 10HNO_3(conc) \longrightarrow 2HIO_3 + 4H_2O + 10NO_2$ **[1]**

14. (a)

(i) $3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$ **[1]**

(ii) $2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{\ 2-} + 4H^+$ **[1]**

(b)

(i) Two, due to presence of two P-OH bonds **[1]**

(ii) Due to high electronegativity of fluorine. **[1]**

(iii) There are no interatomic forces except weak dispersion forces. **[1]**

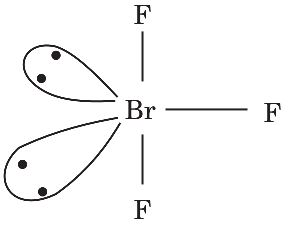
15. (a)

(i) Bond enthalpy of F_2 is lower than that of Cl_2 because 'F' atom is small in size and due to this the electron- electron repulsions between the lone pairs of F-F electrons are very large. Thus, the bond dissociation energy of F_2 is lower than that of Cl_2. **[1]**

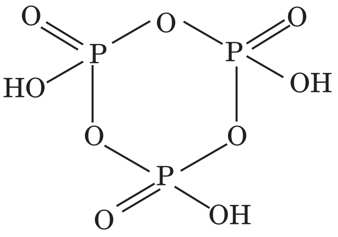
(ii) PH_3 has lower boiling point than NH_3 because $\boldsymbol{NH_3}$ molecule possess intermolecular hydrogen bondings which binds them strongly, whereas, $\boldsymbol{PH_3}$ has weaker van der Waal's forces. Thus PH_3 has a lower boiling point than NH_3. **[1]**

(b)

(i) BrF_3, Bent T-shape **[1]**



(ii) $(HPO_3)_3$ Cyclic Structure **[1]**



(iii) XeF_4, square planar **[1]**

OR

(a)

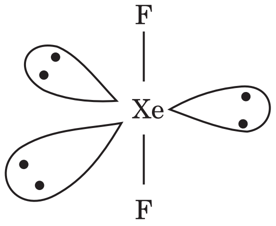
(i) Helium mixed with oxygen under pressure is given to sea- divers for artificial respiration because of its very low solubility in blood. Air is not given because nitrogen present in air being soluble in blood will give a painful sensation called bends by bubbling out blood on moving from high pressure to the atmospheric pressure. Thus, oxygen-helium mixture is used. **[1]**

(ii) Fluorine being the most electronegative atom does not exhibit positive oxidation state because, it does not have d-orbitals for octet expansion and therefore, it shows only a negative oxidation state of -1. **[1]**

(iii) Oxygen shows catenation behaviour less than sulphur because the oxygen atom is smaller in size as compared to sulphur, due to this the lone pair of electrons in O–O bonds in oxygen experiences more repulsions as compared to the S-S bonds and thus, S-S forms strong bond. **[1]**

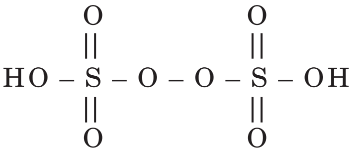
(b)

(i) XeF_2, **[1]**



XeF_2, Shape : Linear

(ii) $H_2S_2O_8$ **[1]**



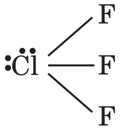
$$HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$$

16. (a) (i) The acidic strength of the halogen acids increases from HF to HI because the stability of the acids decreases from HF to HI on account of decrease in bond dissociation enthalpy of H — X bond from HF to HI. **[1]**

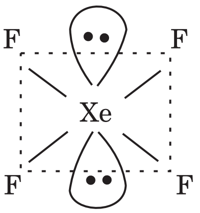
(ii) The difference in melting point and boiling point of oxygen and sulphur is due to the difference in their atomicities oxygen exists as a diatomic (O_2) molecule, while sulphur exists as a polyatomic (S_8) molecule and also oxygen is small in size and have high electro negativities. **[1]**

(iii)Being an element of second period, Nitrogen has no 'd' orbitals and its maximum covalency is restricted to four. Hence, due to the non-availability of d-orbitals, it can't form pentahalides. **[1]**

(b) (i) **[1]**

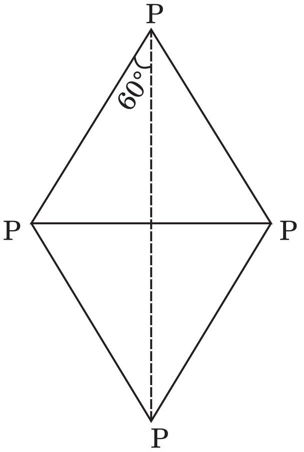


(ii) Structure of XeF_4 **[1]**



OR

(i) White phosphorus is most reactive of all the allotropes of phosphorus. It is because it exists as P_4 discrete tetrahedral units with 60° angle, which results in angular strain and makes it highly reactive. **[1]**



(ii) Since supersonic jets fly in the stratosphere near the ozone layer, they are responsible for the depletion of ozone layer. The oxide emitted from the exhausts of supersonic jet aeroplanes readily combine with ozone to form nitrogen dioxide and diatomic oxygen. **[1]**

$$NO(g)+O_3\ (g)\longrightarrow NO_2\ (g)+O_2\ (g)$$

(iii)The size of a fluorine atom is very small as compared to a chlorine atom. Therefore, the repulsion between electrons in the outer most shell of the two atoms in a fluorine molecule is much greater than that in a chlorine molecule. Hence, it requires less energy to break up the fluorine molecule, making its bond dissociation energy lesser than that of chlorine molecule. **[1]**

(iv) Helium gas is used for filling of balloons for meteorological observations. **[1]**

(v) $XeF_2 + PF_5 \longrightarrow [XeF]^+[PF_6]^-$ **[1]**

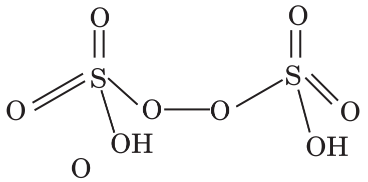
17. (a) *(i)* In NH^+_4 all the four orbitals are bonded where as in NH_3, there is a lone pair of electrons on p, which is responsible for lone pair-bond pair repulsion in NH_3 & reduce the bond angle **[1]**

(ii) Acidic character increases due to decrease in bond enthalpy as we move down the group and due to increasing of size E–H bond breaks more easily. **[1]**

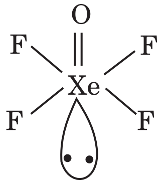
(iii) $HClO_4$ is a stronger acid than HClO because acidic character increases with the increase in oxidation number. Since Cl in $HClO_4$ is in +7 oxidation it is more acidic than HClO where Cl is in +1 oxidation state. **[1]**

(b)

(i) **[1]**



(ii) **[1]**



OR

(a) $P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{Phosphine Gas}}{PH_3 + NaH_2PO_2}$

[1]

(b) N Bartlett first prepared & then he made effort to make first noble gas compound $Xe^+PtF_6^-$ because I.E. of xenon is almost same as oxygen . **[1]**

(c)

(i) The E^o_{cell} value of F_2 is much higher than that of Cl_2

(ii) F_2 has low bond dissociation enthalphy than Cl_2

(iii) F_2 Flurine has **more electronegativity** than Cl_2 Chlorine **[1]**

(d) Cl_2 is used in bleaching wood pulp **[1]**

(e) $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$ **[1]**

18. (a)

(i) $6NaOH + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$ **[1]**

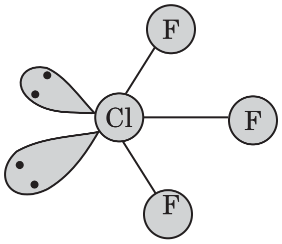
(ii) $XeF_6(s) + 3\,H_2O(l) \longrightarrow XeO_3 + 6\,HF$

[1]

(b) (i) This is because oxygen has a smaller size than sulphur. **[1]**

(ii) Because of small difference between the size of N and F which results in stable N-F bond. NCl_3 is unstable because of large difference between the size of N and Cl which results is weak N-Cl bond. **[1]**

(iii) This is because in ClF_3, Cl is sp^3d hybridised and two lone pairs are present on equatorial positions. **[1]**



OR

(a) *(i)* $P_4 + 10\,SO_2Cl_2 \longrightarrow 4\,PCl_5 + 10SO_2$ **[1]**

(ii) $6\,XeF_4 + 12\,H_2O \longrightarrow 4Xe + 2XeO_3 + 24\,HF + 3\,O_2$

[1]

(b) *(i)* This is because of inert pair effect. As we move down the group, due to poor shielding of inner d- electrons, ns electrons are pulled strongly towards the nucleus. Thus, ns electrons are difficult to release and do not participate in bond formation. **[1]**

(ii) Solid phosphorus pentachloride behaves as an ionic compound because in solid state it exists as $[PCl_4]^+[PCl_6]^-$ having tetrahedral PCl_4^+ and octahedral PCl_6^-. These two combines to form a stable ionic species where PCl_4^+ acts as cation and PCl_6^- acts as anion. **[1]**

(iii) Halogens are strong oxidizing agents because of high electronegativity and high electron affinity which makes them to take electrons very much readily from other elements and oxidise other elements. **[1]**

Topic 4: Group 18 Elements

Summary

- **Electronic configuration:** $ns^2\ np^6$.
- **Atomic and Ionic radii:** They have the largest radii in their respective periods and it increases down the group.
- **Ionization Enthalpy:** Decreases down the group and have highest ionization enthalpy in their respective periods.
- Low melting and boiling points because of weak van der Waal's forces. Increases down the group.
- Due to complete octet of outermost shell, they have less tendency to form compounds. The best characterised compounds are those of xenon with fluorine and oxygen only under certain conditions.
- These gases have several uses. Argon is used to provide inert atmosphere, helium is used in filling balloons for meteorological observations, neon is used in discharge tubes and fluorescent bulbs.
- Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6 by following reactions.

$$Xe(g) + F_2(g) \xrightarrow{\text{673K, 1bar}} XeF_2(s)$$

$$Xe(g) + 2F_2(g) \xrightarrow{\text{873K, 7bar}} XeF_4(s)$$

$$Xe(g) + 2F_2(g) \xrightarrow{\text{573K, 60-70bar}} XeF_6(s)$$

- Xenon trioxide (XeO_3)

$$6XeF_4(g) + 12H_2O \rightarrow 2XeO_3 + 4Xe + 3O_2 + 24HF$$

- Xenon oxyfluorides

$$XeF_4 + H_2O \rightarrow XeOF_2 + 2HF$$

$$XeF_6 + H_2O \xrightarrow[\textit{hydrolysis}]{\textit{partial}} XeOF_4 + 2HF$$

$$XeF_6 + OH_2O \xrightarrow[\textit{hydrolysis}]{\textit{complete}} XeO_2F_4 + 4HF$$

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 4

1 Mark Questions

1. What is the structure of XeF_2 molecule? Draw it. **[DELHI 2011]**

2. Draw the structure of XeF_4 molecule. **[CBSE 2011]**

3. What inspired N. Bartlett for carrying out reaction between Xe and PtF_6? **[CBSE 2013]**

2 Marks Questions

4. Draw the structures of the following molecules:

(i) XeF_6

(ii) $H_2S_2O_7$ **[ALL INDIA 2013]**

5. Complete the following equations:

(i) $C + conc.\ H_2SO_4 \longrightarrow$

(ii) $XeF_2 + H_2O \longrightarrow$ **[ALL INDIA 2014]**

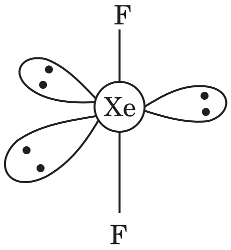
6. Draw the structures of the following:

(i) XeO_3

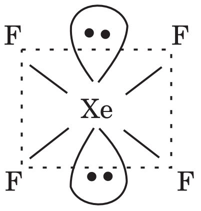
(ii) H_2SO_4 **[ALL INDIA 2011]**

Solutions

1. **[1]**

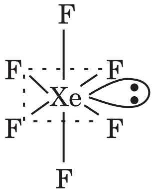


2. **[1]**

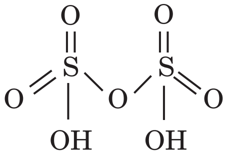


3. N. Bartlett observed that the first ionization enthalpy of molecular oxygen is almost identical with that of xenon. So after preparing red coloured compound $O_2 + PtF_6^-$ he made efforts to prepare $Xe + PtF_6^-$ by mixing PtF_6 and Xe. **[1]**

4. (i) **[1]**



(ii) **[1]**

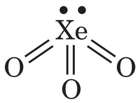


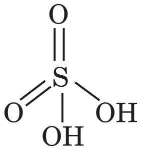
5. (i) $C + conc.\ H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2\,H_2O$

(ii) $XeF_2 + 2H_2O \longrightarrow 2Xe + O_2 + 4HF$

[1] + [1]

6. **[1] + [1]**





Smart Notes ....

CHAPTER 8

d- and f-Block Elements

Chapter Analysis with respect to Last 3 Years' Board Exams

List of Topics	**2016**		**2017**		**2018**	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
General introduction, electronic configuration, occurrence and characteristics of transition metals			3 marks	3 marks		
General trends in properties of the first row transition metals				3 marks		
Metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties	5 marks	5 marks	2, 3 marks	2 marks	2 ,3 marks	2 ,3 marks
Interstitial compounds, alloy formation, preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$.						
Lanthanoids - Electronic configuration, oxidation states, chemical reactvity and lanthanoid contraction and its consequences						
Actinoids - Electronic configuration, oxidation states and comparison with lanthanoids						

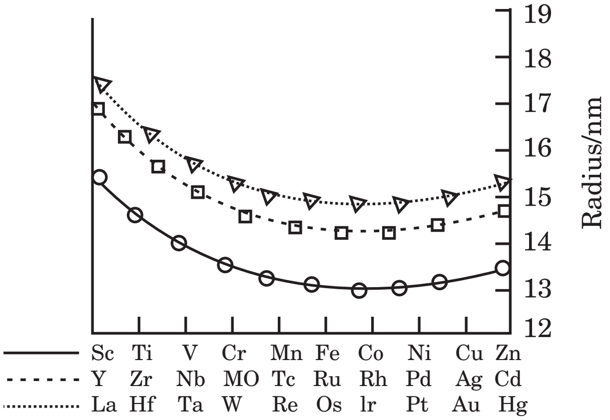
Summary

d-block elements

- The elements of group 3-12 which have incompletely filled *d*-orbitals in the ground state are called d- block elements.
- They are also called transitional elements as their properties are in between those of s and p block elements.
- The electronic configuration is given as $(n - 1)\,d^{1-10}\,ns^{1-2}$.

General properties

- **Physical Properties**
  - ➢ They are all metals, malleable and ductile(except Hg)
  - ➢ They display high tensile strength, high thermal and electrical conductivity
- **Variation in atomic and ionic sizes**
  - ➢ With increasing atomic number, ions of the same charge in given series experience decrease in radius as when a new electron enters a *d* orbital, the nuclear charge increases by unity.
  - ➢ 4*f* orbitals must be filled before 5*d* orbitals which leads to a regular decrease in atomic radii known as Lanthanoid contraction which is responsible for increasing atomic sizes with increasing atomic number.



- **Ionisation Enthalpy**

  The ionization enthalpy in a group decreases from 3*d* to 4*d* series and increases from 4*d* to 5*d* series because of Lanthanoid contraction.
- **Oxidation states**
  - ➢ Transition elements show a great variety of oxidation states in their compounds due to incomplete filling of *d*-orbitals.
  - ➢ Elements in the middle of the group have the maximum number of oxidation states, example: Manganese exhibits oxidation states from +2 to +7.
- **Trends in** $\frac{M^{2+}}{M}$ **electrode potential**

  No regular trend is shown in $E°$ values as ionization and sublimation enthalpy have no regular trend.

- **Magnetic Properties**
  - The two types of elements are diamagnetic and paramagnetic.
  - Diamagnetic substances have paired electrons only like Zn whereas paramagnetic substances have atleast one unpaired electron
- **Colored compound formation**

  The transition elements form colored ions as they have unpaired *d*-electrons.

  When light is absorbed in the visible region, it causes excitation of unpaired *d*-electrons which causes formation of colored compounds.
- **Alloy Formation**
  - *d*- block elements form alloy due to:

    Availability of d-orbitals for bond formation

    High ionic charges

    Similar sizes of the metal ions
  - Some of the alloys are Steel and Brass.
- **Chemical Reactivity**
  - Transition metals differ in chemical reactivity.
  - Many of them are sufficiently electropositive to dissolve in mineral acids while few of them stay unaffected by simple acids.
- **Catalytic Properties**
  - Many of the transition metals and their compounds acts as catalyst, especially oxides.
  - Some of the commonly used catalysts are Iron, Nickel, Cobalt, Platinum and their compounds.
- **Interstitial Compound Formation**
  - These are the compounds formed when small atoms (H, C, and N) get trapped inside the crystal lattices of metals. Example: TiC, Fe_3H, Mn_4N.
  - They are chemically inert, have a good metallic conductivity and are extremely hard.

Compounds of Transition Elements

- **Potassium dichromate ($K_2Cr_2O_7$)**
  - It is a crystalline solid orange in color.
  - It is prepared from the chromate ore using the following reactions:

    $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

  The sodium chromate solution is acidified with sulphuric acid

  $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

  The solution is treated with potassium chloride.

  $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$
  - It is used in preparation of azo compounds and in leather industry.
- **Potassium Permanganate ($KMnO_4$)**
  - It is a crystalline solid dark purple in color.
  - It is prepared commercially as

$$MnO_2 + 2e^- \xrightarrow[\text{Oxidised with air}]{\text{Fused with KOH}} MnO_4^{\,2-}$$

$$MnO_4^{\,2-} \xrightarrow[\text{in alkaline solution}]{\text{Electrolytic oxidation}} MnO_4^{\,-} + 1e^-$$

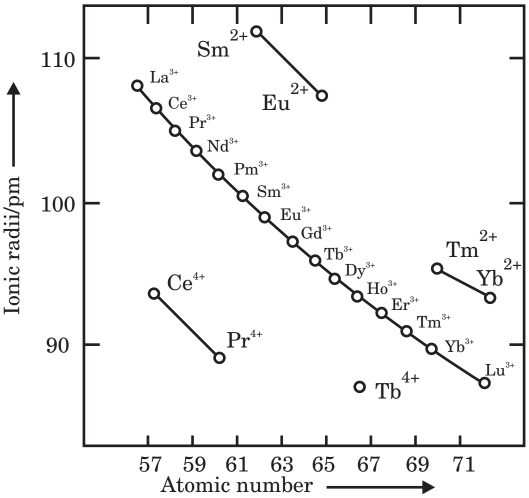
  - It is used in titration, bleaching of silk and in organic synthesis.
- The *f* block elements comprises of two series of elements called Lanthanoids and Actinoids.

- The general electronic configuration for f block elements is $(n-2)f^{1-14}\,(n-1)d^{0-1}\,ns^2$.
  $$\begin{cases} n=6 & \text{for Lanthanoid} \\ n=7 & \text{for Actinoid} \end{cases}$$

Lanthanoids

- **General Properties**
  - ➢ They are soft metals silvery white in color.
  - ➢ They are good conductors of electricity.
- **Atomic and ionic sizes**

  There is an overall decrease in atomic and ionic radii from Lanthanium to Lutelium (with increasing atomic number) due to Lanthanoid Contraction.



- **Oxidation States**

  Some of the elements exhibit +2 and +4 oxidation states but mainly they show +3 oxidation state.

Actinoids

- **General Properties**
  - ➢ Actinoids are radioactive elements.
  - ➢ They have high melting point and are highly electropositive.
- **Atomic and ionic radii**
  - ➢ With increasing atomic number, the electrons are added to the 5f shell resulting in increase in nuclear charge causing the shell to shrink which is known as actinoid contraction.
  - ➢ Due to actinoid contraction, atomic and ionic radii decrease with increasing atomic number
- **Oxidation States**
  - ➢ They generally exhibit +3 oxidation state but the distribution in oxidation states is uneven.
  - ➢ They exhibit higher oxidation states of +4, +5, +6, +7.

Comparison of Lanthanoids with Actinoids

Lanthanoids	**Actinoids**
They are less reactive than actinoids.	They are highly reactive metals.
$4f$ orbital is progressively filled.	$5f$ orbital is progressively filled.
They show limited oxidation state +2, +3, +4	A variety of oxidation states is shown. +3, +4, +5, +6, +7
They are non-radioactive except promethium.	They are radioactive elements.

Applications of *d* and *f* block elements

- Plutonium is used in atomic reactors and in atomic bombs.
- Oxides of lanthanoids are used as abrasives in cleaning of glass
- Iron is extensively used as a building material.
- *d* and *f* block elements are used as catalysts in various reactions.
- MnO_2 is used in dry battery cells.

PREVIOUS YEARS'
EXAMINATION QUESTIONS

▶ 1 Mark Question

1. What is meant by 'lanthanoid contraction'?

[ALL INDIA 2011]

▶ 2 Marks Questions

2. How would you account for the following:
   (i) Cr^{2+} is reducing in nature while with the same d-orbital configuration $(d^4)Mn^{3+}$ is an oxidising agent.
   (ii) In a transition series of metals, the metal which exhibits the greatest number of oxidation states occurs in the middle of the series. [**ALL INDIA** 2011]
3. Complete the following chemical equations:
   (i) $MnO_4^{\ -}(aq)+S_2O_3^{\ 2-}(aq)+H_2O\ (l)\longrightarrow$
   (ii) $Cr_2O_7^{\ 2-}(aq)+Fe^{2+}(aq)+H^+(aq)\longrightarrow$

   OR

   State reasons for the following:
   (i) Cu (I) ion is not stable in an aqueous solution.
   (ii) Unlike $Cr^{3+}, Mn^{3+}, Fe^{3+}$ and the subsequent other M^{3+} ions of the 3d series of elements, the 4d and the 5d series metals generally do not forms stable cationic species.
   [ALL INDIA 2011]
4. Assign reasons for each of the following:
   1. Transition metals generally form coloured compounds.
   2. Manganese exhibits the highest oxidation state of +7 among the 3d series of transition elements. **[DELHI 2011]**
5. Assign reasons for the following:
   1. Copper (I) ion is not known in aqueous solution.
   2. Actinoids exhibit greater range of oxidation states than lanthanoids. **[DELHI 2011]**
6. Complete the following chemical equations:
   (i) $Cr_2O_7^{2-}+H^++I^-\longrightarrow$
   (ii) $MnO_4^-+NO_2^-+H^+\longrightarrow$

   [ALL INDIA 2013]
7. (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}
   (Atomic Nos. Sc = 21, V = 23, Ti = 22, Mn = 25) **[DELHI 2013]**
8. What are the transition elements? Write two characteristics of the transition elements. **[DELHI 2015]**
9. Why do transition elements show variable oxidation states? How is the variability in oxidation states of d-block different from that of the p-block elements? **[ALL INDIA 2015]**
10. Complete the following chemical reaction equations:
    (i) $MnO_4^{\ -}(aq)\ +\ C_2O_4^{\ 2-}(aq)\ +\ H^+(aq)\longrightarrow$
    (ii) $Cr_2O_7^{\ 2-}(aq)\ +\ Fe^{2+}(aq)\ +H^+(aq)\longrightarrow$

    [DELHI 2015]
11. Complete and balance the following chemical equations:
    (a) $Fe^{2+}+MnO_4^-+H^+\longrightarrow$
    (b) $MnO_4^-+H_2O+I^-\longrightarrow$

    [ALL INDIA 2018]

12. Explain the following observations:

(i) Generally there is an increase in density of elements from titanium ($Z = 22$) to copper ($Z = 29$) in the first series of transition elements.

(ii) Transition elements and their compounds are generally found to be good catalysts in chemical reactions.

3 Marks Questions

13. (*i*) E^0 value for the Mn^{3+}/Mn^{2+} couple is positive (+1.5 V) whereas that of Cr^{3+}/Cr^{2+} is negative (– 0.4 V). Why?

(*ii*) Transition metals form colored compounds. Why?

(*iii*) Complete the following equation:

$$2\,MnO_4^{\,-} + 16H^{+} + 5C_2O_4^{\,2-} \longrightarrow$$

[**ALL INDIA 2015**]

14. How would you account for the following?

1. With the same d-orbital configuration (d_4) Cr^{2+} is a reducing agent while Mn^{3+} is an oxidizing agent.
2. The actinoids exhibit a larger number of oxidation states than the corresponding members in the lanthanoid series.
3. Most of the transition metal ions exhibit characteristic in colours in aqueous solutions. **[DELHI 2012]**

15. Explain the following observations giving an appropriate reason for each:

1. The enthalpies of atomization of transition elements are quite high.
2. There occurs much more frequent metal-metal bonding in compounds of heavy transition metals (i.e. 3rd series).
3. Mn^{2+} is much more resistant than Fe^{2+} towards oxidation. **[DELHI 2012]**

16. How would you account for the following?

(i) Many of the transition elements are known to form interstitial compounds.

(ii) The metallic radii of the third (5d) series of transition metals are virtually the same as those of the corresponding group member of the second (4d) series.

(iii) Lanthanoids from primarily +3 ions, while the actinoids usually have higher oxidation states in their compounds, +4 or even +6 being typical. [**ALL INDIA 2012**]

17. How would you account for the following?

(i) Transition metals exhibit variable oxidation states.

(ii) Zr ($Z = 40$) and Hf ($Z = 72$) have almost identical radii.

(iii) Transition metals and their compounds act as catalyst.

OR

Complete the following chemical equations:

(i) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^{+} \longrightarrow$

(ii) $2CrO_4^{2-} + 2H^{+} \longrightarrow$

(iii) $2MnO_4^{-} + 5C_2O_4^{2-} + 16H^{+} \longrightarrow$

[DELHI 2017]

18. How would you account for the following:

(i) Many of the transition elements and their compounds can act as good catalysts.

(ii) The metallic radii of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second series.

(iii) There is a greater range of oxidation states among the actinoids than among the lanthanoids. **[DELHI 2017**]

19. (a) Based on the nature of intermolecular forces, classify the following solids: Silicon carbide, Argon

(b) ZnO turns yellow on heating. Why?

(c) What is meant by groups 12-16 compounds? Give an example. **[ALL INDIA 2017]**

20. How would you account for the following?

(i) The atomic radii of the metals of the third (5*d*) series of transition elements are virtually the same as those of the corresponding members of the second (4*d*) series.

(ii) The E^0 value for the Mn^3/Mn^{2+} couple is much more positive than that for $Cr^3/\ Cr^{2+}$ couple or Fe^{3+}/Fe^{2+} couple.

(iii) The highest oxidation state of a metal is exhibited in its oxide or fluoride.

[DELHI 2014]

21. Give reasons:

(a) E^0 value for Mn^{+3}/Mn^{2+} couple is much more than that for Fe^{+3}/Fe^{2+}

(b) Iron has higher enthalpy of atomization than that of copper.

(c) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured. [**ALL INDIA 2018**]

5 Marks Questions

22. (a) Give reasons for the following:

(i) Mn^{3+} is a good oxidizing agent

(ii) $E^o_{M^{2+}/M}$ values are not regular for first row transition metals (3d series)

(iii) Although 'F' is more electronegative than 'O', the highest Mn fluoride **is** MnF_4, whereas the highest oxide is Mn_2O_7

(b) Complete the following equation:

(i) $2CrO_4^{2-} + 2H^+ \longrightarrow$

(ii) $KMnO_4 \xrightarrow{heat}$

OR

(a) Why do transition elements show variable oxidation states?

(i) Name the elements showing maximum number of oxidation states among the first series of transition metals from Sc (Z = 21) to Zn (Z = 30)

(ii) Name the element which shows only +3 oxidation state

(b) What is lanthanide contraction? Name an important alloy which contains some of the lanthanoid metals **[ALL INDIA 2013]**

23. (a) Complete the following equations:

(i) $Cr_2O_7^{-2} + 2OH^- \longrightarrow$

(ii) $MnO_4^- + 4H^+ + 3e^- \longrightarrow$

(b) Account for the following :

(i) Zn is not considered as a transition element.

(ii) Transition metals form a larger number of complexes.

(iii) The $E°$ value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple.

OR

(i) With reference to structural variability and chemical reactivity, write the difference between lanthanoids and actinoids.

(ii) Name of member of the lanthanoid series which is well known to exhibit +4 oxidation state.

(iii) Complete the following equations:

$MnO_4^- + 8H^+ + 5e^- \longrightarrow$

(iv) Out of Mn^{3+} and Cr^{3+}, which is more paramagnetic and why?
(Atomic nos: Mn = 25, r = 24)

[**ALL INDIA** 2014]

24. (a) Account for the following:

(i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.

(ii) Cr^{2+} is a strong reducing agent.

(iii) Cr^{2+} salts are colored while Zn^{+2} slats are white.

(b) Complete the following equations:

(i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta}$

(ii) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow$

OR

The elements of 3d transition series are given as: Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn

Answer the following:

(i) Write the element which shows maximum number of oxidation states. Give reason.

(ii) Which element has the highest m.p?

(iii) Which element shows only +3 oxidation state?

(iv) Which element is a strong oxidizing agent in +3 oxidation state and why?

[**ALL INDIA** 2016]

25. Assign reasons for the following:

(i) The enthalpies of atomization of transition elements are high.

(ii) The transition metals and many of their compounds act as good catalyst.

(iii) From element to element, the actinoid contraction is greater than the lanthanoid contraction.

(iv) The E_0 value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}.

(v) Scandium (Z = 21) does not exhibit variable oxidation states and yet it is regarded as a transition element.

OR

(a) What may be the possible oxidation state of the transition metals with the following d electronic configurations in the ground state of their atoms:

$3d^3 4s^2,\ 3d^5 4s^2 and\ 3d^6 4s^2$.

Indicate relative stability of oxidation states in each case.

(b) Write steps involved in the preparation of

(i) Na_2CrO_4 from chromite ore and

(ii) K_2MnO_4 from pyrolusite ore.

[DELHI 2016]

26. (a) Account for the following:

(i) Transition metals show variable oxidation states.

(ii) Zn, Cd and Hg are soft metals.

(iii) E° value for the Mn^{3+}/Mn^{2+} couple is highly positive (+1.57 V) as compared to Cr^{3+}/Cr^{2+}.

(b) Write one similarity and one difference between the chemistry of lanthanoid and actionoid elements.

OR

(a) Following are the transition metal ions of 3d series: Ti^{4+}, V^{2+}, Mn^{3+}, Cr^{3+}

(Atomic numbers: Ti = 22, V = 23, Mn = 25, Cr = 24)

Answer the following:

(i) Which ion is most stable in an aqueous solution and why?

(ii) Which ion is a strong oxidising agent and why?

(iii) Which ion is colourless and why?

(b) Complete the following equations:

(i) $2MnO_4^- + 16H^+ + 5S^{2-} \longrightarrow$

(ii) $KMnO_4 \xrightarrow{heat}$ **[ALL INDIA 2017]**

Solutions

1. The regular decrease in the atomic and ionic radii/(having the same charge) of Lathanoids with increasing atomic number is known as Lanthanoid contraction. **[1]**

2. (*i*) Cr^{2+} is reducing as its configuration changes from d^4 to d^3**,** the latter having half filled t_{2g} level whereas Mn^{3+} to Mn^{2+} results in half filled orbitals (d^5) **[1]**

(*ii*) In a transition metal series the oxidation state first increases and then decreases; At the middle it is maximum due to greater number of unpaired electron in (n-l)d and ns orbitals. Also due to presence of more unpaired electrons and more number of partially filled orbitals in the middle of a transition series,these metals exhibit the greatest number of oxidation states. **[1]**

3. (i) $8MnO_4^-(aq) + 3S_2O_3^{2-}(aq) + H_2O\ (l) \longrightarrow$
$8\ MnO_2(s) + 6\ SO_4^{2-}(aq) + 2OH^-(aq)$

[1]

(ii) $Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ Fe^{+2}(aq) \longrightarrow$
$2\ Cr^{3+}(aq) + 6\ Fe^{+3}(aq) + 7H_2O\ (l)$

[1]

OR

(i) In an aqueous medium, Cu^{2+} is more stable than Cu^+. This is because although energy is required to remove one electron from Cu^+ to Cu^{2+}, high hydration energy of Cu^{2+} compensates for it. Because Copper (I) ion is unstable in aqueous solution and undergoes dis-proportionation to give Cu^{2+} and Cu. **[1]**

(ii) Unlike Cr^{3+}, Mn^{3+}, Fe^{3+} and the subsequent other M^{3+} ions of the 3d series of elements, the 4d and the 5d series metals generally do not forms stable cationic species because the atomic radii of 4d and 5d series are greater than that of 3d series elements. So due to poor shielding of d and f orbitals, they do not form stable cationic species. **[1]**

4. 1. Due to presence of unpaired electrons and d-d transition, the transition metals are generally coloured. **[1]**

2. Manganese (Z = 25) exhibits largest number of oxidation states. This is because its electronic configuration is $3d^5 4s^2$ and it has maximum number of electrons (five d electrons and two s electrons) to lose or share. Thus, it can exhibits an oxidation state of +2 to +7 which is the maximum number. **[1]**

5. 1. In aqueous solution Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

$$2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$$

The higher stability of Cu^{2+} ion is aqueous solution may be attributed to its greater negative $\Delta_{hyd}H$ than that of Cu^+ ion. It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

[1]

2. Actinoids exhibit greater range of oxidation states than lanthanoids. This is because there is less energy difference between 5d and 6d orbitals belonging to actinoids than the energy difference between 4d and 5d orbitals in case of lanthanoids. **[1]**

6. (i) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow$ **[1]**

$$2Cr^{3+} + 3I_2 + 7H_2O$$

(ii) $2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow$ **[1]**

$$2Mn^{2+} + 4NO_3^- + 3H_2O$$

7. (a) Cu is the only metal in the first transition series (3d series) which exhibits +1 oxidation state more frequently. This is because the electronic configuration of Cu is $3d^{10}\ 4s^1$ and after losing one electron it acquires a stable $3d^{10}$ configuration. **[1]**

(b) The colour of cations depend upon the number of unpaired electrons present in d-orbital. The electronic configuration of the following cations is as follows:

Sc (Atomic number 21) = $Sd^1s^2$and Sc^{+3} = $3d^\circ 4s^\circ$. As d-orbital is empty, it is colourless.

V (atomic number 23) = $3d^3 4s^2$ and V^{+3} = $3d^2 4s^\circ$. As d-orbital is having 2 unpaired electrons, it undergoes d-d transition and depicts green colour.

Ti (Atomic number 22) = $3d^2\ 4s^2$ and

Ti^{+4} = $3d^\circ 4s^\circ$

As d orbital is empty, it is colourless.

Mn (Atomic number 25) = $3d^5 4s^2$ and Mn^{+2} = $3d^5 4s^0$. As 'd' orbital has 5 unpaired electrons, it depicts pink colour.

Thus, V^{+3} and Mn^{+2} ions are coloured in their aqueous solution due to presence of unpaired electron. **[1]**

8. Elements which in their ground state or in any of their oxidation state **have partially filled d-orbital**. The name 'transition' is given to the elements of d-block only because of their position between d-block and p-block elements. **[1]**

The two characteristics of transition elements are: **[1]**

(i) They show variable oxidation states.

(ii) They generally form coloured compounds.

9. Transition elements show variable oxidation states because electrons in ns and (n–1) d-orbitals are available for bond formation. **[1]**

The oxidation states of d-block differ from each other by unity (due to incomplete filling of d-orbitals) whereas oxidation states of p-block elements normally differ by two units. **[1]**

10. (i) $2MnO_4^{\ -}(aq) + 5C_2O_4^{\ 2-}(aq) + 16H^+(aq)$

$$\longrightarrow 2Mn^{2+}(aq) + 8H_2O + 10CO_2$$

[1]

(ii) $Cr_2O_7^{\ 2-}(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow$

$$2Cr^{3+} + 6Fe^{3+}(aq) + 7H_2O$$

[1]

11. (a) $5Fe^{2+} + 2MnO_4^- + 8H^+ \longrightarrow$ **[1]**

$$5Fe^{+3} + 2Mn^{+2} + 4H_2O$$

(b) $2MnO_4^- + H_2O + I^- \longrightarrow$ **[1]**

$$2MnO_2 + 2OH^- + IO_3^-$$

12. (i) It is due to increase in atomic mass whereas atomic volume decreases from Ti to Cu. Therefore density goes on increasing. The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of the elements from titanium (Z = 22) to copper (Z = 29) in the first series of transition elements. **[1]**

(ii) Transition elements and their compounds are generally found to be good catalysts in chemical reaction because transition elements have the ability to adopt multiple oxidation states and form complexes. **[1]**

13. (i) Because is more stable as it has half-filled configuration $3d^5\ 4s^0$, whereas comparatively negative value of Cr show the extra stability of Cr^{3+} **[1]**

(ii) Due to d-d transition, when visible light falls on a transition metal compound, they absorb certain radiation of visible light and when energy is emitted definite color is observed. **[1]**

(iii) $2MnO_4^{\ -} + 16H^+ + 5C_2O_4^{\ 2-} \longrightarrow$ **[1]**

$$2Mn^{2+} + 10CO_2 + 8H_2O$$

14. 1. Cr^{2+} has d^4 configuration. It gets oxidized, to Cr^{3+} with electronic configuration d^3 which is more stable. Therefore, Cr^{2+} is a reducing agent. Mn^{3+} has d^4 configuration. It gets reduced to Mn^{2+} with d^5 configuration. This is half-filled d-orbital and is stable. Therefore Mn^{3+} is an oxidizing agent. **[1]**

2. Because 5f, 6d and 7s energy levels has small energy gap in the actinoid series. Due to these orbitals actinoids exhibit large number of oxidation states. **[1]**

3. Due to partial absorption of visible light the electron from one orbital gets promoted to another orbital of the d subshell. Due to presence of unpaired electrons transition metals are coloured. **[1]**

15. 1. Due to the presence of metallic bonds as a result of large number of valence electrons. **[1]**

2. The presence of valence electrons and unpaired d-orbital electrons help heavy transition metals to form metallic bonds. **[1]**

3. Due to stability of Mn^{2+} because of half filled-subshell **($3d^5$)** it does not gets oxidized. But Fe^{2+} has **$3d^6$**configuration and it can lose one electron to become $3d^5$ which is stable. Therefore it is easily oxidized. **[1]**

16. (i) Transition metals are large in size and contain lots of interstitial sites. They can trap atoms of other elements (that have small atomic size), such as H, C, N, in the interstitial sites of their crystal lattices. So they are known to form interstitial compounds.

The common examples of interstitial compounds of transition metals are TiC, Mn_4N, Fe_3H, TiH_2 etc. **[1]**

(ii) Metallic radii of third (5d) series of transition metals are virtually same as those of (4*d*) series because of the lanthanoids contraction. This is associated with the intervention of the 4f orbitals which are filled before the 5d series of elements start. The filling of 4f orbitals before 5d orbitals results in regular decrease in atomic radii which compensates the expected increase in atomic size with increasing atomic numbers. **[1]**

(iii)The wide range of oxidation states of actinoids is attributed to the fact that the 5f, 6d and 7s energy levels are of comparable energies. Therefore all these three sub shells can participate. But the most common oxidation state of lanthanoids is +3. **[1]**

17. (i) The variable oxidation states of transition elements is due to the participation of ns and (n – 1) d-electrons in bonding. Lower oxidation state is exhibited when ns-electrons take part in bonding. Higher oxidation states are exhibited when (n – 1) d-electrons take part in bonding. **[1]**

(ii) This is because atomic radii of 4d and 5d transition elements are nearly same. This similarity in size is a consequence of lanthanide contraction which is due to weak shielding of d-electrons. As a result, the radii of *Hf* becomes nearly equal to that of *Zr*. **[1]**

(iii)The catalytic activity of transition elements and their compound is due to the following reasons:

(i) Due to their tendency to shown variable oxidation state transition metal form unstable intermediate compounds and provides a new path for the reaction with lower activation energy.

(ii) In some cases, the transition metals provide a suitable large surface area with free valencies ion on which reactant are adsorbed. **[1]**

OR

(i) $$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$ **[1]**

(ii) $$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$ **[1]**

(iii) $$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$ **[1]**

18. (i) Transition elements have the ability to show variable oxidation state and to form complexes. **[1]**

(ii) Lanthanoid contraction is the result of a poor shielding effect of the 4f electrons and hence metallic radii of second and third transition series are similar. **[1]**

(iii)5f, 6d and 7s levels are of comparable energies and due to larger size and lower ionization energy, there is a greater range of oxidation states among the actinoids. **[1]**

19. (a) On the basis of intermolecular forces : -

(i) Silicon carbide: Covalent or network solid (Covalent Bonding)

(ii) Argon: Non-polar molecular solid which possess dispersion or london forces. **[1]**

(b) Zinc oxide is white in colour at room temperature. On heating it loses oxygen & turns yellow. When you heat ZnO then Oxygen leaves as O_2 leaving behind Zn^{2+} and 2 electrons. Zn^{2+} and the 2 electrons move to the interstitial sites of the crystal . This provides excess electrons in the crystal lattice of ZnO. When light falls on these crystals then these electrons absorb a part of the light in the visible region and hence impart a yellow colour to the ZnO. **[1]**

(c) Some of the compound like *ZnS*, *CdSe* and *HgTe* are example of group 12 – 16 compound. In these compound bonds are having same ionic character along with covalent. **[1]**

20. (i) Due to lanthanoid contraction. **[1]**

(ii) Because Mn^{3+} has the outer electronic configuration of $\mathbf{3}d^4$, and Mn^{2+} has the outer electronic configuration of $3d^5$. Thus, the conversion of Mn^{3+} to Mn^{2+} will be a favourable reaction since $3d^5$ is a very stable configuration as it is half-filled configuration. Hence, E^0 value for Mn^{3+}/Mn^{2+} couple is positive. Cr^{3+} to Cr^{2+} undergoes a change in outer electronic configuration from $3d^3$ to $3d^4$. Fe^{3+} to Fe^{2+} undergoes a change in outer electronic configuration from $3d^5$ to $3d^6$. Both these configurations of the resultant are not stable and hence have a lower E^0 value. **[1]**

(iii)Because of small size and high electronegativity oxygen or fluorine can oxidize the metal to its highest oxidation state. **[1]**

21. (a) Mn^{+3}/Mn^{2+} has large +ve value between Mn^{+3} can be easily reduced to Mn^{+3}. Mn^{+3} has a half- filled d-orbital.

Fe^{+3}/Fe^{2+} has small +ve because Fe^{+3} is more stable than Fe^{3+}/Fe^{2+} to Mn^{2+} has a half-filled **[1]**

(b) Metallic bond in iron is stronger than that of copper. This is due to presence of higher number of unpaired electrons. **[1]**

(c) Compounds of transition elements are coloured due to presence of unpaired electrons in d-orbital as they are working on d-d transition. In Sc^{3+} there are no electrons whereas in Ti^{3+} there is one d- electron. **[1]**

22. (a)

(i) Because +2 oxidation state of Mn is more stable than +3

$Mn^{3+} \xrightarrow{reduction} Mn^{2+}$ **[1]**

(ii) Because values of $IE_1 + IE_2$ are not regular for first row transition metals (3d series) and also sublimation enthalpies are much less for vanadium and manganese. **[1]**

(iii) Although 'F' is more electronegative than 'O', the highest Mn fluoride **is** MnF_4, whereas the highest oxide is Mn_2O_7 because the ability of oxygen to stabilize the higher oxidation states exceeds that of fluorine. Also the ability of oxygen to from multiple bonds with metals favours Mn_2O_7. O can form multiple bonds while F can form single bond. **[1]**

(b) (i) $2Cr_2O_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$ **[1]**

(ii) $KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$ **[1]**

OR

(a) Due to partially filled inner d-subshell **[1]**

(i) Mn **[1]**

(ii) Sc **[1]**

(b) As atomic number increases atomic or ionic radius gradually decreases in lanthanoids, which is called as lanthanoid contraction Misch metal is an alloy which contains some lanthanoid metals. **[2]**

23. (a)

(i) $Cr_2O_7^{-2} + 2OH^- \longrightarrow 2CrO_4^{-2} + H_2O$ **[1]**

(ii) $MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$

[1]

(b) (*i*) In Zn inner 3d-subshell is full filled. **[1]**

(*ii*) Conditions required to form complex are: **[1]**

- Metal ion must have high charge density.
- Metal ion must have vacant orbitals. Transition elements follow these requirements.

Hence, they form complexes.

(*iii*) For Mn '+2' oxidation state is more stable than '+3' oxidation state while for Cr '+3' oxidation state is more stable '+2' oxidation state in iron. **[1]**

OR

(i)

Lanthanoids	Actinoids
They are not radioactive (except Pm)	They are radioactive
They mainly show '+3' oxidation state. They can show upto '+4' oxidation state	They mainly show '+3' oxidation state. They can show upto '+7' oxidation state
Their magnetic nature can be easily explained.	Their magnetic nature cannot be easily explained
Their physical and chemical properties have been studied thoroughly.	Their physical and chemical properties have not been studied thoroughly.

[2]

(ii) Cerium (Ce) **[1]**

(iii) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ **[1]**

(iv) $Mn^{+3} = [Ar]\ 4s^0 3d^4$ (4 unpaired e$^-$)

$Cr^{+3} = [Ar]\ 4s^0 3d^3$ (3 unpaired e$^-$) Mn^{+3}

has more no. of unpaired e$^-$ than Cr^{+3}.

[1]

24. (a)

(i) Mn shows the highest oxidation state of +7 with oxygen because it can form pπ – dπ multiple bonds involving 2p-orbitals of oxygen and 3d orbitals of Mn. On the other hand, Mn shows the highest oxidation state of +4 with F because it forms single bond with F owing of unavailability of 2p-orbitals in F for multiple bonding. **[1]**

(ii) The electronic configuration of Cr^{2+} is **d^4**, whereas the electronic configuration of Cr^{3+} is **d^3** (t^3_{2g}). The electronic configuration of Cr^{3+} is a more stable configuration; hence, Cr^{2+} tends to lose an electron and behaves as a reducing agent. **[1]**

(iii) Cu^{2+} has availability of vacant d-orbitals, thereby allowing for the d-d transition and forming colored salts, whereas Zn^{2+} has no vacant d-orbitals and does not form colored salts. **[1]**

(b)

(i) $2\,MnO_2 + 4\,KOH + O_2 \longrightarrow 2\,K_2MnO_4 + 2\,H_2O$ **[1]**

(ii) $Cr_2O_7^{2-} + 14\,H^+ + 6I^{-1} \longrightarrow 2\,Cr^{3+} + 3\,I_2 + 7\,H_2O$ **[1]**

OR

(i) Mn shows maximum oxidation state of +7 because the valence shell electronic configuration of Mn is **$3d^5 4s^2$**. **[1]**

In Mn, d-orbitals are half-filled so that it can lose all 7 valence electrons. **[1]**

(ii) Cr has the highest melting point due to the availability of maximum number of unpaired electrons, which results in the increase in strength of the metallic bond. **[1]**

(iii) Sc shows only the +3 oxidation state because it has one 3d and two 4s electrons. So, it can lose maximum of three electrons. **[1]**

(iv) Mn shows strong oxidizing character in the +3 oxidation state because it acquires highly stable $3d^5$ configuration in the +2 oxidation states. **[1]**

25. (i) Transition elements because of larger number of unpaired electrons in their atoms, have stronger interatomic interaction and hence stronger bonding between atoms resulting in higher enthalpies of atomization. **[1]**

(ii) The transition metals and many of their compounds act as good catalyst because of their ability to adopt multiple oxidation states and to form complexes. **[1]**

(iii) Because of poor shielding by 5f electrons than that by 4f, actinoid contraction is greater than the lanthanoid contraction. **[1]**

(iv) The E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} because of the much larger third ionization energy of Mn (where the required change is d^5 to d^4). **[1]**

(v) Scandium (Z = 21) is regarded as a transition element because of the presence of incomplete d-orbital ($3d^1 4s^2$) in its ground state. **[1]**

OR

(a) In a transition series, those oxidation states are stable which lead to exactly half-filled or completely-filled d orbitals.

$3d^3 4s^2$ (Vanadium): **[1]**

Oxidation states +2,+3,+4,+5

Stable oxidation state:

+4 as VO^{2+}, +5 as VO_4^{3-}

$3d^5 4s^2$ (Manganese): **[1]**

Oxidation states +2,+3,+4,+5,+6,+7

Stable oxidation states:

+2 as Mn^{2+}, +7 as MnO^-_4

$3d^6 4s^2$ (Iron):

Oxidation states +2,+3, +4, +6 **[1]**

Stable oxidation state:

+2 in acidic medium, +3 in neutral or in alkaline medium.

(b)

(i) $$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$ **[1]**

(ii) $$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$ **[1]**

26. (a)

(i) The variable oxidation states of transition elements are due to the participation of ns and (n-1)d-electrons in bonding. Lower oxidation state is exhibited when ns-electrons take part in bonding. Higher oxidation states are exhibited when (n - 1)d-electrons take part in bonding. In each group, the highest oxidation state increases with the increase in atomic number; reaches the maximum in the middle, and then starts decreasing. **[1]**

(ii) Zn, Cd and Hg are soft metals due to absence of any unpaired electrons resulting in weak metal-metal bonding. **[1]**

(iii) Mn^{2+} exists in half-filled d^5 state which is highly stable while Mn^{3+} is d^4 which is not very stable. Conversion from d^4 to d^5 will be quick and have negative A_G value. Hence, because of the stability factor the $E°$ value is high for this process. While, Cr^{3+} is d^3 is half filled (t^3_{2g}) is stable in nature and Cr^{2+} is d_4 has one extra electron which it would like to donate to attain the stable half filled (t^3_{2g}) configuration. Hence for the process Cr^{3+} to Cr^{2+} the value of $E°$ is less. **[1]**

(b) Similarity: They both show contraction of radii, the progressive decrease in the radii of atoms of the lanthanoid and actionoid elements as the atomic number increases. **[1]**

Difference: Actinoids display a large number of oxidation states while lanthanoids primarily show only three oxidation states. **[1]**

OR

(i)

	Gaseous ions	**Number of un-paired electrons**
(i)	$Ti^{4+}, [Ar]3d^0$	0
(ii)	$V^{2+}, [Ar]3d^3$	3
(iii)	$Mn^{3+}, [Ar]3d^4$	4
(iv)	$Cr^{3+}, [Ar]3d^3$	3

V^{2+} and Cr^{3+} are the most stable ions in aqueous solutions owing to a t_{2g}^3 configuration. **[1]**

(ii) An examination of the $E°$ values for the redox couple M^{3+}/M^{2+} (from electrode potential table) shows that Mn^{3+} ion are the strongest oxidising agents in aqueous solutions. **[1]**

(iii) Only the ions that have electrons in d-orbital and in which d-d transition is possible will be coloured. The ions in which d-orbitals are empty or completely filled will be colourless as no d-d transition is possible in those configurations. From the given transition metal ions, it can be easily observed that only Ti^{4+} has an empty d-orbital, so, it is colourless ion. **[1]**

(b)

(i) $$2MnO_4^- + 16H^+ + 5S^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 5S$$ **[1]**

(ii) $$2KMnO_4 \xrightarrow{heat} K_2MnO_4 + MnO_2 + O_2$$ **[1]**

Smart Notes ....

CHAPTER 9

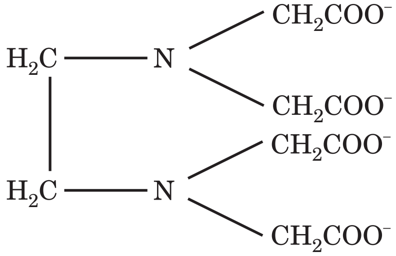
Coordination Compounds

Chapter Analysis with respect to Last 3 Years' Board Exams

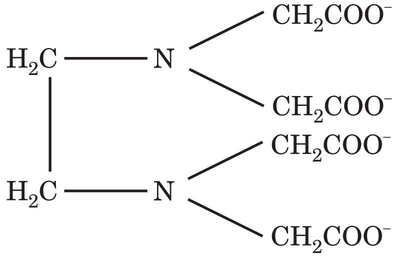
List of Topics	**2016**		**2017**		**2018**	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Coordination compounds - Introduction					(3 marks)	(3 marks)
Ligands, coordination number, colour, magnetic properties and shapes	(3 marks)		(3 marks)	(3 marks)	(1 marks)	(1 mark)
IUPAC nomenclature of mononuclear coordination compounds.		(2 marks)		(2 marks)		
Bonding, Werner's theory, VBT, and CFT						
Structure and stereo isomerism,						
Importance of coordination compounds (in qualitative inclusion, extraction of metals and biological system).						

Summary

- Coordination compounds are formed when metal atoms bound with anions or neutral molecules to form a compound. For example: $\left[Co(NH_3)_6\right]^{3+}$, $\left[Ni(CO)_4\right]$, $\left[CoCl_2(NH_3)_4\right]^{+}$, etc.
- **Double Salt:** It differs from coordination compound in such a way that they dissociate into constituent ions when dissolved in water while coordination compounds will not break into its respective ions. Some examples of double salt are Mohr's salt ($FeSO_4.(NH_4)_2SO_4.6H_2O$), Potash alum $KAl(SO_4)_2.12H_2O$, etc.
- **Coordination entity:** A central metal ion or atom bonded to a fixed number of ions or molecules forms a coordination entity. For example: $[Co(NH_3)_6]^{3+}$ is a coordination entity where a cobalt ion is surrounded by six ammonia molecules.
    - ➢ Here cobalt ion is the **central ion.**
    - ➢ The ammonia molecules arranged in a pattern around the central ion are called **ligands**.
    - ➢ When ligand is bound to metal atom/ ion by single donor atom then it is **unidentate ligand** as in this example ammonia is unidentate.
    - ➢ When a ligand is bound to two donor atoms, it is **didentate ligand**. For example: $C_2O_4^{2-}$ or $H_2NCH_2CH_2NH_2$
    - ➢ When several donor atoms are present in a single ligand, it is **a polydentate ligand**. For example: Ethylenediaminetetraacetate ion which contains several donor atoms.



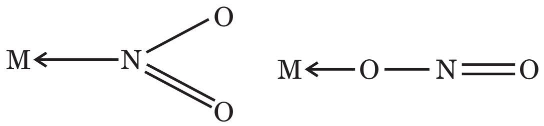
- ➢ **Denticity** is the number of ligating groups in a ligand.
- ➢ When two or more donor atoms are used by ligands to bind a metal ion, it is called a **chelate ligand**. For example:



- ➢ Ligands which can ligate through two different atoms are called **ambidentate ligands**. Some examples are: SCN^- which can coordinate through sulphur or nitrogen atom. NO_2^- can coordinate through nitrogen or oxygen.

$M \longleftarrow SCN$ $\quad$ $M \longleftarrow NCS$

thiocyanato $\quad$ isothiocyanato



- Ligands can also be classified on the basis of charge. It is of three types:

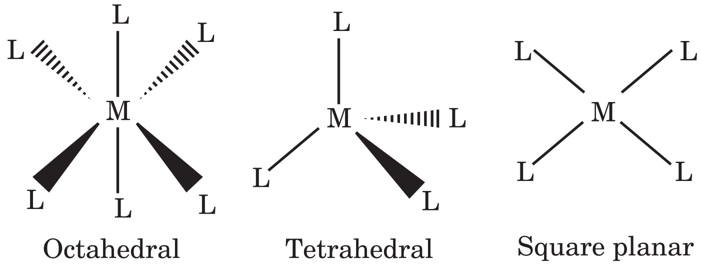
  Cationic ligands: The ligands which carry positive charge are cationic ligands. For example:

  $N_2H_5^+$, NO_2^+ .

  Anionic ligands: The ligands which carry negative charge are anionic ligands. For example: OH^-, CN^-, etc.

  Neutral ligands: Ligands which do not carry any charge are neutral ligands. For example: NH_3, N_2, NO, etc.

- **Coordination sphere:** It is a collective term for central atom/ ion and ligands written together in square brackets. For example: $[Co\ (NH_3)_6]^{3+}$, $K_4\ [Fe\ (CN)_6]$ (here $[Fe\ (CN)_6]^{4-}$ is a coordination sphere while K^+ is a counter ion).
- **Coordination number:** Metal atom/ ion is bonded to some ligand donor atoms. The number of donor atoms linked to the metal gives the coordination number. For example, in the compound $[Co\ (NH_3)_6]^{3+}$, coordination number of Co is 6 and in the compound $[Co\ (en)_3]^{3+}$, coordination number is 6 because en (ethane-1, 2-diamine) is a didentate ligand.
- **Coordination Polyhedron:** The ligand atoms are arranged around the central atom in a definite pattern which forms a coordination polyhedron. Some of the common examples are: square planar, octahedral, tetrahedral, etc.



- **Oxidation number of central atom:** The charge on the central atom when all the ligands are removed along with the elctron pairs shared with it gives the oxidation number of central atom. For example: oxidation number of copper in $[Cu\ (CN)_4]^{3+}$ is 1 and it is written in Roman numeral as Cu (I).
- **Homoleptic and heteroleptic complexes:** When a complex is bound to more than one donor groups, it is a heteroleptic complex. For example: $[Co\ (NH_3)_6]Cl_3$

  When the metal in a complex is bound to just one type of donor atom, it is a homoleptic complex. For example: $[Cu\ (CN)_4]^{3+}$
- **Nomenclature of Coordination Compounds:** It is based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC). There are some rules for naming coordination compounds which are as follows:
  - Cation is named first while naming any coordination entity.
  - Ligands are written before the central atom/ion in alphabetical order.
  - Anioinc ligands are written with –o at the end. There are some terms for some specific molecules written in (). aqua is used for H_2O, ammine for NH_3 , nitrosyl for NO and carbonyl for CO.
  - Number of individual ligands in the coordination entity are represented by some prefixes like mono, di, tri, etc.
  - Oxidation number of the central atom/ion is written in Roman numerals inside parentheses.
  - Cations are named same as the element in complex ion while anions end with –ate.

    For example: Co is written as cobalt if it acts as cation and cobaltate if it is present as anion.
- **Isomerism:** The phenomenon of compounds which have same molecular formula but different structural formulae which are isomers is known as isomerism. For example: C_2H_6O can be written as C_2H_6OH and CH_3OCH_3.

- **Types of isomerism:** Isomerism can either be structural or stereo.
  - **Structural Isomerism:** It can be divided into four types:

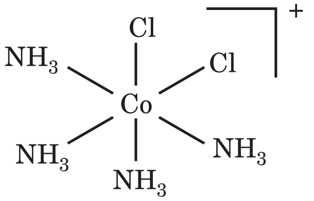
    Ionisation isomerism: When isomers have same molecular formula but different ions in solution, it is called ionisation isomerism. For example: $[Co\ (NH_3)_5SO_4]Br$ and $[Co\ (NH_3)_5Br]SO_4$.

    Linkage isomerism: It arises in compounds which contain ambidentate ligand. For example: $[Co\ (NH_3)_5\ (NO_2)]Cl_2$ where nitrile ligand is bound through oxygen to give red color and nitrile ligand is bound through nitrogen to give yellow color.

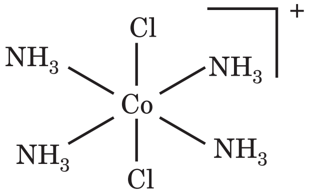
    Coordination isomerism: Ligands interchange between cationic and anionic entities of different metal ions in a complex. Such isomerism is a type of coordination isomerism. For example: $[Co\ (NH_3)_6][Cr\ (C_2O_4)_3]$ and $[Cr\ (NH_3)_6][Co\ (C_2O_4)_3]$

    Hydration isomerism: In this type of isomerism, isomers have same molecular formula but different number of molecules of water. For example: $[Cr\ (H_2O)_5Cl]\ Cl.\ H_2O$ and $[Cr\ (H_2O)_4Cl_2]Cl.\ 2H_2O$
  - **Stereo Isomerism:** It can be of two types:

    Geometrical isomerism (cis-trans isomerism): For a tetra co-ordinated square planar complex, trans-isomer has same groups on opposite sides while cis-isomer has same group on same sides. For example: cis and trans isomer of $[Co\ (NH_3)_4Cl_2]^+$

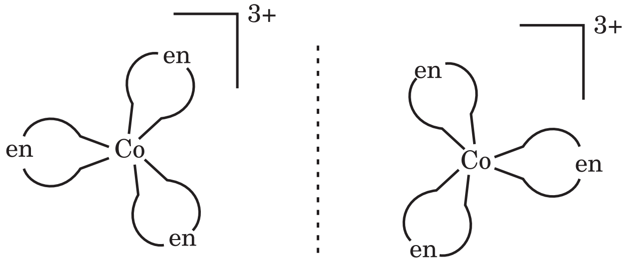


cis



trans

Optical isomerism: Optical isomers also called enantiomers are mirror images which cannot be superimposed on one another. The molecules or ions involved in this isomerism are called chiral. Depending on the direction of rotation of plane polarised light in a polarimeter, there are two forms dextro (d) and laevo (l).



dextro mirror laevo

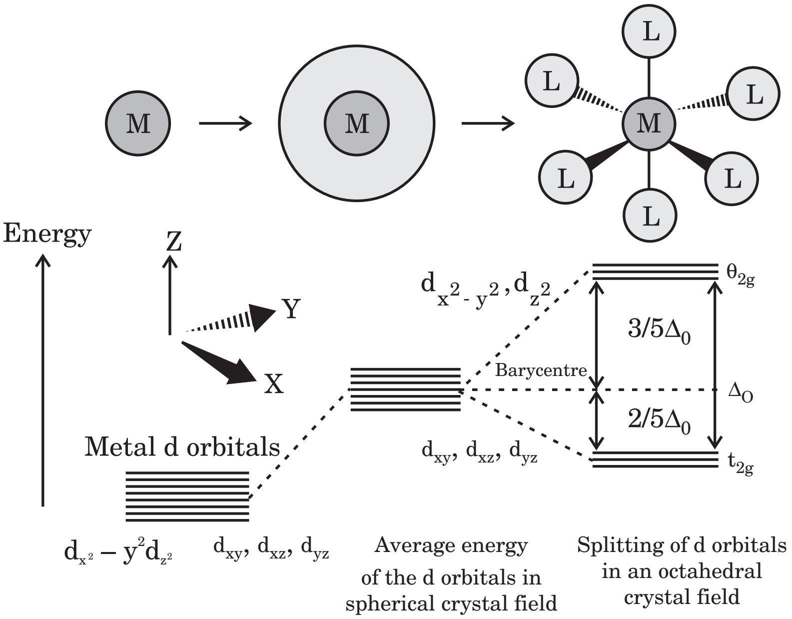
Optical isomers of $[Co(en)_3]^{3+}$

- Bonding in coordination compounds can be explained by different theories like Valence Bond Theory (VBT), Werner's Theory, Crystal Field Theory (CFT), Ligand Field Theory (LFT), and Molecular Orbit Theory (MOT).
- **Werner's Theory of Coordination Compounds:**

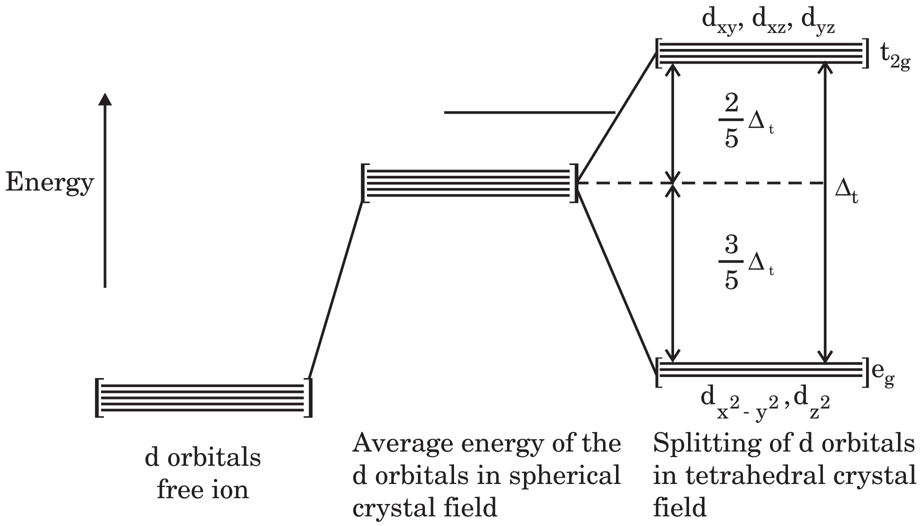
  This theory explained the nature of bonding in complex compounds. Primary and Secondary valency are the different kinds of valencies shown by metals.
  - Primary valency is equal to the oxidation state of the metal which is satisfied by anions.
  - Secondary valencies are similar to coordination number which is satisfied by opposite charged ions, neutral molecules or cations.

- **Limitations of Werner's theory:**
  - ➢ It does not explain the reason of only some elements forming complexes.
  - ➢ It does not explain the magnetic nature of complexes.
  - ➢ It does not explain the directional nature of coordination complexes.
- **Valence Bond Theory:**
  - ➢ A suitable number of vacant orbitals must be present for the formation of coordinate bond in the central metal atom/ion.
  - ➢ *s, p* or *d*-orbitals are appropriately used for hybridization by central metal ion depending on the number of ligands.
  - ➢ The ligands which donate electron pair overlap with the hybridized orbitals.
  - ➢ Outer or inner orbital complexes are formed on the basis of outer or inner *d*-orbitals used.
- **Limitations of Valence Bond Theory:**
  - ➢ Detailed magnetic properties of complex compounds are not explained.
  - ➢ Optical absorption spectra of coordination compounds are not explained by this theory.
  - ➢ It does not differentiate between strong and weak ligands.
  - ➢ Thermodynamic or kinetic stabilities of coordination compounds is not explained by this theory.
  - ➢ Geometry of 4 coordinate complex (square planar or tetrahedral) is not predicted.
- **Crystal Field Theory:**
  - ➢ Ligands are point charges according to this theory.
  - ➢ *d*-orbitals of metal ion split on approaching ligands.
  - ➢ In tetrahedral complexes, t_{2g} orbitals have high energy.
  - ➢ Splitting of *d*-orbitals is large when ligands produce strong fields and splitting is small when ligands produce weak fields.
  - ➢ Ligands are arranged according to increasing field strength as follows:

    $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$



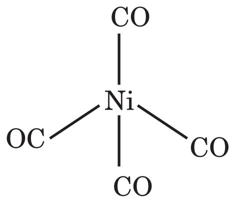
Splitting octahedral crystal field



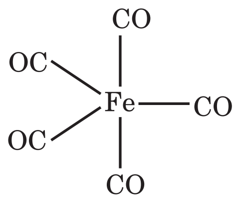
- There is high energy of e_g orbitals in octahedral and lower energy in tetrahedral complexes.

- **Limitations of crystal field theory:**
  - It does not consider the covalent bonding between ligand and central atom.
  - According to this theory anionic ligands exert greatest splitting effect but actually the splitting is small.

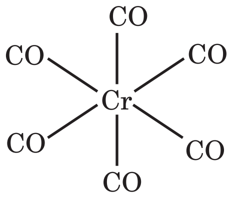
- **Bonding in metal carbonyls:** Homoleptic carbonyls are formed by transition metals. Some examples are pentacarbonyliron (0) is trigonalbipyramidal, tetracarbonylnickel (0) is tetrahedral and hexacarbonyl chromium (0) is octahedral.



$Ni(CO)_4$
Tetrahedral



$Fe(CO)_5$
Trigonal bipyramidal



$Cr(CO)_6$
Octahedral

- Metal-carbon bond possess both *s* and *p* character. There is a synergic effect between the metal and ligand bond which strengthens the bond.

- **Stability of Coordination compounds:** The degree of association between two species gives the stability of complex in solution. Stability is expressed by magnitude of equilibrium constant. Larger the stability constant/ association constant, higher the proportion of the product in solution.

  Consider a reaction: $A + 4B \rightleftharpoons AB_4$

  Here *A* is surrounded by solvent molecules, *B* and the reaction goes in the following order using stability constants:

  $$A + B \rightleftharpoons AB \qquad K_1 = \frac{[AB]}{[A][B]}$$

  $$AB + B \rightleftharpoons AB_2 \qquad K_2 = \frac{[AB_2]}{[AB][B]}$$

  $$AB_2 + B \rightleftharpoons AB_3 \qquad K_3 = \frac{[AB_3]}{[AB_2][B]}$$

  $$AB_3 + B \rightleftharpoons AB_4 \qquad K_4 = \frac{[AB_4]}{[AB_3][B]}$$

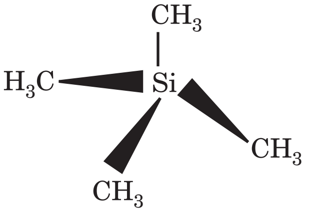
Here K_1, K_2,...... are stepwise stability constants.

$$\beta_4 = \frac{[AB_4]}{[A][B]^4}$$, β_4 is overall stability constant

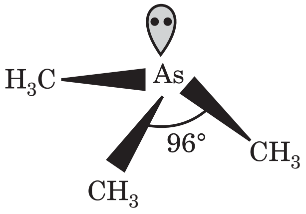
$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$

Dissociation constant or instability constant is the reciprocal of association/ stability constant.

- **Classification of organometallic compounds:** These are divided into two groups as main group organometallics and *d*- and *f*- block organometallics.
  - ➢ **Main Group organometallics:** These are *s*- and *p*- block organometallics. Here are some examples with diagram: Tetramethyl silane, trimethyl arsene, etc.



$Si(CH_3)_4$



$As(CH_3)_3$

  - ➢ *d*- and *f*- block organometallics: The elements of *d*- and *f*- block form these kind of organometallics. Some examples are: Pentamethyl cyclopentadienyl ligand (C_5Me_5) forms *f*- block compounds, $[PtCl_3\ (C_2H_4)^-]$, $(C5H_5)_2Fe$, etc.
- **Applications of complex compounds:**
  - ➢ These compounds are used in qualitative and quantitative analysis.
  - ➢ Stability constants of calcium and magnesium complexes are different which can be used for selective estimation of calcium and magnesium ions.
  - ➢ Purification of metals is carried out by formation and decomposition of coordination compounds.
  - ➢ Extraction processes are carried out using complex formation.
  - ➢ These compounds are used as catalysts. For example, Wilkinson catalyst (rhodium complex) is used for hydrogenation of alkenes.
  - ➢ Medicinal chemistry make use of chelate therapy.

PREVIOUS YEARS'
EXAMINATION QUESTIONS

1 Mark Questions

1. Which of the following is more stable complex and why?

$\left[Co\left(NH_3\right)_6\right]^{3+}$ and $\left[Co(en)_3\right]^{3+}$ **[DELHI 2014]**

2. Give an example of linkage isomerism.

3. Write the coordination number and oxidation state of Platinum in the complex $\left[Pt(en)_2\,Cl_2\right]$.

[ALL INDIA 2018]

2 Marks Questions

4. Explain the following giving an appropriate reason in each case.

1. O_2 and F_2 both stabilize higher oxidation states of metals but O_2 exceeds F_2 in doing so.
2. Structures of xenon fluorides cannot be explained by Valence Bond approach.

[DELHI 2012]

5. Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. What type of isomerism does it exhibit? [DELHI 2014]

6. (i) Write down the IUPAC name of the following complex: $\left[Cr\left(NH_3\right)_2 Cl_2\,(en)\right]Cl$

(en = ethylenediamine)

(ii) Write the formula for the following complex: Pentaamminenitrito-o-Cobalt(III).

[DELHI 2015]

7. (i) Write down the IUPAC name of the following complex: $\left[Pt(NH_3)(H_2O)Cl_2\right]$

(ii) Write the formula for the following complex: Tris – (ethane-1,2-diamine) chromium (III) chloride **[ALL INDIA 2015]**

3 Marks Questions

8. When a coordination compound $CoCl_3.6NH_3$ is mixed with $AgNO_3$, 3 moles of $AgCl$ are precipitated per mole of the compound. Write

(i) Structural formula of the complex

(ii) IUPAC name of the complex

[**ALL INDIA 2016**]

9. Using IUPAC norms write the formulae for the following:

(a) Potassium trioxalatoaluminate(III)

(b) Dichloridobis–(ethane-1,2-diamine) cobalt (III) [**ALL INDIA 2017**]

10. Name the following coordination compounds according to IUPAC system of nomenclature:

(i) $\left[Co(NH_3)_4(H_2O)Cl\right]Cl_2$

(ii) $\left[CrCl_2(en)_2\right]Cl$,

(en = ethane – 1, 2-diamine)

11. 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) $K_2\left[Ni(CN)_4\right]$ **[DELHI 2011]**

12. Explain the following terms giving a suitable example in each case:

(i) Ambident ligand

(ii) Denticity of a ligand

(iii) Crystal field splitting in an octahedral field **[ALL INDIA 2011]**

13. Write the name, the structure and the magnetic behavior of each of the following complexes:

(i) $\left(Pt(NH_3)Cl(NO_2)\right)$

(ii) $\left[Co(NH_3)_4Cl_2\right]Cl$

(iii) $Ni(CO)_4$

(At. Nos. Co = 27, Ni = 28, Pt = 78)

[DELHI 2012]

14. Give the formula of each of the following coordination entities:

(i) Co^{3+} ion is bound to one Cl^-, one NH_3 molecule and two bidentate ethylene diamine (en) molecules.

(ii) Ni^{2+} ion is bound to two water molecules and two oxalate ions.

Write the name and magnetic behavior of each of the above coordination entities.
(At. Nos. Co = 27, Ni = 28) **[ALL INDIA 2012]**

15. Give the formula of each of the following coordination entities:

(i) Co^{3+} ion is bound to one Cl^-, one NH_3 molecule and two bidentate ethylene diamine (en) molecules.

(ii) Ni^{2+} ion is bound to two water molecules and two oxalate ions.

Write the name and magnetic behaviour of each of the above coordination entities.
(At. nos. Co = 27, Ni = 28) **[ALL INDIA 2012]**

16. Write the types of isomerism exhibited by the following complexes:

(i) $\left[Co(NH_3)_5Cl\right]SO_4$

(ii) $\left[Co(en)_3\right]^{3+}$

(iii) $\left[Co(NH_3)_6\right]\left[Cr(CN)_6\right]$ **[DELHI 2013]**

17. Write the IUPAC names of the following coordination compounds:

(i) $\left[Cr(NH_3)Cl_3\right]$

(ii) $K_3\left[Fe(CN)_6\right]$

(iii) $\left[CoBr_2(en)_2\right]^+$

(en = ehylenediamine) **[DELHI 2013]**

18. For the complex $[NiCl_4]^{-2}$, write

(i) The IUPAC name

(ii) The hybridization type

(iii) The shape of the complex (Atomic no. of Ni = 28)

Or

What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_2g and e_g in an octahedral field when

(i) $\Delta_0 > P$

(ii) $\Delta_0 < P$ **[ALL INDIA 2013]**

19. (i) Write the IUPAC name of the complex $\left[Cr\left(NH_3\right)_4 Cl_2\right]Cl$

(ii) What type of isomerism is exhibited by the complex $[Co(en)_3]^{3+}$? (en = ethane-1,2-diamine)

(iii) Why is $[NiCl_4]^{2-}$ paramagnetic but $[Ni(CO)_4]$ is diamagnetic? (At. Nos.: $Cr = 24$, $Co = 27$, $Ni = 28$) **[ALL INDIA 2014]**

20. (i) What type of isomerism is shown by $\left[CO\left(NH_3\right)_5 ONO\right]Cl_2$?

(ii) On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_0 < P$

(iii) Write the hybridization and shape of $[Fe(CN)_6]^{3-}$ (Atomic number of $Fe = 26$) **[ALL INDIA 2015]**

21. (a) For the complex $\left[Fe\left(H_2 0\right)_6\right]^{3+}$, write the hybridization, magnetic character and spin of the complex. (At. number: $Fe = 26$)

(b) Draw one of the geometrical isomers of the complex $\left[Pt\left(en\right)_2 Cl_2\right]^{2+}$ which is optically inactive. **[DELHI 2015]**

22. (a) What is a ligand? Give an example of a bidentate ligand.

(b) Explain as to how the two complexes of nickel, $\left[Ni\left(CN\right)_4\right]^{2-}$ and $Ni\left(CO\right)_4$, have different structures but do not differ in their magnetic behaviour. ($Ni = 28$) **[DELHI 2016]**

23. Giving a suitable example for each, explain the following:

(i) Crystal field splitting

(ii) Linkage isomerism

(iii) Ambidentate ligand

Or

Compare the following complexes with respect to structural shapes of units, magnetic behaviour and hybrid orbitals involved in units

$\left[Co\left(NH_3\right)_6\right]^{3+}$, $\left[Cr\left(NH_3\right)_6\right]^{3+}$, $Ni\left(CO\right)_4$

Atomic number: $Co = 27$, $Cr = 24$, $Ni = 28$ **[DELHI 2017]**

24. (a) What type of isomerism shown by the complex $\left[Co\left(NH_3\right)_5\left(SCN\right)\right]^{+}$?

(b) Why is $[NiCl_4]^{2-}$ paramegnatic while $[Ni(CN)_4]^{2-}$ is diamagnetic? (Atomic number of $Ni = 28$)

(c) Why are low spin tetrahedral complex rarely observed? **[ALL INDIA 2017]**

25. (a) Write the formula of the following coordination compound: Iron (III) hexacyanoferrate (II)

(b) What type of isomerism is exhibited by the complex $\left[Co\left(NH_3\right)_5 Cl\right]SO_4$?

(c) Write the hybridisation and number of unpaired electrons in the complex $\left[CoF_6\right]^{3-}$.

(Atomic No. of $Co = 27$) **[ALL INDIA 2015]**

Solutions

1. $\left[\text{CO(en)}_3\right]^{3+}$ form more stable complexes **[1]**

2. $\left[Co\left(NH_3\right)_5 ONO\right]Cl_2$ and $\left[Co\left(NH_3\right)_5 NO_2\right]Cl_2$ are linkage isomers. In $\left[Co\left(NH_3\right)_5 ONO\right]Cl_2$, the bonding is through oxygen $\left(-ONO\right)$ whereas in $\left[Co\left(NH_3\right)_5 NO_2\right]Cl_2$, the bonding is through nitrogen $\left(-NO_2\right)$ **[1]**

3. Coordination number = 6, Oxidation number = +2

Platinum is bonded with two types of ligands,

Ethylenediamine which is bidentate ligand is of two in number hence $2 \times 2 = 4$,

Chloride which is an unindented ligand is of two in number hence $1 \times 2 = 2$

Hence co-ordination number of Platinum will be $4 + 2 = 6$

Oxidation state of Pt:

$[x + (0 \times 2) + (-1 \times 2)] = 0$

$x + 0 - 2 = 0$

$x = +2$ **[1]**

4. 1. Due to the difference in atomic size of oxygen and fluorine and the property of oxygen to form multiple bonds with metals, O_2 exceeds F_2, stabilising higher oxidation states. **[1]**

2. For explaining the structures of xenon fluorides, we need to use VSEPR and hybridization theories because in VBT, covalent bonds are formed by overlapping of half filled atomic orbital. But xenon has fully filled electronic configuration. Xenon is an inert gas and hence has zero valency, but it combines with strong oxidizing agent like fluorine. Hence, the molecule contains lone pair which affect the shape and structure of the compounds, but the lone pairs are not taken into consideration in valence bond theory. VSEPR theory can explain interaction between lone pair – lone pair and lone pair – bond pair. **[1]**

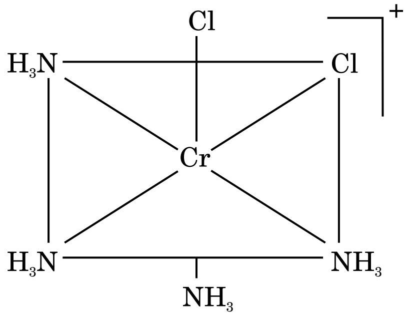
   For example:

   XeF_2, So hybridization of $XeF_2 = sp^3d$

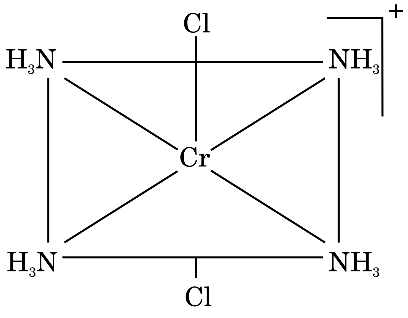
   As per the sp^3d hybridization, the structure should be Trigonal bipyramidal,

   But the actual structure is linear. Thus, valence bond theory cannot explain this but the VSEPR theory explains the linear shape.

5. Tetraamminedichloridochromium (III) ion. The complex exhibits geometric (cis-trans) isomerism. **[1]**



Cis-isomer



trans-isomer **[1]**

6. (i) Diamminedi chlorid ethylene dia minchromium (III) chloride. **[1]**

(ii) $\left[Co\left(NH_3\right)_5\left(ONO\right)\right]^{2+}$ **[1]**

7. (i) Ammineaqua dichlorido platinum (II)

(ii) $\left[Cr\left(en\right)_3\right]Cl_3$ **[1] + [1]**

8. (i) Since 3 moles of $AgCl$ get precipitated, all $3Cl^-$ ions in the coordination compound $CoCl_3.6NH_3$ are present outside the coordination sphere and satisfy the primary valency. Hence, the structural formula of the given compound is $\left[Co\left(NH_3\right)_6\right]Cl_3$. **[1]**

(ii) The IUPAC name of the complex is hexaannminecobalt (III) chloride. **[1]**

9. (a) $K_3\left[Al\left(C_2O_4\right)\right]$ **[1]**

(b) $\left[COCl_2\left(en\right)_2\right]^+$ **[1]**

10. (i) Tetraammineaquachlorocobalt(III) chloride

(ii) Dichloridobis–(ethane-1,2-diamine) chromium (III) chloride **[1] + [1]**

11. (i) Potassiumhexacyanomanganate(II)

Shape: Octahedral **[1]**

Magnetic behavior: Paramagnetic (one unpaired electron)

Hybridization: d^2sp^3

(ii) Pentaaminechloridocobalt (III) chloride [1]

Shape: Octahedral

Hybridization: d^2sp^3

Magnetic behavior: Dimagnetic (no unpaired electrons)

(iii) Potassiumtetracyanonicklate (II) [1]

Shape: Square planar

Hybridization: $d\,sp^2$

Magnetic behavior: Dimagnetic (no unpaired electrons)

12. (i) **Ambident ligand**: a unidentate ligand which can co-ordinate to the central metal atom through more than one co-ordinate bond. e.g. NO_2^-, SCN^- **[1]**

(ii) The number of donor atoms in ligating groups is known as denticity of that ligand. e.g. in $C_2O_4^{2-}$ denticity is 2 **[1]**

(iii) Crystal field splitting in an Octahedral field: The splitting of d-orbitals under the influence of approaching ligand is known as crystal field splitting for example for d^4, configuration is $t_{2g}^3\ and\ e_g^1$ **[1]**

13. (i) Amminechloridonitrito—N-platinum (II),trigonal planar, diamagnetic. **[1]**

(ii) Tetra-ammine dichlorido cobalt (III) chloride, octahedral, diamagnetic **[1]**

(iii) Tetracarbonyl nickel (0), Tetrahedral, diamagnetic **[1]**

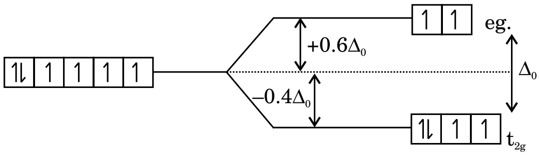
14. (i) $\left[Co\left(NH_3\right)\left(en\right)_2 Cl\right]^{2+}$ **[1]**

Amminebis (ethylenediamine) chloride cobalt (II) ion, diamagnetic. **[½]**

(ii) $\left[Ni\left(H_2O\right)_2\left(C_2O_4\right)_2\right]^{2-}$ **[1]**

Diaquadioxalatonickelate (II) ion, paramagnetic **[½]**

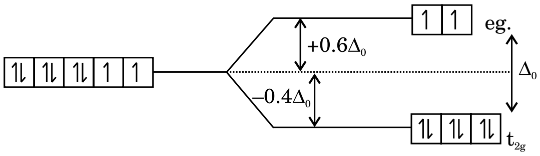
15. (i) $\left[\text{CoClNH}_3(\text{en}_2)\right]^{2+}$ amminebis–(ethane-1, 2-diamine)chloride(III) ion **[1]**



Number of unpaired electrons = 4
So the complex is paramagnetic **[½]**

(ii) $\left[Ni\left(H_2O\right)_2\left(C_2O_4\right)_2\right]^{2-}$ **[1]**

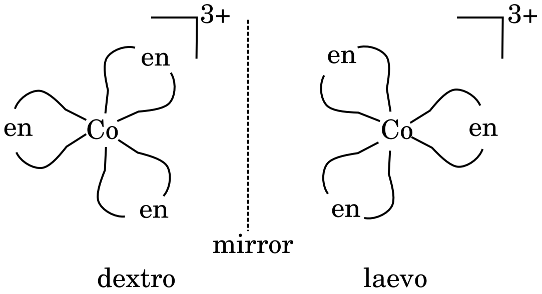
Diaquadioxalatonickelate (II)



Number of unpaired electrons **= 2**
So the complex is paramagnetic. **[½]**

16. (i) ionisation isomerism **[1]**

(ii) Optical isomerism **[1]**



(iii)Coordination isomerism **[1]**

17. (i) Triamminetrichloridochromium(III)

(ii) Potassium hexacyanoferrate(III)

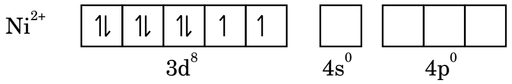
(iii)Dibromidobis-(ethylene-diammine) cobalt (III) ion. **[1+1+1]**

18. (i) Tetrachloridonickelate(II)ion **[1]**

(ii) $\left[NiCl_4\right]^{-2}$ **[1]**

$Ni^{+2} = \left[Ar\right]\ 4s^0 3d^8$

Electronic configuration of Ni^{2+} ion



Cl^- is weak field ligand hence, pairing does not occur

Type of hybridization is sp^3

(iii)Tetrahedral **[1]**

OR

It is the energy difference between lower energy and higher energy d-orbitals after splitting of d-orbitals **[1]**

(i) $\Delta_0 > P$ **[1]**

$t_{2g}^4 e_g^o$

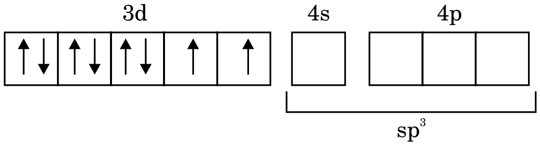
(ii) $\Delta_0 < P$ **[1]**

$t_{2g}^3 e_g^1$

19. Tetraaminedichlorochromium(III) chloride **[1]**

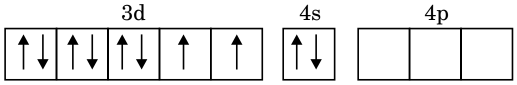
(ii) $\left[Co\left(en\right)_3\right]^{3+}$ shows optical isomerism **[1]**

(iii)$\left[NiCl_4\right]^{2-}$ $Ni^{+2} = \left[Ar\right]\ 4s^0 3d^8$

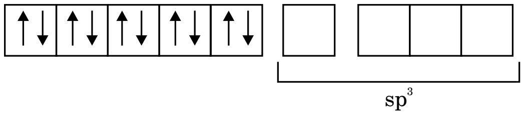


Ni^{+2} has 2 unpaired e⁻ hence, this complex is paramagnetic $[Ni(CO)_4]$ **[1]**

$Ni = \left[Ar\right]\ 4s^2 3d^8$



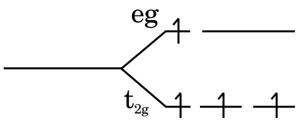
CO is strong field ligand. Hence, pairing occurs.



Ni has zero unpaired electrons, this complex is diamagnetic.

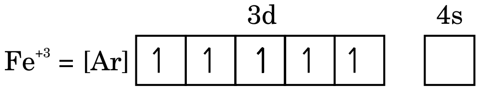
20. (i) Linkage isomerism, whenever ambidentate ligand is present coordination compound shows linkage isomerism. **[1]**

(ii) $t_{2g}^3 e_g^1$,

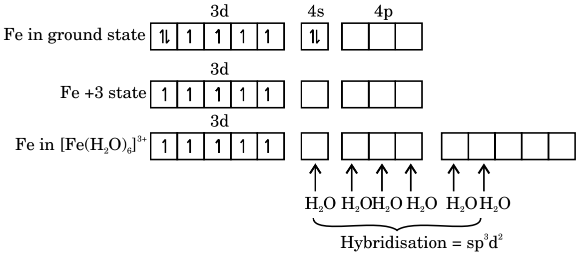


when $\Delta_O < P$ pairing of electron in same orbital is not present. **[1]**

(iii) d^2sp^3, octahedral, $_{26}Fe = [Ar]3d^6 4s^2$ **[1]**



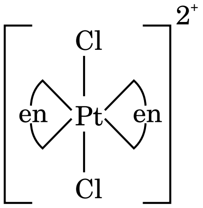
21. (a)



[1+1]

Hybridisation: sp^3d^2, Magnetic character: Paramagnetic, Spin nature of complex: High-spin complex trans-isomer of $\left[Pt(en)_2Cl_2\right]^{2+}$ is optically inactive.

(b) **[1]**



22. (a) Ligand: The ions or molecules that are bound to the central atom/ion in the coordination entity are called ligands. **[1]**

Ex. bidentate ligand: ethane-1,2-diamine or oxalate ion. **[1]**

(b) In $\left[Ni(CN)_4\right]^{2-}$, nickel is Ni^{2+}, $\left(3d^8\right)$, with strong Ligand like CN^-, all the electrons are paired up in four d-orbitals resulting into dsp^2 hybridization giving square planar structure and diamagnetic character. **[1]**

In $Ni(CO)_4$, nickel is in zero valence state, $(3d^8 4s^2)$, with strong Ligand like CO, $4s^2$ electrons are pushed to the d-orbitals resulting into sp^3 hybridization giving tetrahedral shape and diamagnetic in nature.

23. (i) The splitting of the degenerate d orbitals into e_g and t_2g orbitals due to the presence of ligands in a definite geometry is called crystal field splitting. It is denoted by Δ_0 **[1]**

(ii) Linkage isomerism arises in coordination compounds containing ambidentate ligands in which two different atoms of the same ligand can form coordinate bond with metal ion. **[1]**

Example: $\left[Co(NH_3)_5 NO_2\right]Cl_2$ and

$\left[Co(NH_3)_5 ONO\right] Cl_2$

(iii) Ligands which can bind the central metal atom through two different atoms are called ambidentate ligands. **[1]**

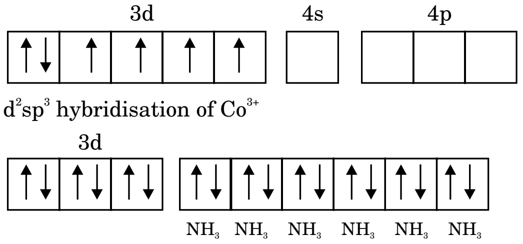
Example: SCN^-, NCS^-

OR

$\left[Co(NH_3)_6\right]^{3+}$

Co^{3+} (Ground State): **[1]**

$3d^6\ 4s^0\ 4p^0$



Structural shape-Octahedral

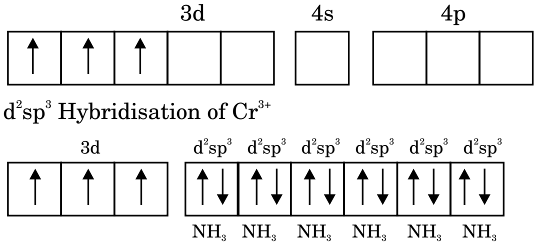
Hybrid Orbitals-d^2sp^3

Magnetic behavior- Diamagnetic

$\left[Cr(NH_3)_6\right]^{3+}$ Cr^{3+} **[1]**

(Ground State):

$3d^3\ 4s^0\ 4p^0$

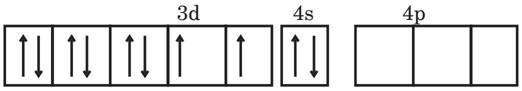


Structural shape-Octahedral

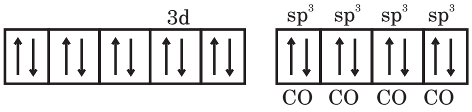
Hybrid Orbitals-d^2sp^3

Magnetic behavior- Paramagnetic

$Ni(CO)_4$



sp^3 hybrid orbitals of Ni



Structural shape- Tetrahedral **[1]**
hybrid orbitals-sp^3
Magnetic behavior - Diamagnetic

24. (a) This complex shows Linkage isomerism **[1]**

(b) Because $\left[NiCl_4\right]^{2-}$ has 2 unpaired electrons and is Paramagnetic. While $\left[Ni(CN)_4\right]^{2-}$ has paired electrons and is diamagnetic. **[1]**

(c) There are only 4 ligands in a tetrahedral complex. So, the crystal field stabilisation energy is roughly $\frac{2}{3}$ of the octahedral field.

The direction of ligand approach in tetrahedral complex does not coincide with the d-orbitals. This reduces the field by a factor of $\frac{2}{3}$. Hence, Δt is roughly $\frac{2}{3} \times \frac{2}{3} = \frac{4}{9}$ of Δo. As a result, all tetrahedral complexes are high-spin since the CFSE is normally smaller than the paring energy. **[1]**

25. (a) $Fe_4\left[Fe(CN)_6\right]_3$ **[1]**

(b) ionisation isomerism **[1]**

(c) Hybridisation $= sp^3d^3$ **[½]**

Number of unpaired electrons is 4. **[½]**

Smart Notes ....

CHAPTER 10

Haloalkanes and Haloarenes

Chapter Analysis with respect to Last 3 Years' Board Exams

List of Topics	2016		2017		2018	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Haloalkanes: Nomenclature, nature of C-X bond, physical and chemical properties				(1 mark)		
Mechanism of substitution reactions, optical rotation	(1 mark)		(3 marks)		(1 mark)	(1 mark)
Haloarenes: Nature of C -X bond, substitution reactions, Directive influence of halogen in monosubstituted compounds only.	(2, 2 marks)	(1, 3 marks)	(3 marks)	(3 marks)		
Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform freons, DDT.						

Topic 1: Introduction, Nomenclature and Preparation of Haloalkanes and Haloarenes

Summary

Haloalkanes are hydrogen atoms in aliphatic hydrocarbons replaced by halogens, whereas Haloarenes are hydrogen atoms replaced in benzene ring by halogens. In haloalkanes, halogen gets connected with the carbon through $(CO_2 + H_2O)$ hybridisation, while in Haloarenes, it is connected with CO_2 hybridisation.

Classification

- **On the Basis of Number of Halogen Atoms**

  It depends on the number of halogen atoms attached to the structure. It may be mono, di, tri or tetra etc. For example,

C_2H_5X

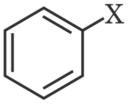
Monohaloalkane

$$\begin{array}{c} CH_2X \\ | \\ CH_2X \end{array}$$

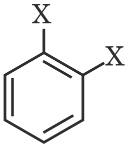
Dihaloalkane

$$\begin{array}{c} CH_2X \\ \| \\ CHX \\ \| \\ CH_2X \end{array}$$

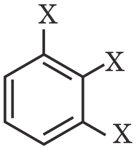
Triyhaloalkane



Monohaloarene



Dihaloarene



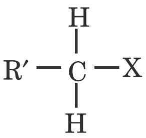
Trihaloarene

- **Compounds Containing** $\text{ppm}\left(\text{mass to mass}\right) = \dfrac{\text{Mass of a component}}{\text{Total mass of solution}} \times 10^6$ **C-X Bond (X= F, Cl , Br, I)**

  ➢ Alkyl halides or haloalkanes (R-X): The series is represented as

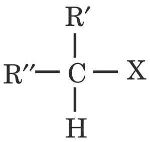
  $$\text{ppm}\left(\text{volume to volume}\right) = \frac{\text{Volume of a component}}{\text{Total volume of solution}} \times 10^6.$$

  It has further 3 categories, i.e., primary, secondary or tertiary depending on the nature of carbon to which halogen is attached.



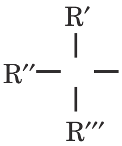
$$\begin{array}{c} H \\ | \\ R'-C-X \\ | \\ H \end{array}$$

Primary (1°)



$$\begin{array}{c} R' \\ | \\ R''-C-X \\ | \\ H \end{array}$$

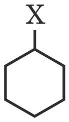
Secondary (2°)



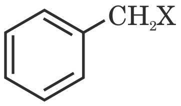
$$\begin{array}{c} R' \\ | \\ R''- \quad - \\ | \\ R''' \end{array}$$

Tertiary (3°)

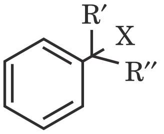
  ➢ Allylic halides: The halogen atom is attached to the carbon atom just adjacent to carbon-carbon double bond.



- Benzylic halides: The halogen atom is attached to the carbon atom right next to an aromatic ring.



(1°)

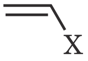


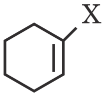
R′ = CH_3, R″ = H(2°)

R′ = R″ = CH3(3°)

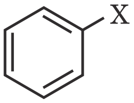
- **Compounds Containing** $\text{ppm}\left(\text{mass to volume}\right) = \frac{\text{Mass of a component}}{\text{Volume of solution}} \times 10^6$ **C-X Bond**

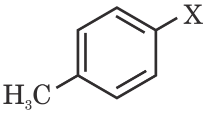
  - Vinylic halides: The halogen atom is attached to the carbon atom just adjacent to carbon-carbon double bond (C=C).





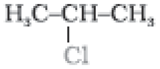
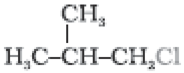
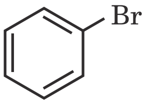
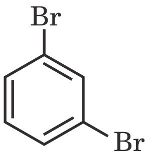
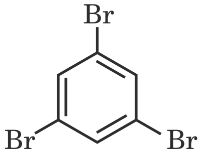
  - Aryl halides: The halogen atom is attached to the carbon atom right next to an aromatic ring.





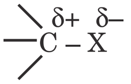
Nomenclature

Alkyl halides are named as halo-substituted hydrocarbons in the IUPAC system of nomenclature. Haloarenes are the common as well as IUPAC names of aryl halides.

Structure	IUPAC Names	Common Names
$CH_3CH_2CH_2Br$	1-Brompropane	n-Propyl bromide
 $H_3C{-}\underset{\mid\atop Cl}{CH}{-}CH_3$	2-Chloropropane	Isopropyl chloride
 $H_3C{-}\overset{CH_3\atop\mid}{CH}{-}CH_2Cl$	1-Chloro-2-methylpropane	Isobutyl chloride
	Bromobenzene	Bromobenzene
	1,3-Dibromobenzene	m-Dibromobenzene
	1,3,5-Tribromobenzene	sym-Tribromobenzene
$H_3C-CHCl_2$	1,1-Dicholoroethane	Ethylidene Chloride

Nature of C-X Bond

They form a polarised bond as the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.



Methods of preparation

- **From Alcohols**

  Alkyl halides are most commonly prepared from alcohols as the hydroxyl group of an alcohol can be easily replaced by any halogen atom.

$$R{-}OH + HX \xrightarrow{ZnCl_2} R{-}X + H_2O$$

$$R{-}OH + NaBr + H_2SO_4 \longrightarrow R{-}Br + NaHSO_4 + H_2O$$

$$3R{-}OH + PX_3 \longrightarrow 3R{-}X + H_3PO_3 \quad (X = Cl, Br)$$

$$R{-}OH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl$$

$$R{-}OH \xrightarrow[X_2=Br_2, I_2]{\text{red } P/X_2} R{-}X$$

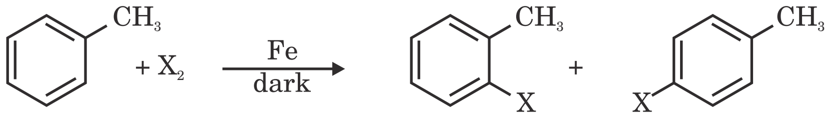
$$R{-}OH + SOCl_2 \longrightarrow R{-}Cl + SO_2 + HCl$$

From Hydrocarbons

- **By free radical halogenation:** Under certain conditions we can obtain mixture of isomeric mono and polyhaloalakanes**.**

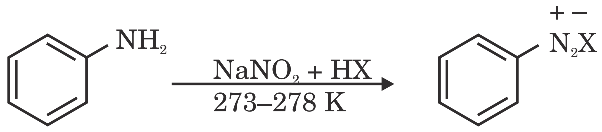
$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

- **By electrophilic substitution:** This requires the presence of Lewis acid catalyst like iron or iron(III) chloride. Chloride and bromide compounds can be prepared from this method but not fluoro compounds due to the high reactivity of fluorine.

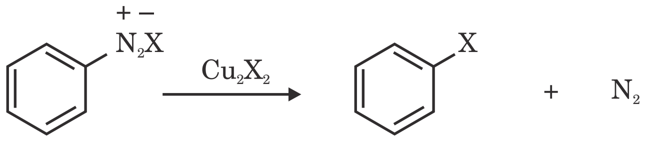


o-Halotoluene p-Halotouene

- **Sandmeyer's reaction:** This requires suspension of primary aromatic amine in cold aqueous mineral acid in the presence of sodium nitrate. A diazonium salt is formed which on reaction with cuprous chloride or bromide will replace diazonium group by Cl or Br.



Benzene diazonium
halide



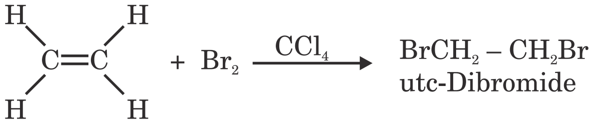
Aryl halide
X = Cl, Br

- **From alkenes**

(i) Addition of hydrogen halides: This requires a reaction of alkyl halide with hydrogen chloride, bromide or iodide.

$$\underset{}{CH_3CH = CH_2} + H\text{–}I \longrightarrow \underset{\text{minor}}{CH_3CH_2CH_2I} + \underset{\text{major}}{CH_3CHICH_3}$$

(ii) Addition of halogens: The following reaction takes place in presence of $M = \frac{\text{Number of moles of solute}}{\text{Volume of solution}} = \frac{W_B \times 1000}{M_B \times V(ml)}$.



- **Halogen Exchange**

The reaction in which the alkyl iodides are prepared by the reaction of alkyl chlorides/ bromides with NaI in dry acetone is known as **Finkelstein Reaction.**

$$R\text{–}X + NaI \longrightarrow R\text{–}I + NaX$$

$X = Cl, Br$

The reaction in which alkyl fluorides are prepared by the reaction of alkyl chlorides/ bromides with metallic fluoride is known as **Swarts Reaction**.

$$H_3C\text{–}Br + AgF \longrightarrow H_3C\text{–}F + AgBr$$

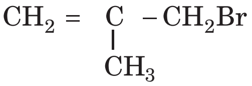
PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 1

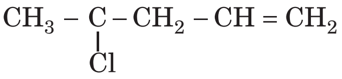
1 Mark Questions

1. Write the IUPAC name of the following compound: $CH_2 = CHCH_2Br$ **[ALL INDIA 2011]**
2. How would you convert ethanol to ethene? **[ALL INDIA 2011]**
3. Give the IUPAC name of the following compound. **[ALL INDIA 2013]**



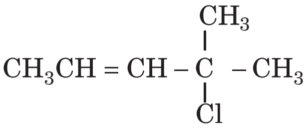
$CH_2 = \underset{|\\ CH_3}{C} - CH_2Br$

4. Write the IUPAC name of: **[DELHI 2013]**



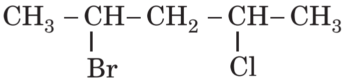
$CH_3 - \underset{|\\ Cl}{C} - CH_2 - CH = CH_2$

5. Write the IUPAC name of **[DELHI 2013]**

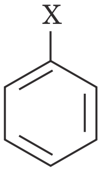
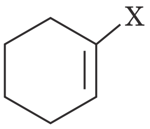


$CH_3CH = CH - \overset{CH_3\\ |}{\underset{|\\ Cl}{C}} - CH_3$

6. Write the IUPAC name of the following compound **[DELHI 2013]**



$CH_3 - \underset{|\\ Br}{CH} - CH_2 - \underset{|\\ Cl}{CH} - CH_3$

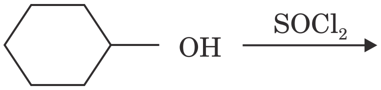
7. Write the IUPAC name of $(CH_3)_2CHCH(Cl)CH_3$. **[DELHI 2013]**
8. Write the structure of an isomer of compound C_4H_9Br which is most reactive towards reaction S_N1. **[ALL INDIA 2016]**
9. Out of the  and  which is an example of allylic halide? **[DELHI 2017]**

2 Marks Questions

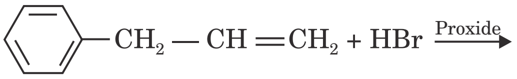
10. Draw the structure of major monohalo product in each of the following reactions:

[DELHI 2014]

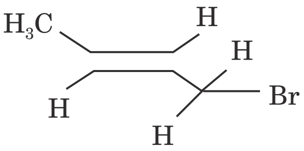
(i)



(ii)



11. (a) State the IUPAC name of the following compound:



(b) Complete the following chemical equations:

$CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{Peroxide}}$

[DELHI 2016]

Solutions

1. 3-bromoprop-1-ene / 3-bromopropene [1]

2. $CH_3CH_2OH \xrightarrow[443\text{ K}]{H_2SO_4} CH_2 = CH_2 + H_2O$ [1]

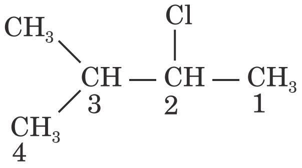
3. 3-bromo-2-methylprop-1-ene [1]

4. 4-chloropent-1-ene [1]

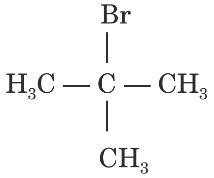
5. 4-bromo-4-methylpent-2-ene [1]

6. 2-Bromo-4-chloro-pentane [1]

7. 2-chloro-3-methylbutane [1]

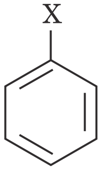


8. The isomer of C_4H_9Br, which is the most reactive towards S_N1 reaction, is the one that forms tertiary carbonation upon the elimination of the leaving group. Its structure is shown below:



$H_3C - \overset{Br}{\underset{CH_3}{C}} - CH_3$ [1]

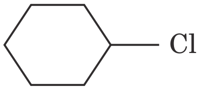
9. allylic halides



[1]

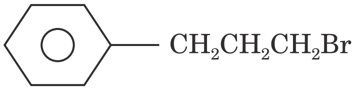
An allylic halide is the one where the carbon atom next to a double bonded carbon atom carries one or more halogen atoms.

10. (i)



[1]

(ii)



[1]

11. (a) 1-Bromobut-2-ene [1]

(b) $CH_3CH_2CH_2CH_2Br$ [1]

Topic 2: Properties of Haloalkanes and Haloarenes Including Polyhalogen Compounds

Summary

Physical Properties

- **Melting and boiling points**

  Because of the polarity of halogen compounds, the intermolecular forces of attraction are stronger due to which the boiling and melting points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons. The decreasing order of boiling points of some alkyl hydrides is: RI>RBr>RCl>RF. The boiling points of some isomers are high due to the symmetry.

- **Density**

  The density of alkyl hydrides increases with the number of carbon atoms and halogen atoms and their atomic masses.

- **Solubility**

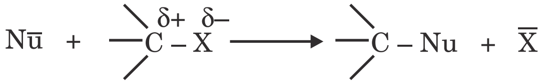
  The solubility of haloalkanes in water is quiet low because of strong hydrogen and carbon bond which is not easy to overcome or break. However, haloalkanes are soluble in solvent molecules because of the new intermolecular interactions between haloalkanes and solvent molecules which do not require much energy.

Chemical Reactions

- **Reactions of Haloalkanes**

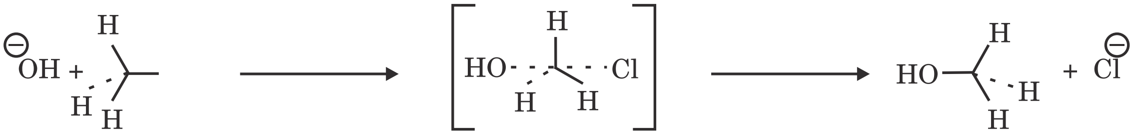
  ➢ **Nucleophilic substitution reactions**

  A nucleophile reacts with a partial positive charge on a carbon atom of the haloalkanes, which then gets substituted by the nucleophile and separates out as halide ion.



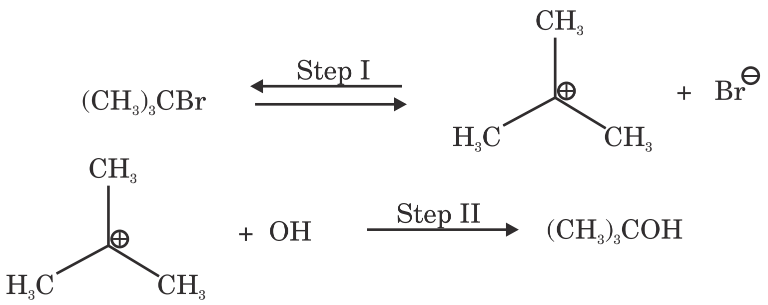
  ➢ **Substitution nucleophilic bimolecular** ($m = \frac{\text{Number of moles of solute}}{\text{Mass of solvent}} = \frac{W_B \times 1000}{W \times W_A}$)

  In this case of nucleophilic substitution, a new carbon-OH bond is formed while simultaneously breaking the carbon-halide bond. Since both the steps take place simultaneously, this process is called **Inversion of configuration**.



  ➢ **Substitution nucleophilic unimolecular** ($\text{Normality} = \frac{\text{Number of gram equivalent of solute}}{\text{Volume of solution in L}}$)

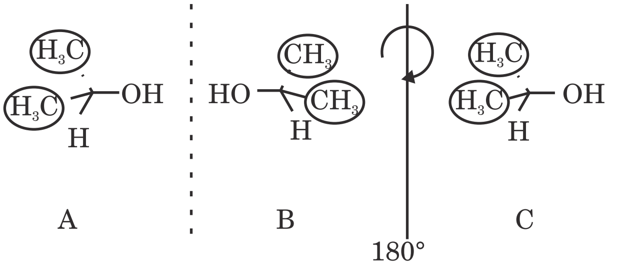
  These reactions require a presence of polar protic solvents like water or alcohol and follow the first order kinetics in which the reaction rate depends on only one reactant. This happens in two steps. In first step, bromide ion is separated out and then in the next step carbocation formed is attacked upon by the nucleophile.



- **Stereochemical aspects of nucleophilic substitution reactions**

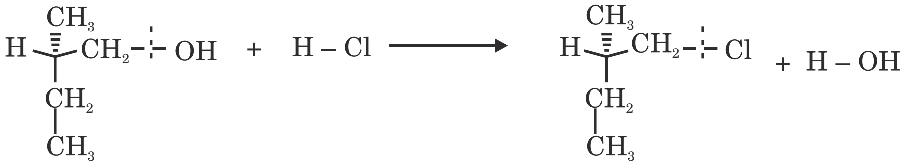
  (i) Plane polarised light and optical activity: Those compounds which rotate the plane polarised light when passed through their solutions are called optically active compounds. If the light is rotated to the right by the compound, then it is called dextrorotatory and is represented by placing a positive sign before the degree of rotation. If the light is rotated to the left by the compound, then it is called laevorotatory and is represented by placing a positive sign before the degree of rotation. These isomers are called optical isomers and the phenomenon is called optical isomerism.

  (ii) Molecular asymmetry, chirality and enantiomers: A carbon atom is called asymmetric carbon or stereocentre if the spatial arrangement of four groups around the central carbon is tetrahedral. The molecule so formed is referred to as asymmetric molecule. The super imposable objects when placed in front of the mirror are said to be achiral and the property is called as chirality. Those objects which are non-super imposable are known as chiral. For ex, propanol.



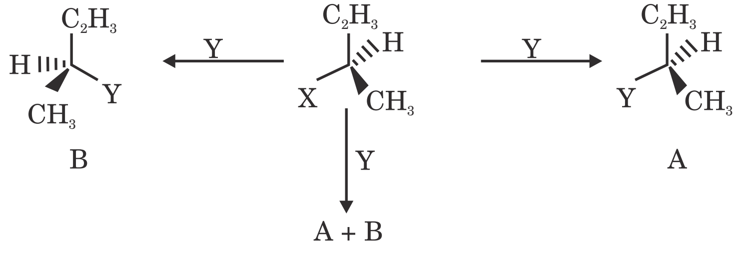
Enantiomers are stereoisomers which are related to each other as non-super imposable mirror images. When the rotation due to one isomer is cancelled by the rotation of other isomer in a mixture containing two equal enantiomers is known as racemic mixture and this process is known as racemisation.

(iii) Retention: The preservation of integrity of the spatial arrangement of bonds during transformation or a chemical reaction is known as retention.



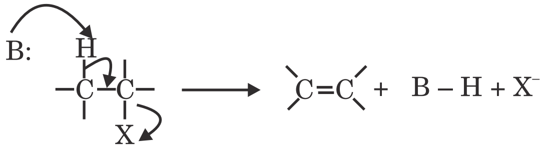
(–) –2-Methy|butan-1-ol (+)-1-ch|oro-2-methy|butane

(iv) Inversion, retention and racemisation: If in a chemical reaction, compound A is produced, the process is called retention of configuration. If compound B is produced, then it is called inversion of configuration. If a mixture is produced, then the process is called racemisation.



- **Elimination reactions**

  This reaction requires the presence of alcoholic potassium hydroxide when a haloalkane with **β**-hydrogen is heated with it and the process is known as **β**-elimination.



B = Base ; X = Leaving group

- **Reaction with metals**

  The compounds obtained when chlorides or bromides react with certain metals are known as organo-metallic compounds. Grignard reagents of the form, RMgX, are obtained in such reactions.

$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{CH_3CH_2MgBr}$$

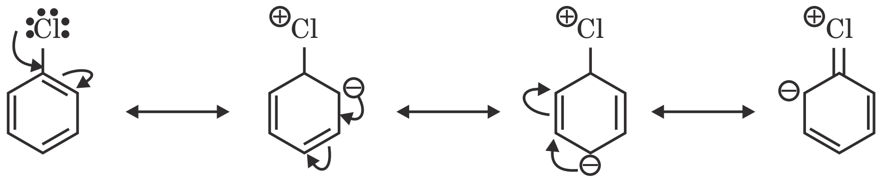
Wurtz reaction: The reactions in which alkyl halides reacts with sodium in dry ether to produce hydrocarbons with double the number of carbon atoms present in the halide.

$$2RX + Na \longrightarrow RR + NaX$$

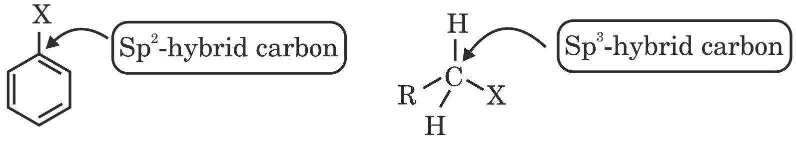
- **Reaction of Haloarenes**

  - **Nucleophilic substitution**

(i) **Resonance effect:** The electron pairs on halogen atom are in conjugation with π- electrons of the ring. The following resonating structures can be formed.

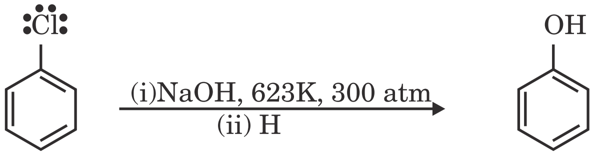


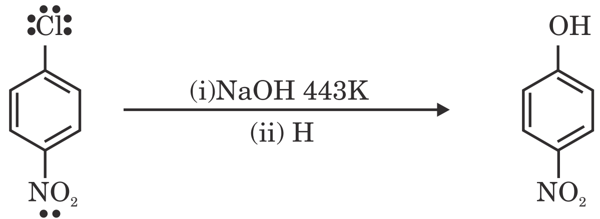
(ii) **Difference in hybridisation of carbon atom in C-X bond:** In haloalkanes, halogen gets connected with the carbon through sp^3 hybridisation, while in Haloarenes, it is connected with sp^2 hybridisation.

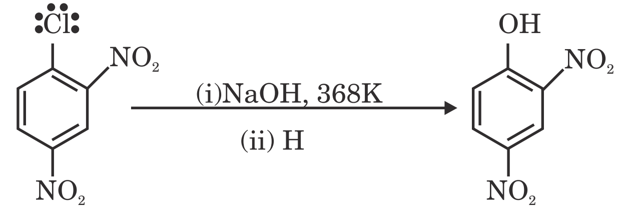


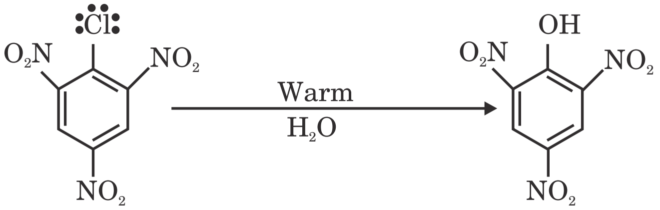
(iii) **Instability of phenyl cation:** In Haloarenes, the phenyl cation formed is not stabilized by resonance due to self-ionisation.

(iv) **Replacement by hydroxyl group:** Phenol is formed by heating chlorobenzene in aqueous sodium hydroxide solution.



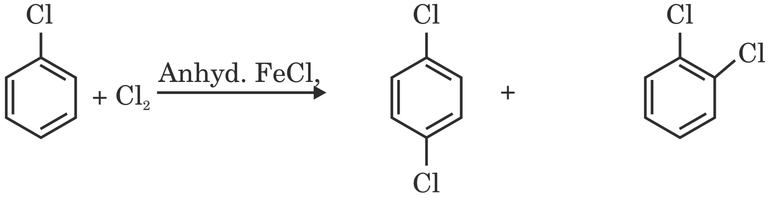






- **Electrophilic substitution reactions**

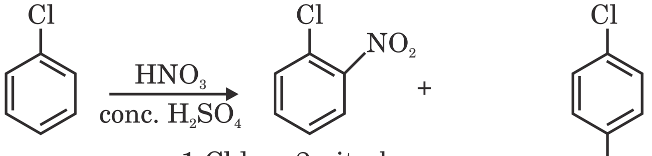
(i) Halogenation:



1, 4-Dichlorobenzene (Major)

1, 2-Dichlorobenzene (Minor)

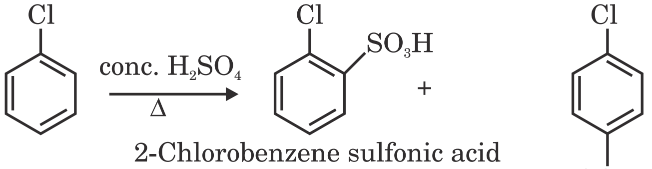
(ii) Nitration:



1-Chloro-2-nitrobenzene (Minor)

1-Chloro-4-nitrobenzene (Major)

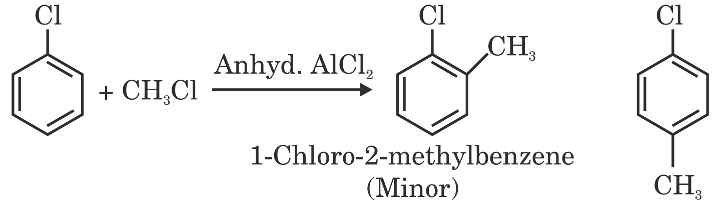
(iii) Sulphonation:



2-Chlorobenzene sulfonic acid (Minor)

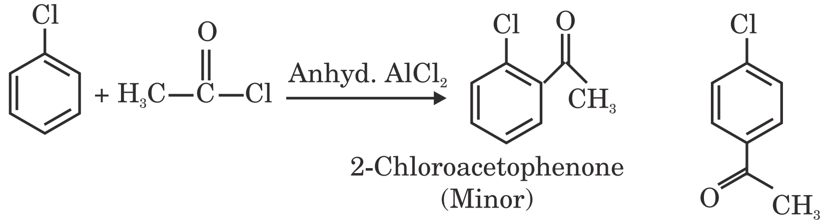
4-Chlorobenzene sulfonic acid (Major)

(iv) Friedel-Crafts reaction:



1-Chloro-2-methylbenzene (Minor)

1-Chloro-4-methylbenzene (Major)



2-Chloroacetophenone (Minor)

4-Chloroacetophenone (Major)

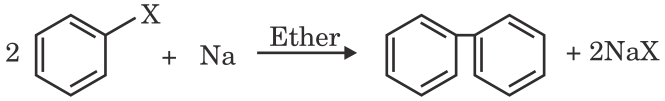
- **Reaction with metals**

  (i) Wurtz-Fittig reaction

  Alkylarene is obtained on reaction of a mixture of alkyl halide and aryl halide with sodium in dry ether.

  (ii) Fittig reaction

  Analogous compounds are also formed in which two aryl groups are joined together.



- **Polyhalogen Compounds**
  - **Dichloromethane (Methylene chloride):** It is prepared industrially by the direct chlorination of methane.

$$CH_4 + 2Cl_2 \xrightarrow{h\upsilon} CH_2Cl_2 + 2HCl$$

  Fractional distillation is used to separate the mixture so obtained. It is used as a solvent, as a paint remover, as a propellant in aerosols and also as a metal cleaning and finishing solvent.

  - **Trichloromethane (Chloroform):** It is manufactured by chlorination of methane followed by separation by fraction.

$$CH_4 + 3Cl_2 \xrightarrow[\text{Sunlight}]{h\upsilon} CHCl_3 + 3HCl$$

  It is extensively used as solvent for waxes, resins, rubber, fats etc. Earlier, chloroform was used as anesthetic but at present this practice has been dropped as it is slowly oxidized by air in the presence of light to form highly poisonous phosgene gas. Therefore, it is stored in closed dark coloured bottles completely filled so that air is kept out.

- **Triiodomethane (Iodoform):** It is prepared by heating ethanol or acetone with sodium hydroxide or Na_2CO_3 and I_2 in water. It is insoluble in water and thus forms yellow precipitate of CHI_3.

$$CH\ CH_2OH + 6NaOH + 4I_2 \xrightarrow{\Delta} CHI_3 + 5NaI + HCOONa + 5H_2O$$

$$CH_3COCH_3 + 4NaOH + 3I_2 \xrightarrow{\Delta} CHI_3 + 3NaI + CH_3COONa + 3H_2O$$

It is used as an antiseptic for dressing wounds.

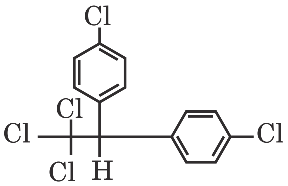
- **Tetrachloromethane (Carbon tetrachloride):** It is prepared by chlorination of methane and by action of chlorine on CS_2 in the presence of $AlCl_3$ as catalyst.

$$CS_2 + 3Cl_2 \xrightarrow[\Delta]{AlCl_3} CCl_4 + \underset{(\text{Sulphur dichloride})}{SCl_2}$$

$$CH_4 + 4Cl_2 \xrightarrow{h\upsilon} CCl_4 + 4HCl$$

It is used in fire extinguisher. Also, it is used as solvent for fats, resins etc.

- **Freons:** The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases.
- **p, p'-Dichlorodiphenyltrichloroethane(DDT):** It is non-biodegradable and extremely stable. It is used as an insecticide. It is manufactured by the condensation of chlorobenzene with chloral in the presence of sulphuric acid. It was earlier used to control malaria and typhoid but due to its highly toxic nature, it was banned in India and USA.



DDT

PREVIOUS YEARS'

EXAMINATION QUESTIONS

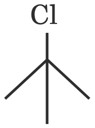
TOPIC 2

1 Mark Questions

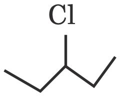
1. What happens when CH_3-Br is treated with KCN?

[DELHI 2013]

2. Which compound in the following pair undergoes faster $S_N{}^1$ reaction?



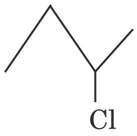
and

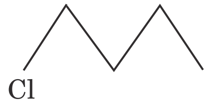


[DELHI 2013]

3. Identify the chiral molecule in the following pair:

[ALL INDIA 2014]

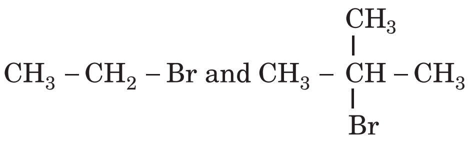




4. Which would undergo S_N2 reaction faster in the following pair: **[ALL INDIA 2015]**

$$C_6H_5CH_2CH_2CH_2Br \text{ and } C_6H_5-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$$

5. Which would undergo S_N2 reaction faster in the following pair and why? **[DELHI 2015]**



$$CH_3-CH_2-Br \text{ and } CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{CH}}}}-CH_3$$

6. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt. **[DELHI 2016]**

7. Out of chlorobenzene and benzylchloride, which one gets easily hydrolysed by aqueous NaOH and why? **[ALL INDIA 2018]**

2 Marks Questions

8. Account for the following: **[DELHI 2013]**

(i) The C – Cl bond length in chlorobenzene is shorter than that in $CH_3 - Cl$

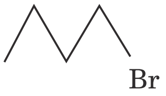
(ii) Chloroform is stored in closed dark brown bottles.

9. (a) Why does p-dichlorobenzene have a higher melting point than its o- and m- isomers?

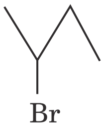
(b) Why is Butan-2-ol optically inactive?

[DELHI 2013]

10. (i) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction?



(a)



(b)

(ii) Out of S_N1 and S_N2, which reaction occurs with

(a) Inversion of configuration

(b) Racemisation **[CBSE 2014]**

11. Explain as to why haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions.

Or

Which compound in each of the following pairs will react faster in S_N2 reaction with –OH? Why?

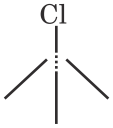
(i) CH_3Br or CH_3I

(ii) $(CH_3)_3CCl$ or CH_3Cl **[DELHI 2016]**

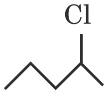
12. A solution of KOH hydrolyses $CH_3CHClCH_2CH_3$ and $CH_2CH_2CH_2CH_2Cl$. Which one of these is more easily hydrolyzed?

13. Which one in the following pairs undergoes S_N1 substitution reaction faster and why?

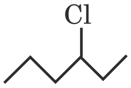
(i)



Or



(ii)

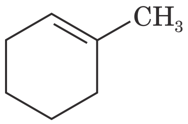


Or

[DELHI 2017]

14. Complete the following reaction equations:

(i)



+ Hl →

(ii) $CH_3CH_2CH = CH_2 + HBr \rightarrow$

[DELHI 2017]

3 Marks Questions

15. Answer the following:

(i) Haloalkanes easily dissolves in organic solvents, why?

(ii) What is known as a racemic mixture? Give an example.

(iii) Of the two bromoderivatives, $C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)Br$, which one is more reactive in S_NI substitution reaction and why? **[DELHI 2011]**

16. Rearrange the compounds of each of the following sets in order of reactivity towards displacement:

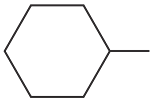
(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane

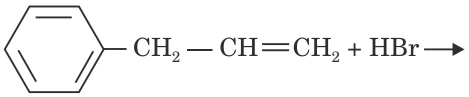
(iii) 1-Bromobutane, 1-Bromo-2, 2-dimethylpropane, 1-Bromo-2-methylbutane **[ALL INDIA 2011]**

17. (a) Draw the structures of major monohalo products in each of the following reactions:

(i)



$CH_2OH \xrightarrow{PCl_2}$

(ii) 

(b) Which halogen compound in each of the following pairs will react faster in S_N2 reaction:

(i) CH_3Br or CH_3I

(ii) $(CH_3)_3C - Cl$ or $CH_3 - Cl$

[ALL INDIA 2014]

18. How do you convert the following:

(i) Prop-1-ene to Propan-2-ol

(ii) Bromobenzene to 2-bromoacetophenone

(iii) 2-bromobutane to But-2-ene

Or

What happens when

(i) Ethyl chloride is treated with NaI in the presence of acetone,

(ii) Chlorobenzene is treated with Na metal in the presence of dry ether,

(iii) Methyl chloride is treated with KNO_2? Write chemical equations in support of your answer. **[DELHI 2014]**

19. Give reasons:

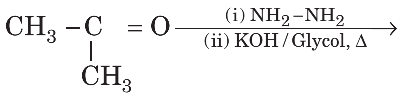
(a) n-Butyl bromide has higher boiling point than t-butyl bromide.

(b) Racemic mixture is optically inactive.

(c) The presence of nitro group ($-NO_2$) at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions. **[DELHI 2015]**

20. Predict the products of the following reactions:

[DELHI 2015]

(i) 

$$CH_3-\underset{\underset{CH_3}{|}}{C}=O \xrightarrow[\text{(ii) KOH / Glycol, }\Delta]{\text{(i) }NH_2-NH_2}$$

(ii) $C_6H_5-CO-CH_3 \xrightarrow{NaOH/I_2} ? + ?$

(iii) $CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} ?$

21. How do you convert:

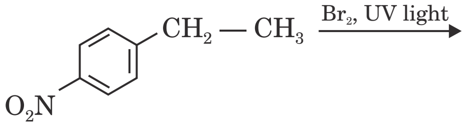
(i) Chlorobenzene to biphenyl

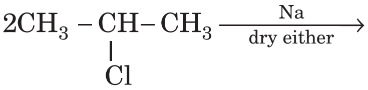
(ii) Propene to 1-iodopropane

(iii) 2-bromobutane to but-2-ene

Or

Write the major products(s) in the following:

(i) 

(ii) 

$$2CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow[\text{dry either}]{Na}$$

(iii) $CH_3-CH_2-Br \xrightarrow{AgCN}$

[ALL INDIA 2016]

22. The following compounds are given to you:

2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

(a) Write the compound which is most reactive towards S_N2 reaction.

(b) Write the compound which is optically active.

(c) Write the compound which is most reactive towards β-elimination reaction.

[ALL INDIA 2017]

23. (i) State one use each of DDT and iodoform.

(ii) Which compound in the following couples will react faster in displacement and why?

(a) 1-Bromopentane or 2-bromopentane

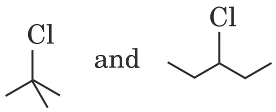
(b) 1-Bromo-2-methylbutane or 2-bromo-2methylbutane.

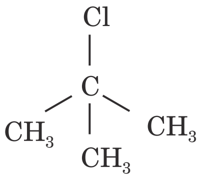
Solutions

1. $CH_3Br + KCN \rightarrow CH_3CN + KBr$

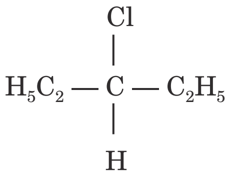
When methyl bromide reacts with Potassium cyanide we get Methyl Cyanide and potassium bromide. It is a nucleophilic substitution reaction. [1]

2. [1]



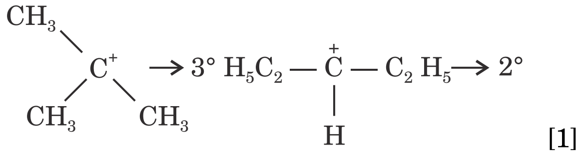


I



II

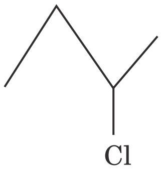
The carbocation formed when compounds I and II undergo S_N1 reaction are shown below:



[1]

As 3° carbocation is more stable than 2° carbocation, hence compound I undergoes faster S_N1 reaction.

3. A molecule which has chiral carbon, i.e. all four different groups attached to carbon is called chiral molecule. [1]



4. $C_6H_5-CH_2-CH_2-CH_2-Br$, because [1]

$$\text{Rate of } S_N2 \propto \text{stability of T.S.} \propto \frac{1}{\text{Steric hinderance}}$$

5. Primary alkyl halides will undergo S_N2 reactions faster than tertiary alkyl halides because of less steric hindrance experienced while approaching nucleophile. Hence, out of the given pair, primary alkyl halide (CH_3CH_2Br) would undergo S_N2 reaction faster. [1]

6. $C_6H_5N_2^+Cl^- + KI \rightarrow C_6H_5I + KCl + N_2$ [1]

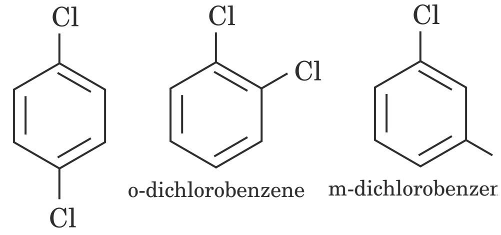
7. Benzylchloride will get easily hydrolysed as the halogen is attached to 1° carbon atom. [1]

8. (i) This is due to partial double bond character of C – Cl bond (due to resonance in C_6H_5Cl). [1]

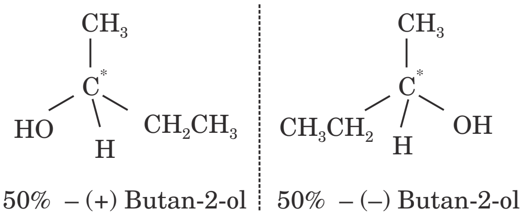
(ii) Chloroform in the presence of air gets oxidized to phosgene. Phosgene is carbonyl chloride and is represented as $COCl_2$. To prevent the formation of phosgene, chloroform is stored in dark coloured bottles. The reaction is represented as [1]

$$CHCl_3 + \frac{1}{2}O_2 \longrightarrow COCl_2 + HCl$$

9. (a) p-dichlorobenzene has higher melting point than ortho and meta isomer. This is because the para isomer is having a symmetrical structure and therefore, its packing is more efficient as compared to the ortho and meta isomer, therefore, it shows higher melting point. [1]

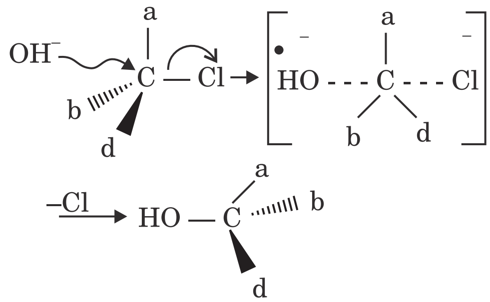


(b) The (+) – Butan-2-ol is optically inactive because it is a racemic mixture and exists in two enantiomeric forms which are non-superimposable mirror images of each other. Both the isomers are present in equal amounts therefore, it does not rotate the plane of polarized light and is optically inactive. [1]

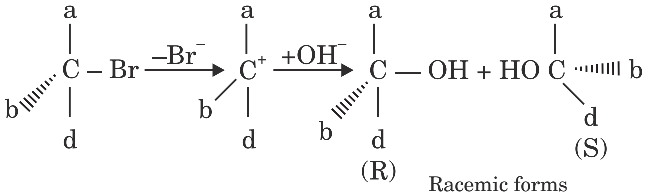


10. (i) Compound (b), i.e., $CH_3CHBrCH_2CH_3$ possesses chiral centre and undergoes faster S_N2 reaction. [1]

(ii) (a) Inversion of configuration results in S_N2 reaction as there is formation of intermediate transition state in which there is simultaneous attack and migration of leaving group. [½]



(b) Racemisation in S_N1 reaction is due to attack of nucleophile on both sides of the planar carbocation. [½]



Racemic forms
(Optically inactive mixture)

11. Aryl halides are less reactive towards nucleophilic substitution because of the following reasons:

Aryl halides are less reactive towards nucleophilic substitution because of the following reasons:

1. The primary reaction of aromatic compounds is Electrophilic substitution because of the aromaticity which benzene possess. [1]
2. Benzene itself acts as a nucleophile which isn't in the favour of nucleophilic substitution reactions.
3. In haloarenes the C-X bond (carbon halogen bond) has a double bond character due to the lone pair of halogens. Whereas the C-X bond in alkyl halides is comparatively weaker with respect to the resonance stabilised C-X bond in aryl halides. [1]

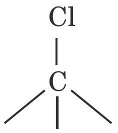
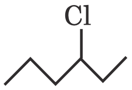
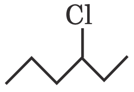
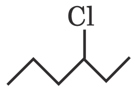
Thus we can conclude that haloalkanes are more reactive than haloarenes

OR

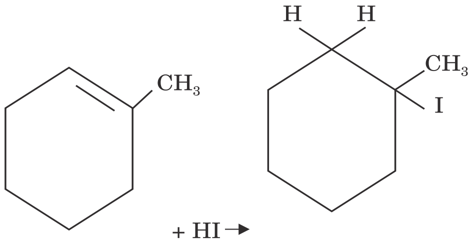
(i) CH_3I, because iodine is a better leaving group due to its larger size. [1]

(ii) CH_3Cl, the presence of bulky group on the carbon atom in $(CH_3)_3CCl$ has an inhibiting effect. [1]

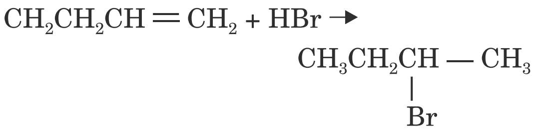
12. $CH_2CH_2CH_2CH_2Cl$ undergoes hydrolysis more easily than $CH_3CHClCH_2CH_3$. $CH_2CH_2CH_2CH_2Cl$ being a primary alkyl halide has less steric hindrance than $CH_3CHClCH_2CH_3$ which is a secondary alkyl halide. [2]

13. i.  will undergo S_N1 reaction faster than  because  is a tertiary alkyl halide and  is a secondary alkyl halide. Tertiary carbocation is more stable than secondary carbocation. [1]

ii.  will undergo S_N1 reaction faster than  because  is a secondary alkyl halide and  is a primary alkyl halide. Secondary carbocation is more stable than primary carbocation. [1+1]

14. (i) 

+ HI →

(ii) 

$$CH_2CH_2CH=CH_2 + HBr \rightarrow \underset{\underset{Br}{|}}{CH_3CH_2CH}-CH_3$$

[1+1]

15. (i) Haloalkanes dissolve in organic solvents because the new intermolecular attraction between haloalkanes and organic solvent molecules have the same strength as the one being broken in the separate haloalkanes and solvent molecules. Moreover haloalkanes are nonpolar molecules and organic solvents are also non polar, therefore they easily get dissolved in it. [1]

(ii) Racemic mixture is an equimolar mixture of two enantiomers and is hence optically inactive, e.g. (± butan-2-ol). [1]

(iii) The carbocation intermediate derived from $C_6H_5CH(C_6H_5)Br$ i.e. $C_6H_5\overset{+}{C}HC_6H_5$ is more stable as compared to the carbocation $C_6H_5\overset{+}{C}HCH_3$ obtained from $C_6H_5CH(CH_{3)}Br$ because it is stabilized by two phenyl groups due to resonance. So it is more reactive in S_N1 substitution. [1]

16. (i) 1-Bromopentane > 2-Bromopentane > 2-Bromo -2-methyl butane. [1]

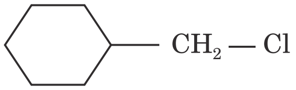
(ii) 1- Bromo-2 - methyl butane> 3-Bromo-2-methyl butane> 2-Bromo-2-methyl butane

[1]

(iii) 1- Bromobutane> 1-Bromo- 2-methyl butane> 1-Bromo-2, 2-dimethyl propane

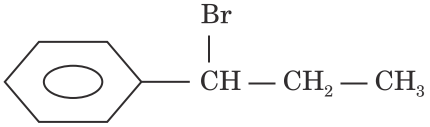
[1]

17. (a) (i)



[1]

(ii)

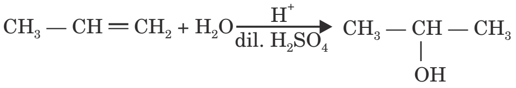


[1]

(b) (i) CH_3I [½]

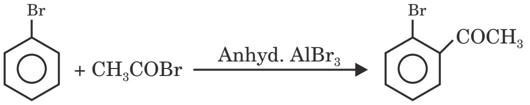
(ii) CH_3Cl [½]

18. (i)



$CH_3—CH=CH_2 + H_2O \xrightarrow[\text{dil. } H_2SO_4]{H^+} CH_3—\underset{\underset{OH}{|}}{CH}—CH_3$

(ii)



(iii)

$CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow[\Delta]{\text{Alc. KOH}} CH_3-CH=CH-CH_3$

[1+1+1]

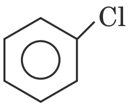
OR

(i) $C_2H_5Cl + NaI \xrightarrow{\text{Acetone}} C_2H_5I + NaCl$ [1]

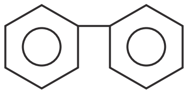
Ethyliodide

(Finkelstein reaction)

(ii) 2



$+ 2\,Na \xrightarrow{\text{Ethane}}$ [1]



+ 2 Na (Fitting reaction)

Diphenyl

(iii) $CH_3Cl + KNO_2 \longrightarrow CH_3ONO + KCl$ [1]

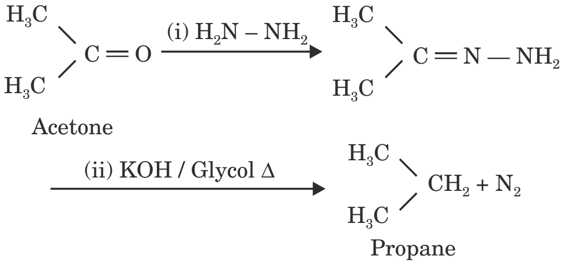
Methyl nitrite

19. (a) n-butyl bromide is a straight chain molecule having larger surface area and therefore, has stronger intermolecular forces. On the other hand, butyl bromide $(CH_3)_3CBr$ is branched molecule, so it has a smaller surface area. Hence, it has weaker intermolecular forces. [1]

(b) Racemic mixture is an equimolar solution of two enantiomers (d and l forms) and thus, the rotation due to one isomer is cancelled by the rotation due to another. Therefore, it has zero optical rotation and hence, it is optically inactive. [1]

(c) This is because nitro group ($–NO_2$) at o/p positions withdraw the electrons from the benzene ring. The reduced electron density at o/p positions for haloarenes facilitates the attack of nucleophile. The negative charge in the carbanion formed, at o/p positions with respect to halogen atom is stabilised through the presence of nitro groups (NO_2) respectively. [1]

20. (i)



(Wolff Kishner Reduction)

[1]

(ii) $C_6H_5-CO-CH_3 \xrightarrow{NaOH/I_2} CHI_3\downarrow + C_6H_5COONa$

Acetophenone Iodoform (Yellow)

[1]

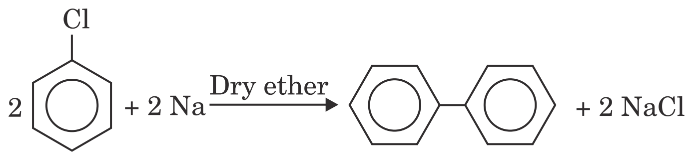
(iii) $CH_3-COONa \xrightarrow{NaOH/CaO} CH_4 + Na_2CO_3$

Sodium acetate Methane

(Decarboxylation Reaction) [1]

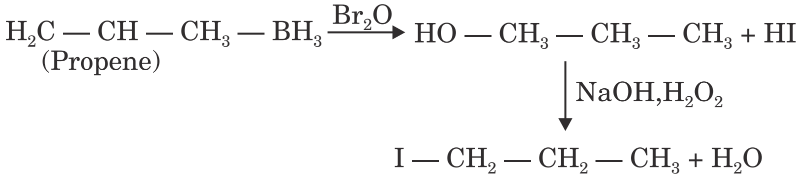
21. [1+1+1]

(i)



(Chlorobenzene) (Biphenyl)

Fittig Reaction



$$\begin{array}{l} H_2C - CH - CH_3 - BH_3 \xrightarrow{Br_2O} HO - CH_3 - CH_3 - CH_3 + HI \\ \qquad\qquad\qquad\qquad\qquad \downarrow NaOH,H_2O_2 \\ \qquad\qquad\qquad\qquad I - CH_2 - CH_2 - CH_3 + H_2O \end{array}$$

(ii) (Propene) (l-lodopropane)

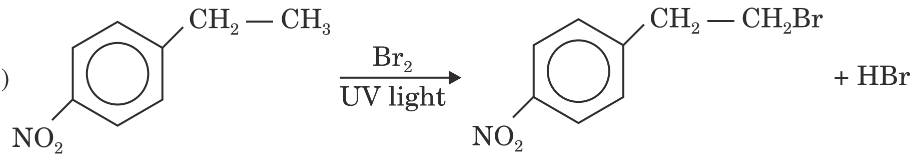
$$\underset{\underset{Br}{|}}{CH_3 - CH} - CH_2 + CH_3 \xrightarrow[\text{Alcohol}]{\text{KOH}} CH_3 - CH = CH - CH_3$$

(iii) (2-Bromobutane) (But-2-ene)

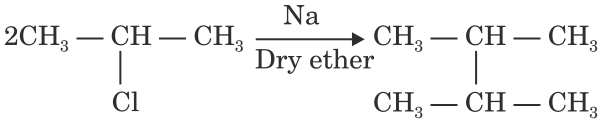
OR

[1+1+1]

(i)



(ii)



$$2CH_3 - \underset{\underset{Cl}{|}}{CH} - CH_3 \xrightarrow[\text{Dry ether}]{\text{Na}} \begin{array}{c} CH_3 - CH - CH_3 \\ | \\ CH_3 - CH - CH_3 \end{array}$$

Wurtz Reaction

(iii) $CH_3 - CH_2 - Br \xrightarrow{AgCN} CH_3 - CH_2 - NC$

22. (a) 1- Bromopentane is most reactive towards S_N2 reaction. **[1]**

(b) 2-Bromo-2-methylbutane **[1]**

(c) 2- Bromopentane is most reactive towards β-elimination reaction with product of pent-1-ene pent-2-ene. **[1]**

23. (i) Use of DDT: It is used as an insecticide. **[1]**

Use of iodoform: It is used as an antiseptic.

(ii) (a) 1 – Bromopentane will undergo faster S_N2 displacement reaction than 2- bromopentane because 1- bromopentane has less steric hindrance than 2 – bromopentane. This is because 1- bromopentane is a primary alkyl halide whereas 2-bromopentane is a secondary alkyl halide. **[1]**

(b) 1- Bromo-2-methylbutane will undergo S_N2 reaction faster than 2- Bromo-2- methylbutane because 1- Bromo-2-methylbutane has less steric hindrance than than 2- Bromo-2-methylbutane. This is because 1- Bromo-2-methylbutane is a primary alkyl halide whereas 2- Bromo-2-methylbutane is a tertiary alkyl halide

[1]

Smart Notes ....

Smart Notes ....

CHAPTER 11

Alcohols, Phenols and Ethers

Chapter Analysis with respect to Last 3 Years' Board Exams

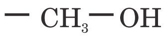
List of Topics	2016		2017		2018	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Alcohols: Nomenclature, methods of preparation, physical and chemical properties	(1, 1 mark)	(1 mark)	(1 mark)			
Identification of primary, secondary and tertiary alcohols						
Mechanism of dehydration, uses with special reference to methanol and ethanol					(3 marks)	(3 marks)
Phenols: Nomenclature, methods of preparation, physical and chemical properties	(3 marks)	(3 marks)			(1 marks)	(1 marks)
Acidic nature of phenol, electrophillic substitution reactions, uses of phenols			(3 marks)	(2 marks)		
Ethers: Nomenclature, methods of preparation, physical and chemical properties, uses					(2 marks)	(2 marks)

Topic 1: Alcohols and Phenols

Summary

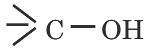
- **Alcohols:** Alcohols have the general formula as $C_nH_{2n+1}OH$ and they are obtained when one hydrogen atom in alkane is replaced by –OH group.
- **Classification of alcohols:**
  - Alcohols which have one hydroxyl group are called monohydric alcohols.
  - Alcohols which have 2 hydroxyl groups are called dihydric alcohols.
  - Alcohols which have 3 hydroxyl groups are called trihydric alcohols.
  - Alcohols which have many hydroxyl groups are called polyhyric alcohols.
  - Monohydric alcohols are further classified according to the hybridization of the carbon atom to which hydroxyl group is attached as shown below:

(i) **Compounds containing** $C_{sp^3}-OH$ **bond:** In this type of alcohols the –OH group is attached to an sp^3 hybridised carbon atom of an alkyl group.



Primary (1°)

Secondary (2°)

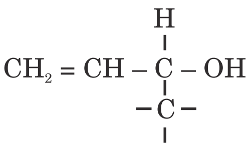


Tertiary (3°)

(ii) **Allylic alcohols:** In this type of alcohols the –OH group is attached to an sp^3 hybridised carbon next to the C-C double bond, which is an allylic carbon.

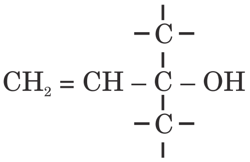
$CH_2 = CH - CH_2 - OH$

Primary



$CH_2 = CH - \overset{H}{\underset{-C-}{C}} - OH$

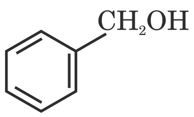
Secondary



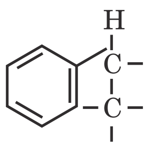
$CH_2 = CH - \overset{-C-}{\underset{-C-}{C}} - OH$

Tertiary

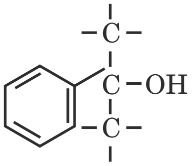
(iii) **Benzylic alcohols:** In this type of alcohols the –OH group is attached to a sp^3-hybridised carbon atom attached to the benzene ring.



Primary



Secondary

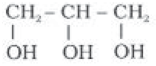
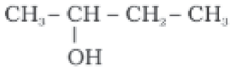


Tertiary

(iv) **Vinylic alcohol:** In this type of alcohols –OH group is bonded to the C-C double bond i.e. to a vinylic carbon or to an aryl carbon.

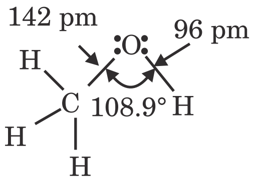
$CH_2 = CH - OH$

- Common and IUPAC names of some alcohols are given below in the table:

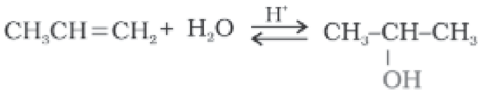
Compound	**Common name**	**IUPAC name**
CH_3-OH	Methyl alcohol	Methanol
$CH_3-CH_2-CH_2-OH$	n-Propyl alcohol	Propan-1-ol
 $\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$	Glycerol	Propane-1, 2, 3-triol
 $CH_3-\underset{OH}{CH}-CH_2-CH_3$	Sec-Butyl alcohol	Butan-2-ol

- **Structure of alcohol:**

In alcohols, the oxygen of the –OH group is attached to sp^3 hybridized carbon by a sigma bond.

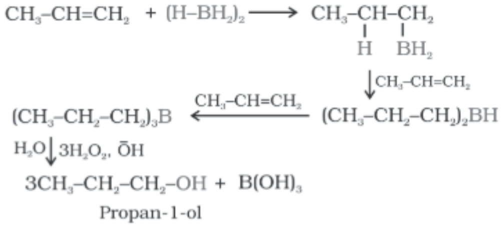


- **Preparation of Alcohols:**
  - **From alkenes:** alcohol is prepared when alkenes react with water in presence of acid as catalyst.



$$CH_3CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3-\underset{OH}{CH}-CH_3$$

  - **By hydroboration-oxidation:**



  - **From carbonyl compounds:**

(i) **By reduction of aldehydes and ketones:** Corresponding alcohols are produced by the reduction of aldehydes and ketones by addition of hydrogen in the presence of catalysts.

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$$

$$RCOR' \xrightarrow{NaBH_4} R-\underset{OH}{CH}-R'$$

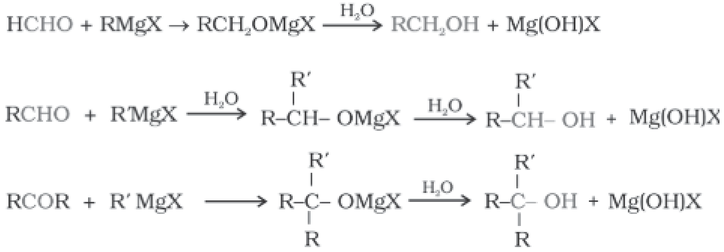
(ii) **By reduction of carboxylic acids and esters:** In the presence of strong agent, lithium aluminium hydride, carboxylic acids are reduced to primary alcohols.

$$RCOOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} RCH_2OH$$

Commercially, acids are reduced to alcohols by first converting them to esters and then following catalytic hydrogenation.

$$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[\text{Catalyst}]{H_2} RCH_2OH + R'OH$$

- **From Grignard reagents:** The reaction of Grignard reagent with formaldehyde produces a primary alcohol, with other aldehydes it reacts to give secondary alcohols and tertiary alcohols are produced on reaction of Grignard reagent with ketones.



$$HCHO + RMgX \rightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg(OH)X$$

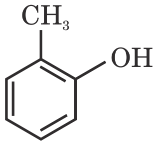
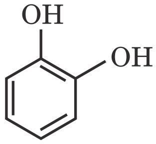
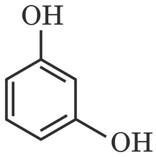
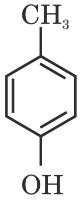
$$RCHO + R'MgX \xrightarrow{H_2O} R-\overset{\overset{R'}{|}}{C}H-OMgX \xrightarrow{H_2O} R-\overset{\overset{R'}{|}}{C}H-OH + Mg(OH)X$$

$$RCOR + R'MgX \longrightarrow R-\underset{\underset{R}{|}}{\overset{\overset{R'}{|}}{C}}-OMgX \xrightarrow{H_2O} R-\underset{\underset{R}{|}}{\overset{\overset{R'}{|}}{C}}-OH + Mg(OH)X$$

➢ **Phenols:**

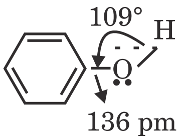
- It is the simplest hydroxyl derivative of benzene. In its substituted compounds the terms ortho (1, 2- disubstituted), meta (1, 3 –disubstituted) and para (1, 4- disubstituted) are often used in common names.

➢ **Common name and IUPAC name of some phenols are given below in the table:**

Compound	**Common name**	**IUPAC name**
	o-Cresol	2-Methylphenol
	Catechol	Benzene-1, 2-diol
	Resorcinol	Benzene-1, 3-diol
	p-Cresol	4-Methyphenol

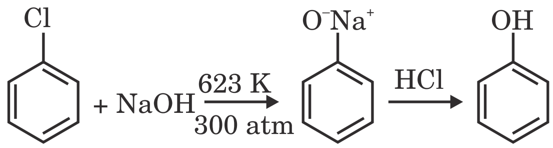
➢ **Structure of Phenols:**

In phenols, the –OH group is attached to the sp^2 hybridised carbon of an aromatic ring.

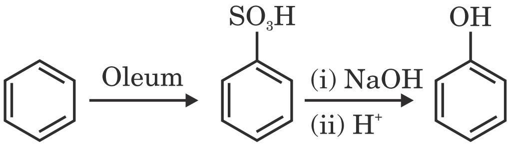


➢ **Preparation of Phenols:**

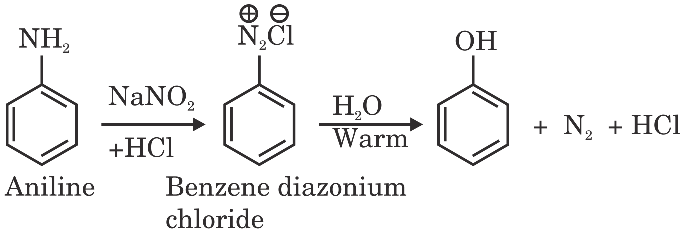
- **From haloarenes:**



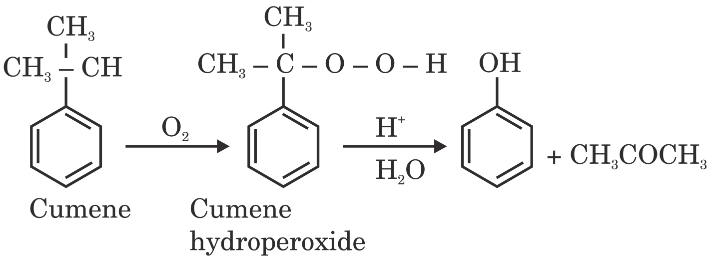
- **From benzenesulphonic acid:**



- **From diazonium salts:**



- **From cumene:**

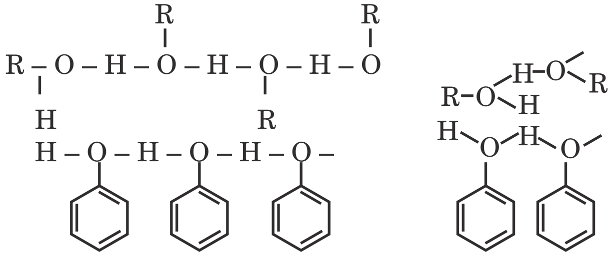


➢ **Physical properties of alcohols and phenols:**

- **Boiling Points:** With increase in the number of carbon atoms van der Waal's forces increase which in turn increases the boiling point of alcohols and phenols. With increase of branching in carbon chain the Van der Waals forces decreases with decrease in surface area which in turn decreases the boiling point of alcohols.

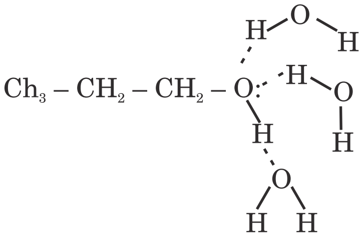
  The high boiling points of alcohols and phenols is mainly because of the presence of intermolecular hydrogen bonding in them which is lacking in ether and hydrocarbons.

  The –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding as shown below:



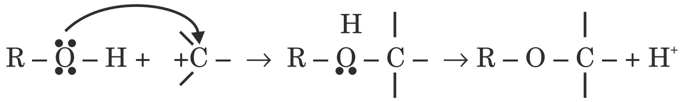
- **Solubility:** Solubility of alcohols and phenols in water is because of their ability to form hydrogen bonds with water molecules.

  With increase in the size of the aryl/alkyl groups the solubility decreases.



➢ Chemical Reactions

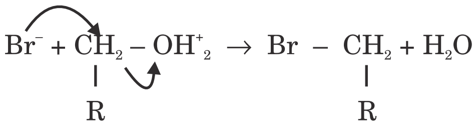
Alcohols react as nucleophiles and electrophiles. When alcohols react as nucleophile the bond between –OH is broken.



$$R-\ddot{\underset{\cdot\cdot}{O}}-H + {}^{+}C< \rightarrow R-\overset{H}{\underset{\cdot\cdot}{O}}-\overset{|}{\underset{|}{C}}- \rightarrow R-O-\overset{|}{\underset{|}{C}}- + H^{+}$$

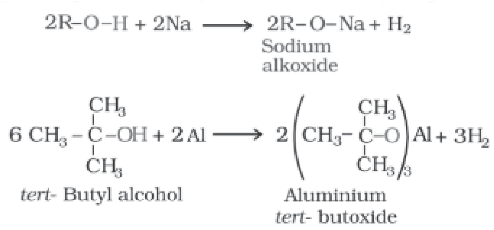
When they react as electrophile the bond between C-O is broken.

$$R-CH_2-OH+\overset{+}{H} \rightarrow R-CH_2-\overset{+}{OH_2}$$



$$Br^{-} + \underset{R}{\underset{|}{CH_2}}-OH^{+}_{2} \rightarrow Br-\underset{R}{\underset{|}{CH_2}} + H_2O$$

- **Reactions of alcohols and phenols involving cleavage of O-H bond:**
    1. **Acidity of alcohols and phenols:**
        (i) **Reaction with metals:** They react with active metals like sodium, potassium and aluminium to give corresponding alkoxides/phenoxides and hydrogen.



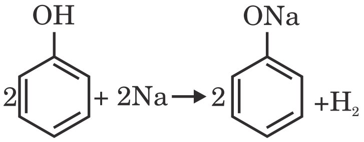
$$2R-O-H + 2Na \longrightarrow 2R-O-Na + H_2$$

Sodium alkoxide

$$6\,CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH + 2\,Al \longrightarrow 2\left(CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-O\right)_3Al + 3H_2$$

tert- Butyl alcohol

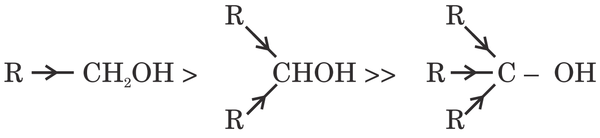
Aluminium *tert*- butoxide



Phenol Sodium phenoxide

(ii) **Acidity of alcohols:** The polar nature of O-H brings the acidic character in alcohols. The electron releasing group increase electron density on oxygen which decreases the polarity of O-H bond hence decreases the acid strength.

The acid strength of alcohols decrease in the following order:



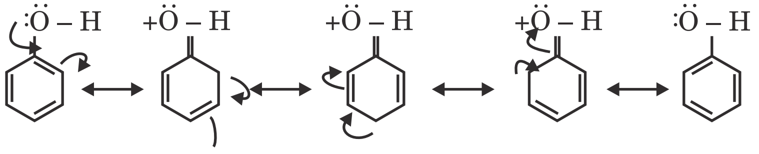
$$R\rightarrow CH_2OH > \begin{matrix}R\searrow\\ \\ R\nearrow\end{matrix}CHOH \gg \begin{matrix}R\searrow\\ R\rightarrow\\ R\nearrow\end{matrix}C-OH$$

Primary Secondary Tertiary

Alcohols are weaker acids than water.

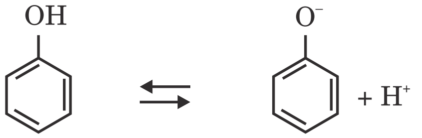
Alcohols act as Bronsted bases due to the presence of unshared electron pairs on oxygen.

(iii) **Acidity of phenols:** Phenols are more acidic than alcohols and water. In phenol the hydroxyl group is attached directly to the sp^2 –hybridised carbon of the benzne ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, causes the oxygen of –OH group to be positive.

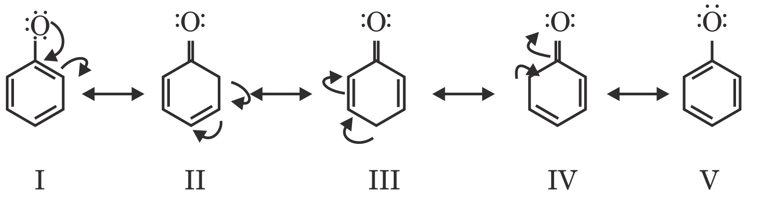


The ionization of an alcohol and a phenol takes place producing alkoxide and phenoxide ions as shown below:

$$R-\ddot{\underset{..}{O}}-H \rightleftharpoons R-\ddot{\underset{..}{O}}:^{-} + H^{+}$$



In alkoxideion, the negative charge is localized on oxygen while in phenoxide ion, the charge is delocalized. The delocalization of negative charge makes phenoxide ion more stable and favours the ionization of phenol.



2. **Esterification:** Esters are formed when alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides.

The reactions are given below:

$$Ar/RO-H + R'-COOH \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + H_2O$$

$$Ar/R-OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + R'COOH$$

$$R/ArOH + R'COCl \xrightarrow{\text{Pyridine}} R/ArOCOR' + HCl$$

- **Reactions involving cleavage of C-O bond in alcohols:**

  Only alcohols undergo this type of reactions which involves cleavage of C-O bond. In phenols this type of reaction takes place only with zinc.

1. **Reaction with hydrogen halides:**

$$R-OH + HX \xrightarrow{ZnCl_2} R-X + H_2O$$

2. **Reaction with phosphorus trihalides:**

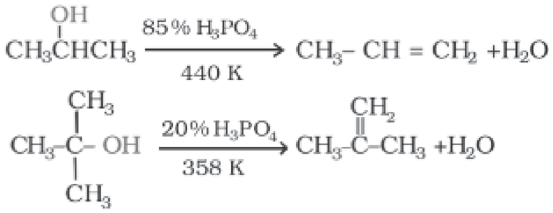
$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3 \quad (X = Cl, Br)$$

3. **Dehydration:**

Dehydration of ethanol is given below:

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$$

Dehydration of secondary and tertiary alcohols take place under milder condition and reaction is shown below:



$$CH_3\overset{OH}{C}HCH_3 \xrightarrow[440\ K]{85\%\ H_3PO_4} CH_3-CH=CH_2 + H_2O$$

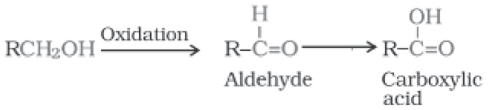
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow[358\ K]{20\%\ H_3PO_4} CH_3-\overset{CH_2}{\overset{\|}{C}}-CH_3 + H_2O$$

The order of dehydration of alcohols is shown as:

Tertiary > Secondary > Primary

4. **Oxidation:**

Primary alcohol can be oxidized to aldehyde which on further oxidizing gives carboxylic acid which depends on the type of oxidizing agent used.



$$RCH_2OH \xrightarrow{Oxidation} \underset{Aldehyde}{R-\overset{H}{C}=O} \longrightarrow \underset{Carboxylic\ acid}{R-\overset{OH}{C}=O}$$

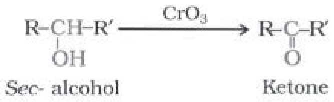
As an oxidizing agent CrO_3 can be used for isolating aldehyde.

$$RCH_2OH \xrightarrow{CrO_3} RCHO$$

Pyridinium chloromate (PCC) can be used an oxidizing reagent to get aldehyde from primary alcohols.

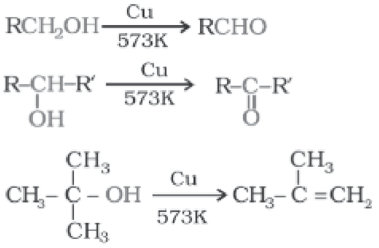
$$CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$$

On oxidizing secondary alcohols gives ketone using CrO_3 as an oxidizing agent.



$$\underset{Sec\text{-}\ alcohol}{R-\underset{OH}{CH}-R'} \xrightarrow{CrO_3} \underset{Ketone}{R-\underset{O}{\overset{}{\underset{\|}{C}}}-R'}$$

5. **Dehydrogenation:**



$$RCH_2OH \xrightarrow[573K]{Cu} RCHO$$

$$R-\underset{OH}{CH}-R' \xrightarrow[573K]{Cu} R-\underset{O}{\underset{\|}{C}}-R'$$

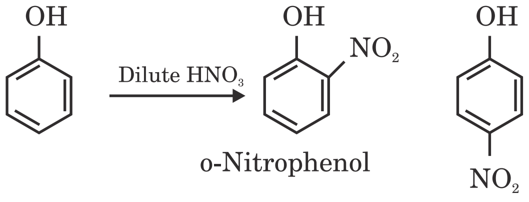
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow[573K]{Cu} CH_3-\overset{CH_3}{C}=CH_2$$

- **Reactions of phenols:**

Following are the reactions of phenols:

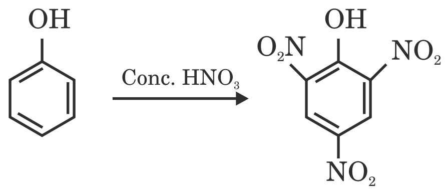
1. **Electrophilic aromatic substitution:**

(i) **Nitration:**



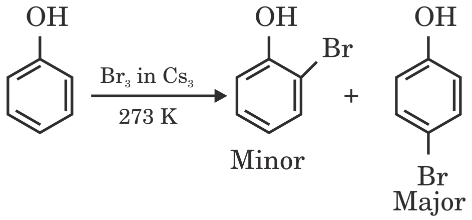
o-Nitrophenol

p-Nitrophenol

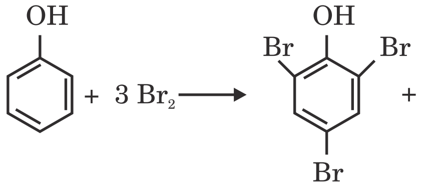


2.4.6-Trinitrophenol
(Picric acid)

(ii) **Halogenation:**

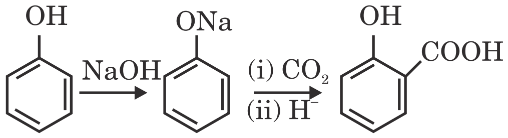


Treatment of phenol with bromine water is shown below:



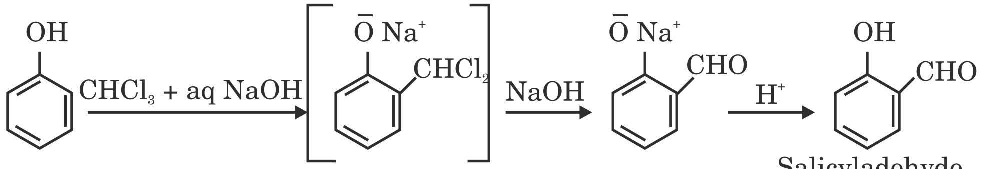
2,4,6-Tribomophenol

2. **Kolbe's reaction:**



2-Hydroxybenzoic acid
(Salicylic acid)

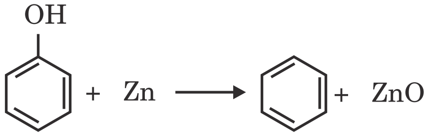
3. **Reimer- Tiemann reaction:**



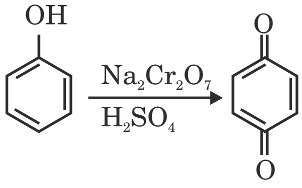
Intermediate

Salicyladehyde

4. **Reaction of phenol with zinc dust:**



5. **Oxidation:**



benzoquinone

- **Some commercially important alcohols are given below:**

1. **Methanol:**
   - **Physical properties:**

   Methanol is also known by the name 'wood spirit'.

   It is a colourless liquid which boils at 337 K.

   In paints, varnishes it is used as a solvent.

   - **Preparation of Methanol:**By catalytic hydrogenation of carbon monoxide.

$$CO + 2H_2 \xrightarrow[\substack{200\text{-}300\ atm \\ 573\text{-}673\ K}]{ZnO\text{-}Cr_2O_3} CH_3OH$$

2. **Ethanol:**
   - **Physical properties:**

   It is a colourless liquid which boils at 351 K.

   It is made unfit for drinking by mixing it with some copper sulphate which gives it some colour and pyride which gives it a foul smell. This complete process is called denaturation of alcohol.

   - **Preparation of Ethanol:**

   Ethanol is prepared by fermentation of glucose and fructose in presence of enzyme, Zymase, which is found in yeast.

   Glucose and fructose are produced from sugar in the presence of enzyme, invertase.

   The reactions are given below:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} \underset{Glucose}{C_6H_{12}O_6} + \underset{Fructose}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH + 2CO_2$$

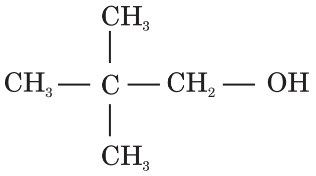
PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 1

1 Mark Questions

1. Draw the structure of hex-l-en-3-ol compound. **[DELHI 2012]**
2. Draw the structural formula of 2-methylpropan -2-ol molecule. **[ALL INDIA 2012]**
3. What happens when ethyl chloride is treated with aqueous KOH? **[DELHI 2013]**
4. Which of the following isomers is more volatile: o-nitrophenol or p-nitrophenol? **[DELHI 2014]**
5. Write the IUPAC name of the given compound



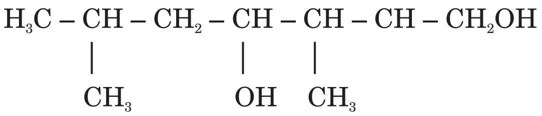
$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ CH_3 & — & C & — & CH_2 — OH \\ & & | & & \\ & & CH_3 & & \end{array}$$

[ALL INDIA 2015]

6. Write IUPAC name of given compound:

[ALL INDIA 2016]

7. Write the IUPAC name of the following compound:



$$\begin{array}{l} H_3C - \underset{\underset{CH_3}{|}}{CH} - CH_2 - \underset{\underset{OH}{|}}{CH} - \underset{\underset{CH_3}{|}}{CH} - CH - CH_2OH \end{array}$$

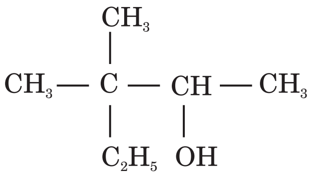
[DELHI 2016]

8. Give the IUPAC name of the following compound:

$$H_2C = CH - \underset{\underset{OH}{|}}{CH} - CH_2 - CH_2 - CH_3$$

[DELHI 2017]

9. Write the IUPAC name of the following:



$$\begin{array}{ccccccc} & & CH_3 & & & & \\ & & | & & & & \\ CH_3 & — & C & — & CH & — & CH_3 \\ & & | & & | & & \\ & & C_2H_5 & & OH & & \end{array}$$

[ALL INDIA 2018]

2 Mark Questions

10. How will you convert the following?

(i) Propan-2-ol to propanone.

(ii) Phenol to 2,4,6 – tribromophenol?

[DELHI 2013]

11. Explain the following giving one example for each:

1. Reimer-Tieman reaction.
2. Friedel Craft's acetylation of anisole.

[DELHI 2011]

12. How would you obtain:

(i) Picric acid (2, 4, 6-Trinitrophenol) from phenol.

(ii) 2-Methylpropene from 2-methylpropanol?

[DELHI 2011]

13. Explain the mechanism of the following reaction:

$$CH_3-CH_2-OH \xrightarrow{H^+,443K} CH_2=CH_2+H_2O$$

[ALL INDIA 2013]

14. Write the mechanism of the following reaction:

$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$$

[ALL INDIA 2014]

15. How are the following conversions carried out?

(i) Benzyl chloride to benzyl alcohol

(ii) Methyl magnesium bromide to 2-methylpropan-2-ol.

3 Mark Questions

16. How would you obtain the following:

(i) Benzoquinone from phenol

(ii) 2-Methylpropan-2-ol from methyl magnesium bromide

(iii)Propan-2-ol from propene

[ALL INDIA 2011]

17. 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-l-propanol **[ALL INDIA 2012]**

18. 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) But-1-en-2-ol

(iii) 2-methyl-1-proponal **[ALL INDIA 2012]**

19. How will you convert:

(i) Propene to Propan- 1-ol?

(ii) Ethanal to Propan-2-ol? (**DELHI 2013)**

20. (a) Write the mechanism of the following reaction:

$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$$

(b) Write the equation involved in Reimer-Tiemann reaction. **(DELHI 2014)**

21. Give reasons for the following:

(i) p-nitrophenol is more acidic than p-methyl phenol.

(ii) Bond length of $C-O$ bond in phenol is shorter than that in methanol.

(iii) $(CH_3)_3C-Br$ on reaction with sodium methoxide $(Na^{+-}OCH_3)$ gives alkene as the main product and not an ether.

(ALL INDIA 2015)

22. Name the reagents which are used in the following conversions:

(i) A primary alcohol to an aldehyde

(ii) Butan -2 - one to butan-2-ol

(iii)Phenol to 2, 4, 6-tribromophenol

[DELHI 2016]

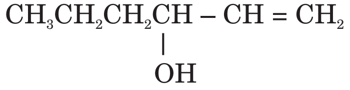
23. Explain the following observations:

i. The boiling point of ethanol is higher than that of methoxymethane.

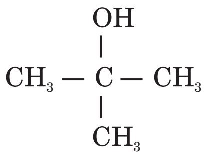
ii. Phenol is more acidic than ethanol.

iii. o- and p- nitrophenols are more acidic than phenol. **[DELHI 2017]**

Solutions

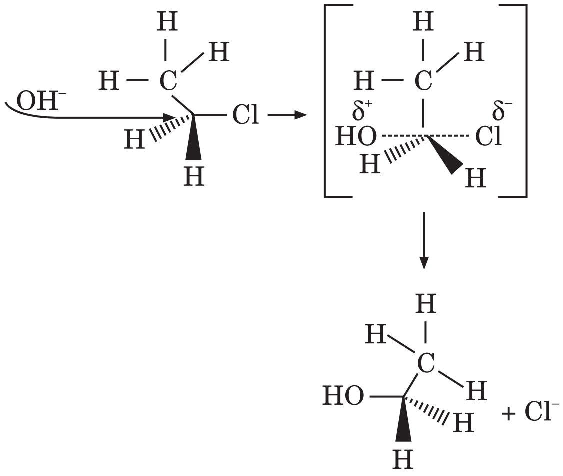
1.  **[1]**

$$CH_3CH_2CH_2\underset{\substack{|\\OH}}{CH}-CH=CH_2$$

2.  **[1]**

$$CH_3-\overset{\substack{OH\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_3$$

3. When C_2H_5Cl reacts with aq. KOH, substitution Nucleophilic bimolecular (S_N2) reaction takes place and ethanol is formed.



Ethanol

And inversion of configuration also takes place. **[1]**

4. o-nitrophenol is more volatile because of the presence of intra-molecular hydrogen bonding.

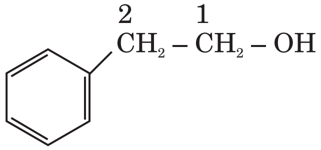
ortho nitrophenol has intra molecular H-bonding, and weak van-der-waal's forces exist between its molecules.

In case of para nitrophenol strong H-bonding exists between the molecules which makes separation of molecules tougher, i.e., molecules need more energy to be separated and hence more temperature.

Thus, the boiling point of p-nitrophenol increases in comparison to o-nitrophenol and consequently o-nitrophenol becomes more volatile. **[1]**

5. 2, 2-Dimethyl propan-1-ol **[1]**

6. 2-phenylethanol

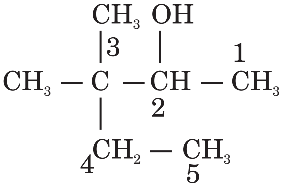


[1]

7. 2,5-Dimethylhexane -1,3-diol **[1]**

8. Hex-1-en-3-ol **[1]**

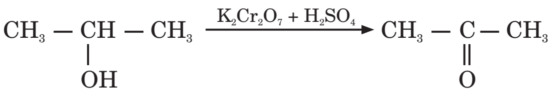
9.



$$\overset{1}{CH_3}\text{—}\overset{CH_3}{\underset{4CH_2-\underset{5}{CH_3}}{\overset{|3}{\underset{|}{C}}}}\text{—}\underset{2}{\overset{OH}{\overset{|}{CH}}}\text{—}CH_3$$

(3,3-dimethylpentan-2-ol) **[1]**

10. (i) Propan-2-ol to propanone:

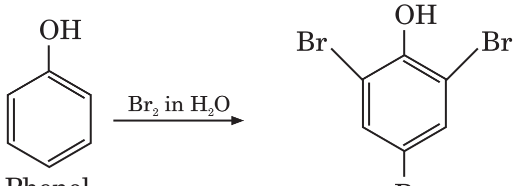


$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{K_2Cr_2O_7 + H_2SO_4} CH_3-\underset{O}{\underset{\|}{C}}-CH_3$$

Propane – 2 – ol Propanone

[1]

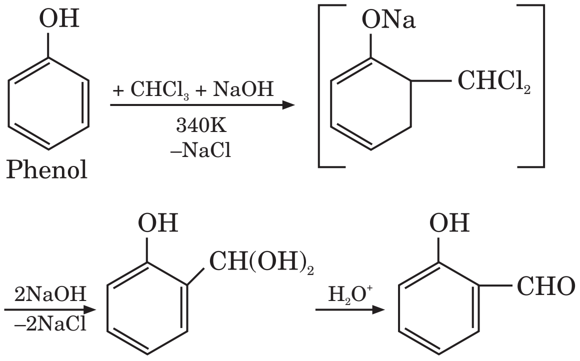
(ii) Phenol to 2, 4, 6-tribromophenol:



Phenol 2, 4, 6 – Tribromophenol

[1]

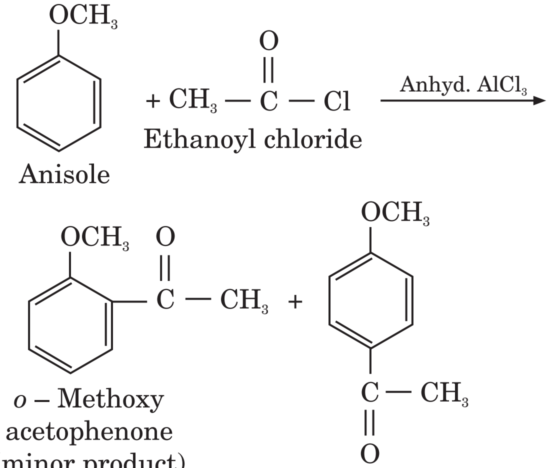
11. **1.** When phenol is treated with chloroform in presence of aqueous NaOH at 340 K followed by hydrolysis, it gives salicylaldehyde.



Salicyaldehyde

[1]

2. When anisole is treated with acetylchloride in presence of anhydrous $AlCl_3$, 2-methoxy acetophenone is formed.

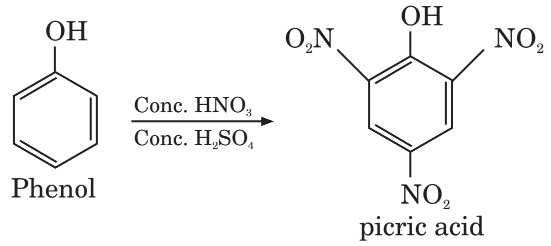


o – Methoxy acetophenone (minor product)

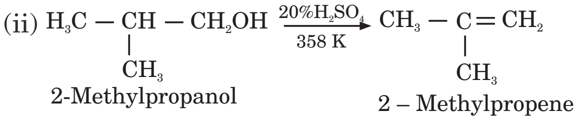
p – Methoxy acetophenone (major product)

[1]

12. (i)



[1]



(ii) $\underset{\text{2-Methylpropanol}}{H_3C - \underset{CH_3}{\underset{|}{CH}} - CH_2OH} \xrightarrow[358\text{ K}]{20\%H_2SO_4} \underset{\text{2 – Methylpropene}}{CH_3 - \underset{CH_3}{\underset{|}{C}} = CH_2}$

[1]

13. Step-I: protonation

$$CH_3 - CH_2 - \ddot{\underset{..}{O}}H \xrightarrow{H^{\oplus}} CH_3 - CH_2 - \overset{\oplus}{\underset{..}{O}}H_2 \quad [1]$$

Step-II: formation of carbocation

$$CH_3 - CH_2 - \overset{\oplus}{\underset{..}{O}}H_2 \rightarrow CH_3 - \overset{\oplus}{C}H_2 \text{ (carbocation)}$$

[½]

Step-III: deprotonation

$$CH_3 - \overset{\oplus}{C}H_2 \rightarrow CH_2 = CH_2 + H^+ \quad [½]$$

14. Step-I:

$$CH_3 - CH_2 - OH \xrightarrow{HBr} \underset{\text{(oxonium ion)}}{CH_3 - CH_2 - \overset{\oplus}{O}H_2}$$

[1]

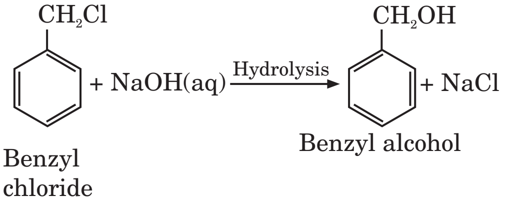
Step-II:

$$CH_3 - CH_2 - \overset{\oplus}{O}H_2 \longrightarrow CH_3\overset{\oplus}{C}H_2 + H_2O \quad [½]$$

Step-III:

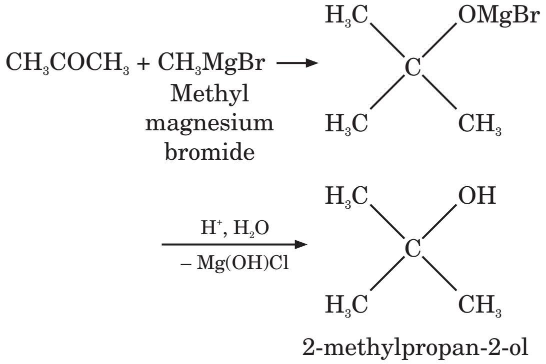
$$CH_3\overset{\oplus}{C}H_2 \xrightarrow{Br^-} CH_3 - CH_2 - Br \quad [½]$$

15. (i) Benzyl chloride to benzyl alcohol,



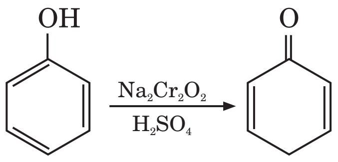
[1]

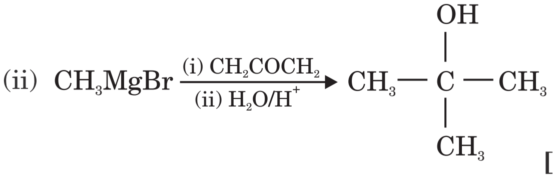
(ii) Methyl magnesium bromide to 2-methylpropan-2-ol.



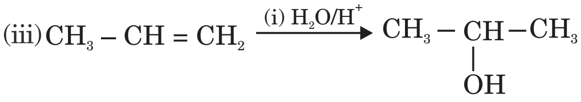
[1]

16. (i) **[1]**





(ii) $CH_3MgBr \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } CH_2COCH_2} CH_3 - \overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}} - CH_3$ **[1]**



(iii) $CH_3 - CH = CH_2 \xrightarrow{\text{(i) } H_2O/H^+} CH_3 - \underset{OH}{\underset{|}{CH}} - CH_3$

[1]

17. (i) $\underset{\text{Butan-1-ol}}{CH_3 - CH_2 - CH_2 - CH_2 - OH} \xrightarrow{CrO_3-H_2SO_4,\ [O]}$

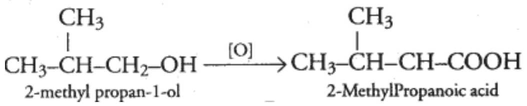
$$\underset{\text{Butanoic acid}}{CH_3 - CH_2 - CH_2 - COOH}$$

[1]

(ii) $\underset{\text{But-2-enol}}{CH_3 - CH = CH - CH_2 - OH} \xrightarrow{PCC,\ [O]}$

$$\underset{\text{Butanoic acid}}{CH_3 - CH = CH - CHO}$$

[1]



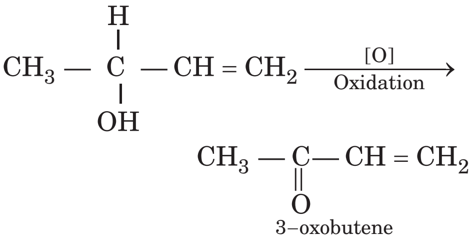
(iii) $\underset{\text{2-methyl propan-1-ol}}{CH_3 - \overset{CH_3}{\overset{|}{CH}} - CH_2 - OH} \xrightarrow{[O]} \underset{\text{2-MethylPropanoic acid}}{CH_3 - \overset{CH_3}{\overset{|}{CH}} - CH - COOH}$

[1]

18. (i) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{Oxidation}]{[O]}$

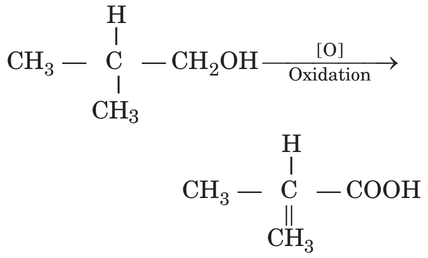
$$\underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

[1]



(ii) $CH_3 - \overset{H}{\overset{|}{\underset{OH}{\underset{|}{C}}}} - CH = CH_2 \xrightarrow[\text{Oxidation}]{[O]}$ **[1]**

$$\underset{\text{3–oxobutene}}{CH_3 - \underset{O}{\underset{\|}{C}} - CH = CH_2}$$

(iii) 

$$CH_3-\underset{CH_3}{\overset{H}{C}}-CH_2OH\xrightarrow[\text{Oxidation}]{[O]}$$

$$CH_3-\underset{\overset{\|}{CH_3}}{\overset{H}{C}}-COOH$$

[1]

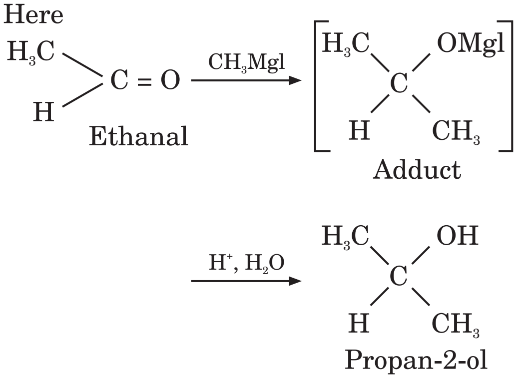
19. (i) $CH_3CH = CH_2 + HBr \xrightarrow{Peroxide}$ Propene

$$CH_3CH_2CH_2Br + KOH \xrightarrow{\Delta} CH_3CH_2CH_2OH$$

Propan-1-ol

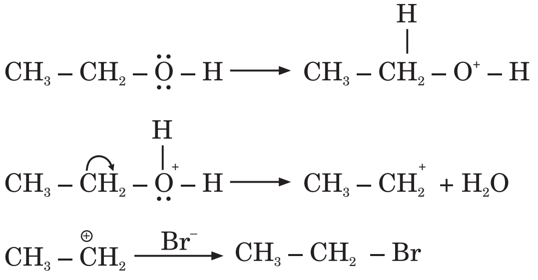
[1½]

(ii) Ethanal to propan-2-ol
Here



[1½]

20. (a) Mechanism of the reaction

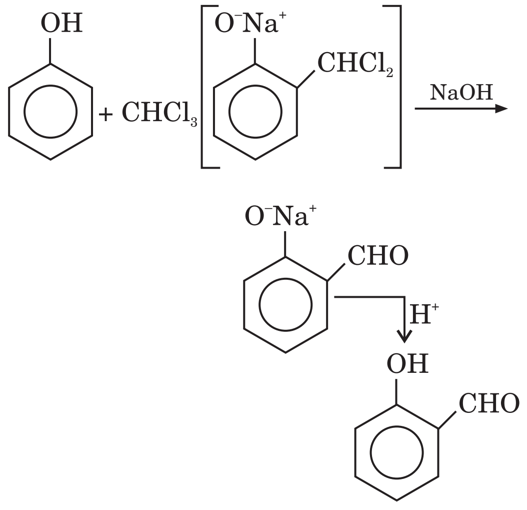


$$CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H \longrightarrow CH_3-CH_2-\overset{H}{O^+}-H$$

$$CH_3-CH_2-\overset{H}{\overset{+}{\ddot{O}}}-H \longrightarrow CH_3-\overset{+}{CH_2} + H_2O$$

$$CH_3-\overset{\oplus}{C}H_2 \xrightarrow{Br^-} CH_3-CH_2-Br$$

This is an S_N2 reaction mechanism. **[1½]**

(b) 

Salicylaldehyde

Reimer-Tiemann reaction

[1½]

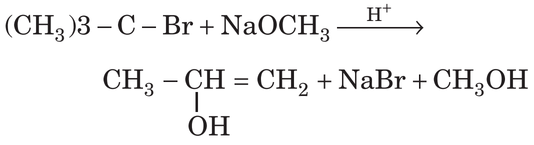
21. (i) NO_2 group is electron withdrawing group & methyl group is electron releasing group. Withdrawing group help in increasing acidic nature, whereas electron releasing group decreases acidic nature of phenol.

[1]

(ii) Due to sp^2 hybridized C and resonance in phenol to which –OH group is attached, where as in CH_3OH, C is sp^3 hybridized.

Bond length in $sp^3 > sp^2$ **[1]**

(iii) Because alkoxides are not only nucleophiles but strong bases as well. They react with 3° alkyl halides leading to **elimination reaction.**



$$(CH_3)3-C-Br + NaOCH_3 \xrightarrow{H^+} CH_3-\underset{OH}{CH} = CH_2 + NaBr + CH_3OH$$

[1]

22. **(i) PCC (Pyridinium chlorochromate)/** HCl, $KMnO_4$ **(any one)** **[1]**

(ii) $\boldsymbol{LiAlH_4}$**,** $\boldsymbol{NaBH_4}$ **(any one)** **[1]**

(iii) Aqueous $\boldsymbol{Br_2}$ **[1]**

23. (i) Hydrogen bonding in ethanol causes the boiling point of ethanol to be higher than that of methoxymethane. **[1]**

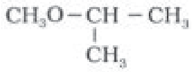
(ii) Phenol on releasing a proton forms phenoxide in which is resonance stabilized. So, phenol is more acidic than ethanol. **[1]**

(iii) NO^{-}_{2} group has -I effect or electron withdrawing inductive effect making it easier for the release of proton. **[1]**

Topic 2: Ethers

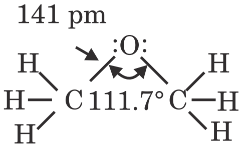
Summary

- They are represented by $R-0-R^{'}$ and have the general formula $C_nH_{2n+2}O$.
- **Ethers are classified into 2 categories:**
    - **Simple or symmetrical:** When the alkyl or aryl groups attached to the oxygen atom are the same. Example: $C_2H_5OC_2H_5$
    - **Mixed or unsymmetrical:** When the alkyl or aryl groups attached to the oxygen atom are different. Example: $C_2H_5OCH_3$
- **Common names and IUPAC names of some ethers are given below:**

Compound	**Common name**	**IUPAC name**
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OCH_3$	Diethyl ether	Ethoxyethane
$C_6H_5OCH_3$	Methylphenyl ether	Methoxybenzene
 $CH_3O-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$	Methyl isopropyl ether	2-Methoxypropane

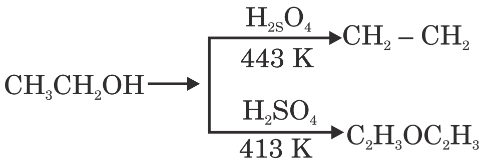
- **Structure of ether:**

The four electron pairs in ether, i.e. the two bond pairs and the two lone pairs of electrons are arranged approximately in tetrahedral arrangement as shown below:



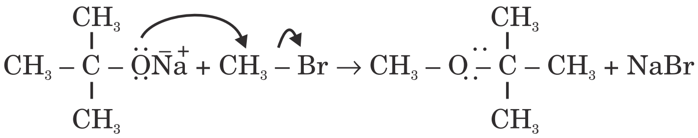
Methoxymethane

- **Preparation of Ethers:**
    - **By dehydration of alcohols:** In the presence of protic acid. The product which is formed in the reaction depends on the conditions of the reaction.



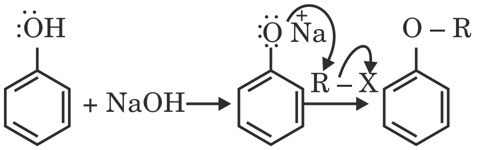
- **Williamson synthesis:** In this method alkyl halide reacts with sodium alkoxide.

$$R - X + R - \ddot{\underset{\cdot\cdot}{O}}\ Na \longrightarrow R - \ddot{\underset{\cdot\cdot}{O}} - R + Na\,X$$



$$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - \ddot{\underset{\cdot\cdot}{O}}\overset{-}{\ }\overset{+}{Na} + CH_3 - Br \rightarrow CH_3 - \ddot{\underset{\cdot\cdot}{O}} - \underset{CH_3}{\overset{CH_3}{C}} - CH_3 + NaBr$$

Phenols can also be converted to ethers using this method of preparation.

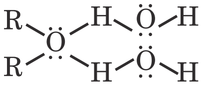


➢ Physical properties of ethers:

- The boiling point of ethers is lower than alcohols but is comparable to those of alkanes of the comparable molecular masses. The example is given below:

Formula	$CH_3(CH_2)_3CH_3$ n-Pentane	C_2H_5-O-C_2H_5 Ethoxyethane	$CH_3(CH_2)_3$-OH Butan-1-ol
b.p./K	309.1	307.6	390

- The solubility of ethers in water is comparable to those of alcohols of the same molecular masses and this is because of the ability of the oxygen of the ether to form hydrogen bonds with water molecules.

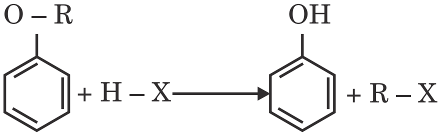


➢ Chemical reactions of Ethers:

1. **Cleavage of C-O bond:** This cleavage takes place under severe conditions using excess of hydrogen halides.

$$R–O–R + HX \longrightarrow RX + R–OH$$

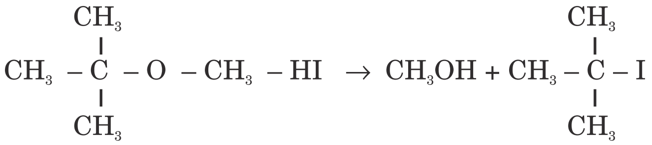
$$R–OH + HX \longrightarrow R–X + H_2O$$



$$R–O–R' + HX \longrightarrow R–X + R'–OH$$

If one of the alkyl group is tertiary group then the halide formed will also be a tertiary halide.

Example:



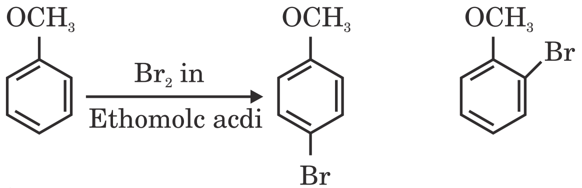
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3-HI \rightarrow CH_3OH+CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I$$

The order of reactivity of hydrogen halides is given below:

HI > HBr > HCl

2. **Electrophilic substitution:**

(i) **Halogenation:**

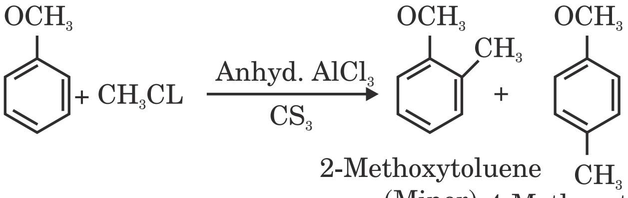


Anisole

p-Bromoanisole (Major)

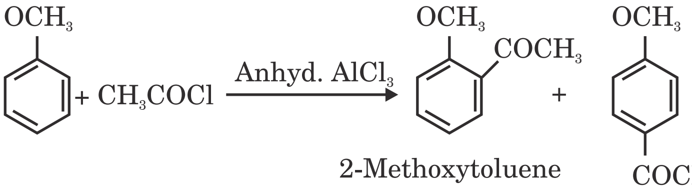
o-Bromoanisole (Minor)

(ii) **Friedel – Crafts reaction:**



2-Methoxytoluene (Minor)

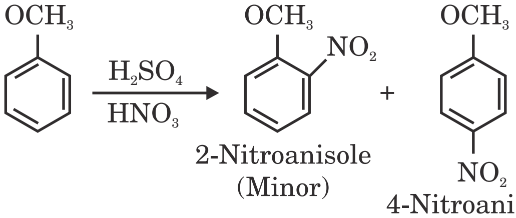
4-Methoxytoluene (Major)



2-Methoxytoluene (Minor)

4-Methoxytoluene (Major)

(iii) **Nitration:**



2-Nitroanisole (Minor)

4-Nitroanisole (Major)

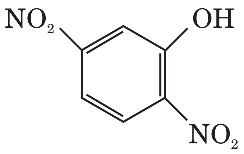
PREVIOUS YEARS'

EXAMINATION QUESTIONS

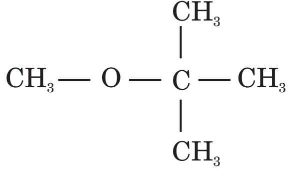
TOPIC 2

1 Mark Questions

1. Write the IUPAC name of the given compound: **[DELHI 2015]**



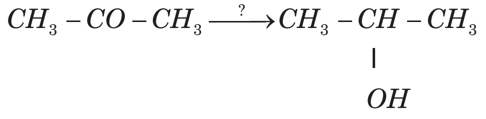
2. Write the IUPAC name of the following compound: **[DELHI 2016]**



$$CH_3-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

2 Mark Questions

3. **Write the equations involved in the following reactions:**
   (i) Reimer – Tiemann reaction
   (ii) Williamson synthesis **[ALL INDIA 2014]**
4. **Name the reagents used in the following reactions:**
   (i)



$$CH_3-CO-CH_3 \xrightarrow{?} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

   (ii) $C_6H_5-CH_2-CH_3 \xrightarrow{?} C_6H_5-COO^-K^+$

[DELHI 2015]

5. (a) Arrange the following compounds in the increasing order of their strength: p-cresol, o-nitrophenol, phenol
   (b) Write the mechanism (using curved arrow notation) of the following reaction:

$$CH_2=CH_2 \xrightarrow{H_3O^+} CH_2-CH_2^+ + H_2O$$

[ALL INDIA 2017]

OR

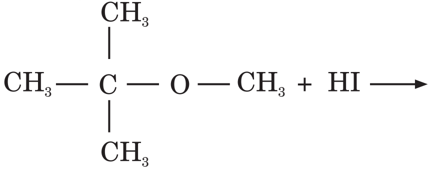
Write the structures of the products when Butan-2-ol reacts with the following:
(a) CrO_3
(b) $SoCl_2$

6. How do you convert the following:
   (a) Ethanol to Propanone **[ALL INDIA 2018]**
7. Illustrate the following reactions giving a chemical equation for each:
   (i) Kolbe's reaction.
   (ii) Williamson synthesis.

3 Mark Questions

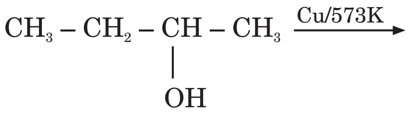
8. **Write the final product(s) in each of the following reactions:**

(a)



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_3 + HI \longrightarrow$$

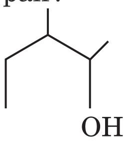
(b)



$$CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{Cu/573K}$$

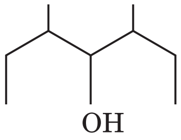
(c) $C_6H_5-OH \xrightarrow[(ii)\quad H^+]{(i)\ CHCl_3 + aq.NaOH}$ **[ALL INDIA 2016]**

9. (a) Identify the chiral molecule in the following pair?



(i)

and



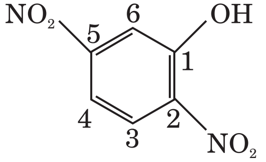
(ii)

   (b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.
   (c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH.

[ALL INDIA 2018]

Solutions

1. **2, 5-Dinitrophenol**

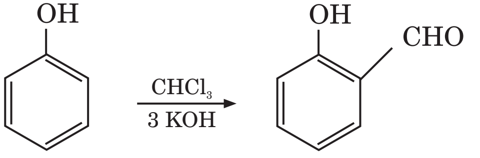


[1]

2. **2-methoxy-2-methyl Propane** **[1]**

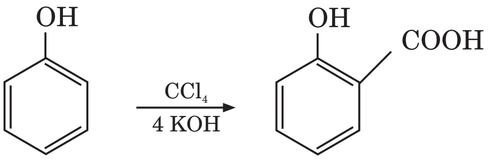
3. (i)

*** Reimer Tiemann Formylation**



(Salicylaldehyde) **[1]**

*** Reimer-Tiemann carboxylation**



(Salicylic acid)

(ii) Williamson's synthesis

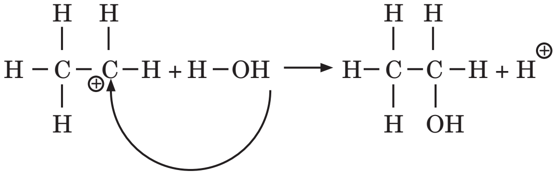
$$C_2H_5-Br+C_2H_5O^-Na^+ \xrightarrow{heat} C_2H_5-O-C_2H_5+\ NaBr$$ **[1]**

4. (i) Sodium borohydride$\left(NaBH_4\right)$ **[1]**

(ii) Alkaline potassium permanganate $\left(KMnO_4+KOH\right)$ **[1]**

5. (a) Below is the increasing order of the compounds according to their strength:
P-Cresol < Phenol < o-Nitrophenol. **[1]**

(b)

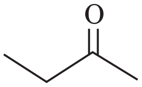


$$H-\underset{H}{\overset{H}{C}}-\overset{H}{\overset{\oplus}{C}}-H+H-OH \longrightarrow H-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H+H^{\oplus}$$

[1]

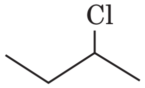
OR

(a) **[1]**



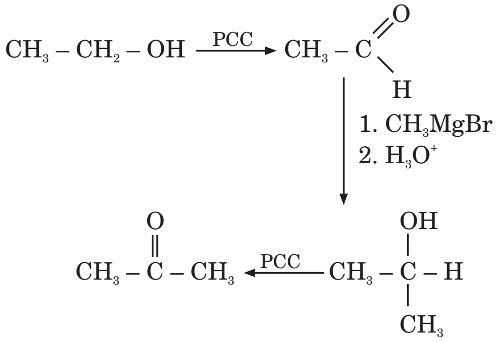
Butan-2-one

(b) **[1]**

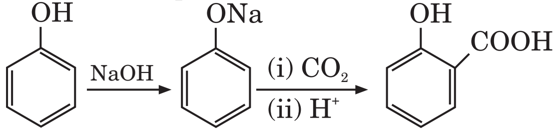


2-chloro-butane

6. **[1]**



7. **(i)** Kolbe's reaction: In this reaction, phenol reacts with sodium hydroxide to form sodium phenoxide. Sodium phenoxide formed reacts with carbon dioxide to form ortho hydroxy benzoic acid or salicylic acid as the main product.



2-Hydroxybenzoic acid
(Salicylic acid)

[1]

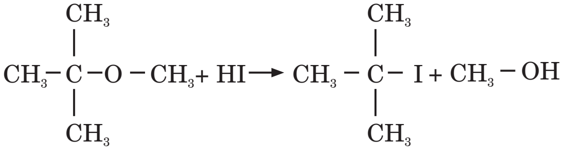
(ii) Williamson synthesis:
It is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide reacts with sodium alkoxide to form ether.

$$R-X+R'-\ddot{\underset{\cdot\cdot}{O}}Na \longrightarrow R-\ddot{\underset{\cdot\cdot}{O}}-R'+NaX$$

[1]

8. The final products in each reaction will be:

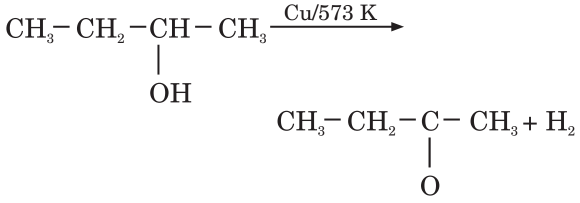
(a)



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3+HI \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I+CH_3-OH$$

[1]

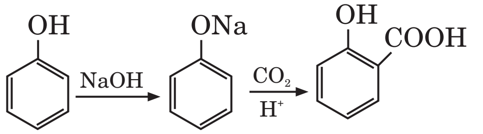
(b)



$$CH_3-CH_2-\underset{OH}{CH}-CH_3 \xrightarrow{Cu/573\ K} CH_3-CH_2-\underset{O}{C}-CH_3+H_2$$

[1]

(c)

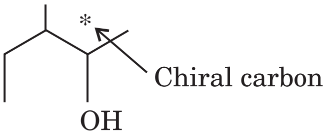


Phenol

2-Hydroxybenzoic acid

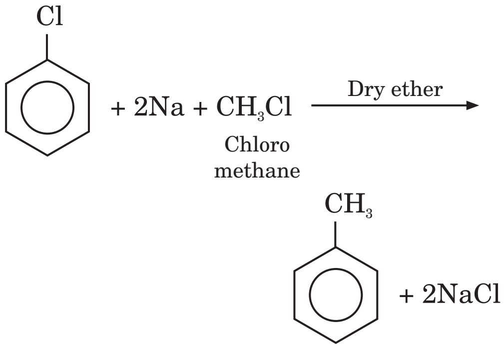
[1]

9. (a)



[1]

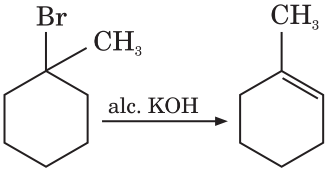
(b)



Toluene

[1]

(c)



[1]

Smart Notes ....

CHAPTER 12

Aldehydes, Ketones & Carboxylic Acids

Chapter Analysis with respect to Last 3 Years' Board Exams

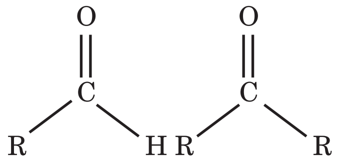
List of Topics	**2016**		**2017**		**2018**	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Aldehydes and Ketones: Nomenclature, nature of carbonyl group			(1, 1 mark)		(3,3 marks)	(3,3 marks)
Methods of preparation, physical and chemical properties						
Mechanism of nucleophillic addition, reactivity of alpha hydrogen in aldehydes: uses		(3 marks)		(5 marks)		
Carboxylic Acids: Nomenclature, acidic nature,		(2 marks)				

Topic 1: Aldehydes and ketones

Summary

They are the organic compounds containing carbon-oxygen double bond. (> C = O)

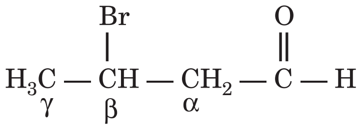
- The carbonyl group is bonded with a carbon and hydrogen in aldehydes and it is bonded to two carbon atoms in ketones.



Aldehyde Ketone

Nomenclature

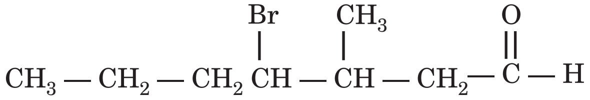
- **Common Names**
  - ➢ Instead of IUPAC names, common names are used for aldehydes and ketones.
  - ➢ The location of the substituent in the carbon chain is indicated by Greek letters α, β, γ etc, α-carbon being the one directly linked to the aldehyde group, carbon the next, and so on.



$$\underset{\gamma}{H_3C} - \underset{\beta}{\overset{\overset{Br}{|}}{CH}} - \underset{\alpha}{CH_2} - \overset{\overset{O}{\|}}{C} - H$$

β-Bromobutyraldehyde

- **IUPAC Names**
  - ➢ They are derived from IUPAC names of corresponding alkanes, by replacing ending e with –al in aldehydes and –one in ketones.
  - ➢ Longest carbon chain is numbered starting from the carbon of the aldehyde group while in case of ketones the numbering begins from the end nearer to the carbonyl group.



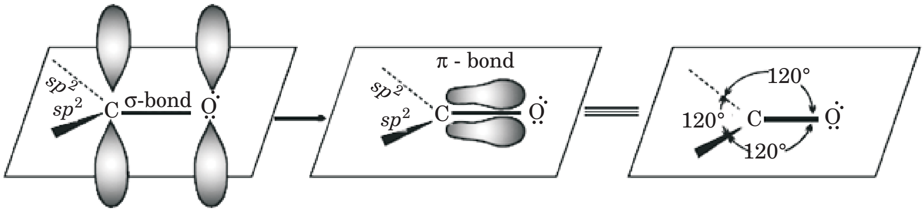
$$CH_3 - CH_2 - CH_2\,\overset{\overset{Br}{|}}{CH} - \overset{\overset{CH_3}{|}}{CH} - CH_2 - \overset{\overset{O}{\|}}{C} - H$$

4-Bromo-3-methylheptanal

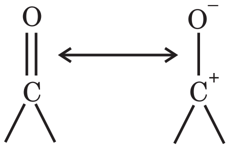
Structure of the Carbonyl Group

- The carbonyl carbon atom forms three sigma bonds and a π bond with oxygen and is sp^3 hybridized.

- The angles between the bonds is 120° as shown below

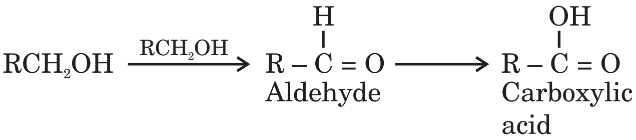


- As oxygen is more electronegative than oxygen, the carbon-oxygen double bond is polarized.



Preparation of Aldehydes and Ketones

- **Oxidation of alcohols**
- By oxidation of primary and secondary alcohols, aldehydes and ketones are prepared.

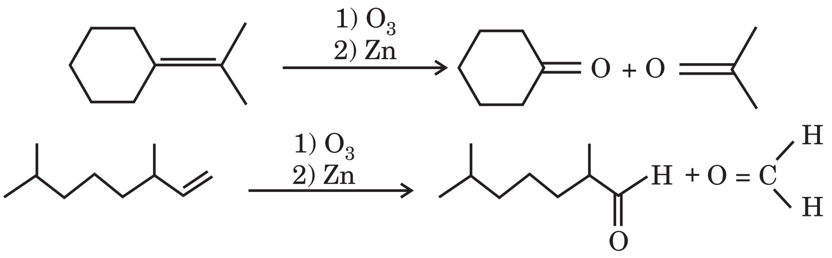


$$RCH_2OH \xrightarrow{RCH_2OH} \underset{\text{Aldehyde}}{R-\overset{H}{\overset{|}{C}}=O} \longrightarrow \underset{\text{Carboxylic acid}}{R-\overset{OH}{\overset{|}{C}}=O}$$

- Secondary alcohols are oxidized in presence of CrO^3 to ketones.
- **Dehydrogenation of alcohols**

$$\underset{1°\ \text{Alcohol}}{R-CH_2-OH} \xrightarrow[573K]{Cu} \underset{\text{Aldehyde}}{RCHO + H_2}$$

- **Using hydrocarbons**
    - ➢ Using ozonolysis of alkenes



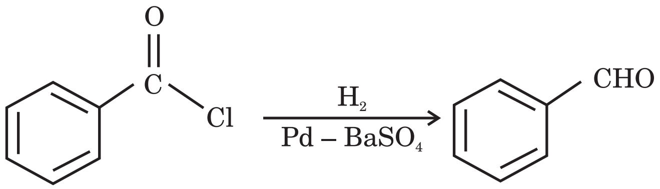
- ➢ By hydration of alkynes

Addition of water to ethyne in the presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde

Preparation of Alhehydes

- **Rosenmund Reaction:**

Acid chloride is hydrogenated in presence of a catalyst (Palladium on Barium Sulphate)



Benzoyl chloride Benzaldehyde

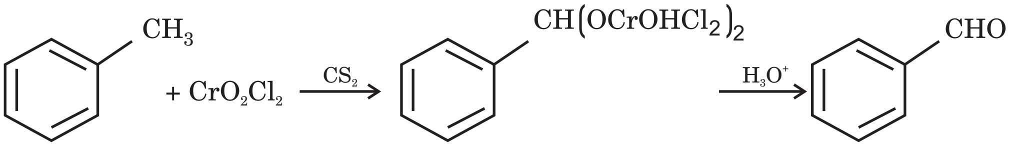
- **Stephen Reaction:**

Nitrites are reduced to imine which on hydrolysis gives aldehyde.

$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3\overset{+}{O}} RCHO$$

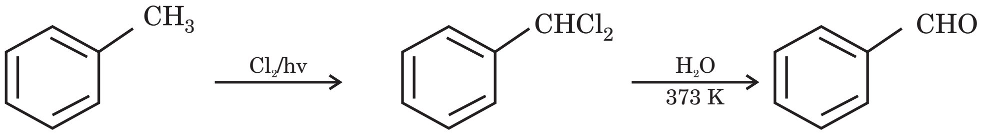
- **From hydrocarbons**
  - By oxidation of methylbenzene

Etard Reaction:



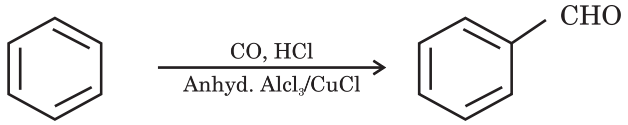
Toluene Chromium complex Benzaldehyde

By side chain chlorination followed by hydrolysis



Toluene Benzal chloride Benzaldehyde

Gatterman-Koch Reaction:

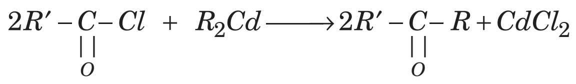


Benzal chloride Benzaldehyde

Preparation of Ketones

- **Using acyl chlorides**

$$2R - Mg - X \ + \ CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$

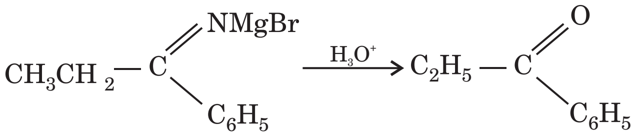


$$2R'-\underset{\underset{O}{||}}{C}-Cl + R_2Cd \longrightarrow 2R'-\underset{\underset{O}{||}}{C}-R + CdCl_2$$

- **Using nitriles**

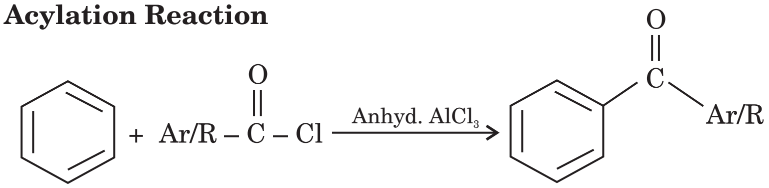
When nitriles are treated with Grignard reagent followed by hydrolysis, it gives ketones.

$CH_3 — CH_2 — C \equiv N + C_6H_5MgBr \xrightarrow{\text{ether}}$



Propiophenone
(1-Phenylpropanone)

- **Acylation Reaction**

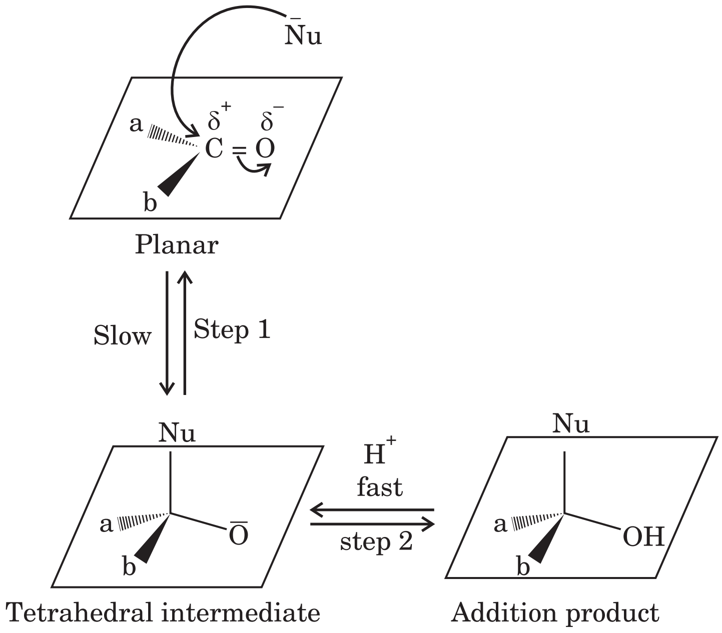


Physical Properties

- A large amount of aldehydes are liquids at room temperature.
- As aldehydes and ketones have hydrogen bonding capacity, they are soluble in water(upto 4 carbon atoms)
- Most of them have high boiling point when compared to hydrocarbons and higher than those of alcohols.

Chemical Properties

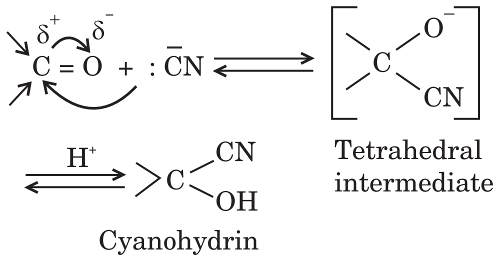
Nucleophilic Addition Reactions



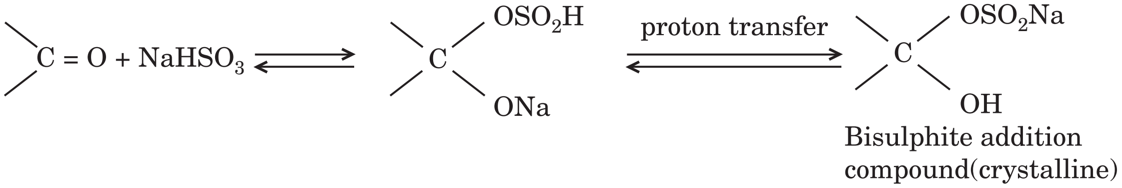
- **Addition of hydrogen cyanide:**

Cyanohydrins are obtained when aldehydes and ketones are treated with

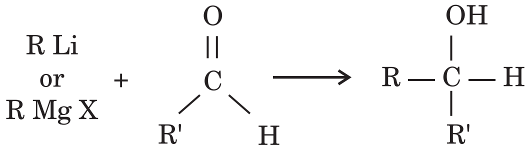
$$HCN + OH^- \rightleftharpoons :\bar{C}N + H_2O$$



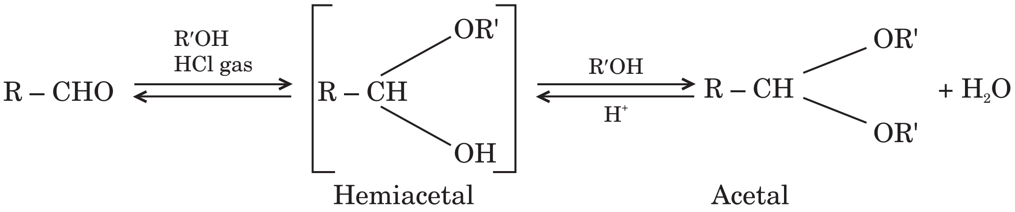
- **Addition of sodium hydrogensulphite**



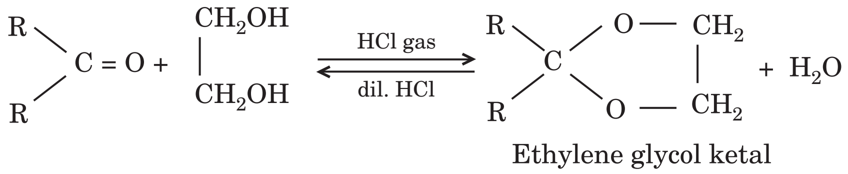
- **Addition of Grignard Reagent**



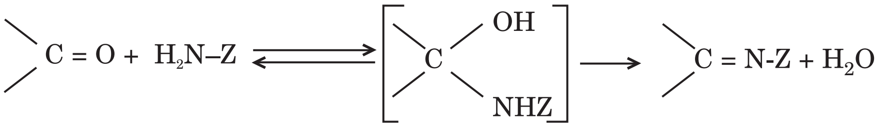
- **Addition of alcohols**



Ketones don't react with monohydric alcohols but react with dihydric alcohols to give ketals.



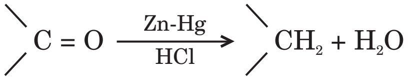
- **Addition of ammonia**



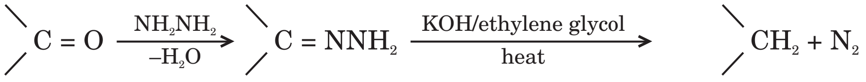
Reduction Reactions

- **Clemmensen Reduction or Wolf Kishner Reduction:**

The carbonyl group is reduced to CH_2 group as shown below



(Clemmensen reduction)



(wolff-Kishner reduction)

- **Reduction to alcohols**

In presence of $NaBH_4$, a primary alcohol is obtained while in presence of $LiAIH_4$, a secondary alcohol is obtained.

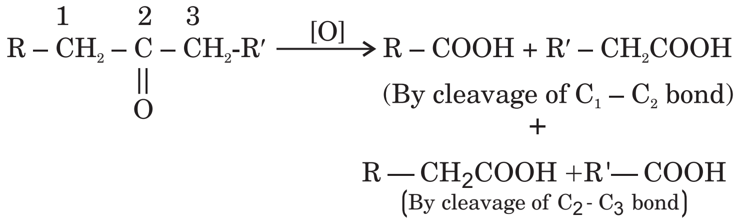
$$R-CHO+2[H]\xrightarrow{LiAlH_4}R-CH_2-OH$$

Oxidation

- On oxidation, aldehydes result in carboxylic acids on treatment with nitric acid, and mild oxidizing agents like Tollen's reagent and Fehling's reagent.

$$R-CHO\xrightarrow{[O]}R-COOH$$

- Ketones are oxidized by strong oxidizing agents at high temperatures which involves the cleavage of carbon-carbon bond.



$$R-\overset{1}{CH_2}-\underset{\underset{O}{\|}}{\overset{2}{C}}-\overset{3}{CH_2}\text{-}R' \xrightarrow{[O]} R-COOH+R'-CH_2COOH$$

(By cleavage of $C_1 - C_2$ bond)

+

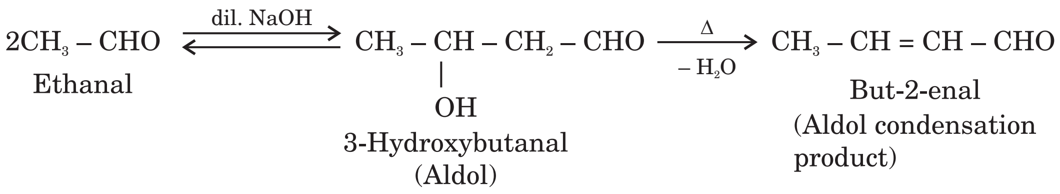
$R-CH_2COOH + R'-COOH$

(By cleavage of $C_2 - C_3$ bond)

Reactions due to α hydrogen

- Aldol Condensation

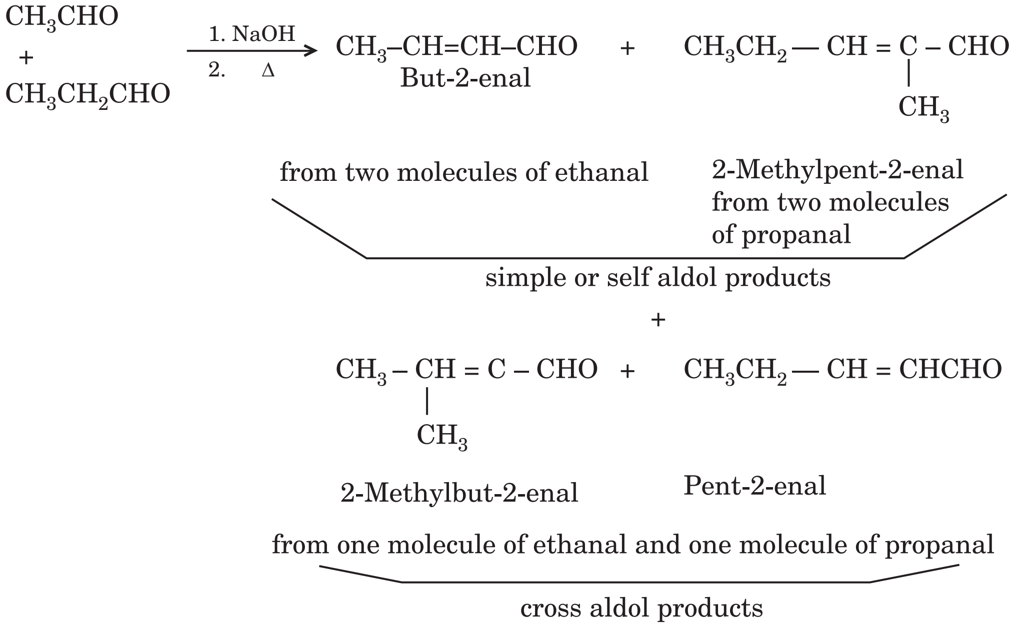
β hydroxyl aldehydes or β hydroxyl ketones are obtained when Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst.



$$\underset{\text{Ethanal}}{2CH_3-CHO} \xrightleftharpoons{\text{dil. NaOH}} \underset{\substack{\text{3-Hydroxybutanal}\\\text{(Aldol)}}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO} \xrightarrow[-H_2O]{\Delta} \underset{\substack{\text{But-2-enal}\\\text{(Aldol condensation product)}}}{CH_3-CH=CH-CHO}$$

- **Cross Aldol Condensation**

  When two different aldehydes or/and ketones undergo aldol condensation, it is known as cross aldol condensation.



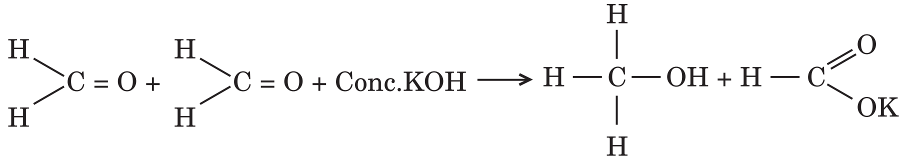
$$\begin{matrix}CH_3CHO\\+\\CH_3CH_2CHO\end{matrix}\xrightarrow[2.\ \Delta]{1.\ NaOH}\underbrace{\underbrace{\underset{\text{But-2-enal}}{CH_3-CH=CH-CHO}}_{\text{from two molecules of ethanal}}+\underbrace{CH_3CH_2-CH=\underset{\substack{|\\CH_3}}{C}-CHO}_{\text{2-Methylpent-2-enal from two molecules of propanal}}}_{\text{simple or self aldol products}}$$

$$+$$

$$\underbrace{\underbrace{CH_3-CH=\underset{\substack{|\\CH_3}}{C}-CHO}_{\text{2-Methylbut-2-enal}}+\underbrace{CH_3CH_2-CH=CHCHO}_{\text{Pent-2-enal}}}_{\substack{\text{from one molecule of ethanal and one molecule of propanal}\\\text{cross aldol products}}}$$

Other Reactions

- **Cannizzaro Reaction**:
  In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.

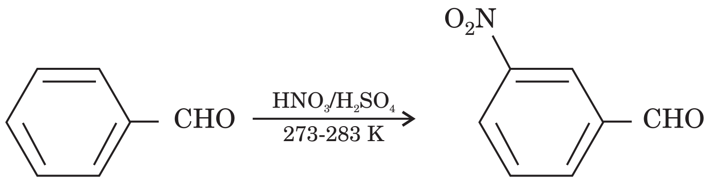


$$2\,HCHO + \text{Conc.KOH} \longrightarrow \underset{\text{Methanol}}{H-\overset{\substack{H\\|}}{\underset{\substack{|\\H}}{C}}-OH} + \underset{\text{Potassium formate}}{H-C\begin{matrix}\nearrow O\\\searrow OK\end{matrix}}$$

Methanol Potassium formate

- **Electrophilic Substitution**

  Aromatic aldehydes and ketones undergo this reaction.



Benzaldehyde m-Nitrobenzaldehyde

Uses of Aldehydes and Ketones

- Formalin solution (Formaldehyde) is used in preserving biological specimens and to prepare polymer products.
- Many aldehydes and ketones have a pleasant smell and flavor.
- Acetaldehyde is used as a starting material to manufacture acetic acid, polymers and drugs.

PREVIOUS YEARS’

EXAMINATION QUESTIONS

TOPIC 1

1 Mark Questions

1. Draw the structure of 4-chloropentan-2-one. **[DELHI 2011]**

2. Draw the structure of 3-methylbutanal. **[DELHI 2011]**

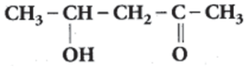
3. Arrange the following compounds in an increasing order of their reactivity in nucleophilic addition reactions: ethanol, propanal, propanone, butanone. **[All INDIA 2012]**

4. Write the structure of 3-methyl butanal. **[DELHI 2013]**

5. Write the structure of 4-chloropentan-2-one. **[DELHI 2013]**

6. Write the structure of p-Methylbenzaldehyde molecule. **[DELHI 2013]**

7. Write the IUPAC name of the compound. **[DELHI 2014]**



$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$

8. Write the structural formula of 1-phenylpentan-1-one. **[DELHI 2017]**

9. Draw the structural formula of 1-phenylpropan-1-one molecule.

2 Marks Questions

10. Write the reagents used in the following reactions:

(i) $C_6H_5-CO-CH_3 \xrightarrow{?} C_6H_5-CH_2-CH_3$

(ii) $CH_3-COOH \xrightarrow{?} CH_3-COCl$

OR

Arrange the following compounds in increasing order of their property as indicated:

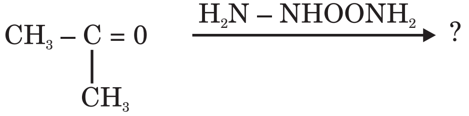
(i) CH_3CHO, C_6H_5CHO, $HCHO$ (Reactivity towards nucleophilic addition reaction)

(ii) 2,4-dinitrobenzoic acid, 4-methoxybenzoic acid, 4-nitrobenzoic acid (Acidic character) **[All INDIA 2015]**

3 Marks Questions

11. Predict the products of the following reactions:

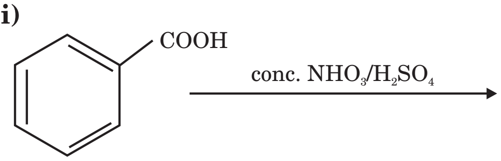
(i)



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=0 \xrightarrow{H_2N-NHOONH_2} ?$

(ii) $C_6H_5-CH_2-CH_3 \xrightarrow[\text{(b) } H^+]{\text{(a) } KMnO_4/KOH} ?$

(iii)



[All INDIA 2015]

12. (A), (B) and (C) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers (A) and (C) give positive Tollen’s test whereas isomer (B) does not give Tollen’s test but gives positive iodoform test. Isomers (A) and (B) on reduction with Zn (Hg)/conc. HCl give the same product (D).

(a) Write the structures of (A), (B), (C) and (D).

(b) Out of (A), (B) and (C) isomers, which one is least reactive towards addition of HCN? **[All INDIA 2018]**

5 Marks Questions

13. (a) Give chemical tests to distinguish between:

(i) Propanal and propanone

(ii)Benzaldehyde and acetophenone

(b) How would obtain:

(i) But-2-enal from ethanol.

(ii)Butanoic acid from butanol

(iii)Benzoic acid from ethylbenzene

OR

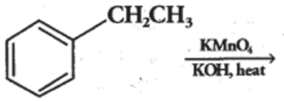
(a) Describe the following giving chemical equations

(i) Cannizzaro reaction

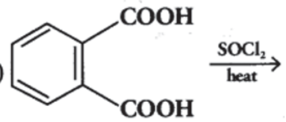
(ii)Decarboxylation

(b) Complete the following chemical equations:

(i)



(ii)



(iii)$C_5H_5CONH_2 \xrightarrow{H_2O\,/\,heat}$

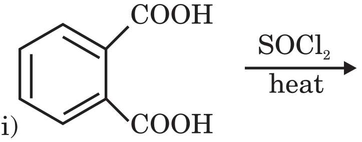
[DELHI 2011]

14. (a) Illustrate the following name reactions:
   (i) Cannizzaro's reaction
   (ii) Clemmensen reduction
(b) How would you obtain the following:
   (i) But-2-enal from ethanal
   (ii) Butanoic acid from butanol
   (iii) Benzoic acid from ethylbenzene

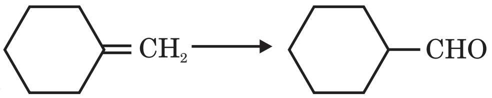
[All INDIA 2011]

OR

(a) Give chemical tests to distinguish between the following:
   (i) Benzoic acid and ethyl benzoate
   (ii) Benzaldehyde and acetophenone
(b) Complete each synthesis by giving missing reagents or products in the following:

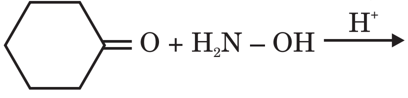
(i) 

(ii) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

(iii) 

[DELHI 2012]

15. (a) Write the products of the fallowing reactions:

(i) 

(ii) $2C_6H_5CHO + \text{Conc. } NaOH \longrightarrow$

(iii) $CH_3COOH \xrightarrow{Cl_2/P}$

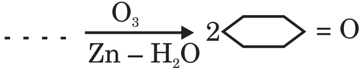
(b) Give simple chemical tests to distinguish between the following pairs of compounds:
   (i) Benzaldehyde and Benzoic acid
   (ii) Propanal and Propanone

OR

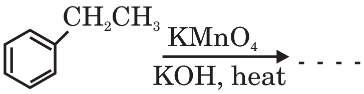
(a) Account for the following:
   (i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN.
   (ii) Carboxylic acid is a stronger acid than phenol.
(b) Write the chemical equations to illustrate the following name reactions:
   (i) Wolff-Kishner reduction
   (ii) Aldolcondesnation
   (iii) Cannizzaro reaction

[DELHI 2014]

16. (*a*) Complete the following reaction statements by giving the missing starting material, reagent or product as required:

(i) 

(ii) 

(iii) 

(*b*) Describe the following reactions:
   (*i*) Cannizaro reaction
   (*ii*) Cross aldol condensation

OR

(a) How would you account for the following?
   (i) Aldehydes are more reactive than ketones towards nucleophiles.
   (ii) The boiling points of aldehydes and ketones are lower than of the corresponding acids.
   (iii) The aldehydes and ketones undergo a number of addition reactions.
(*b*) Give chemical tests to distinguish between:
   (i) Acetaldehyde and benzaldehyde
   (ii) Propanone and propanol

17. (*a*) Explain the mechanism of a nucleophilic attack on the carbonyl group of an aldehyde or a ketone.

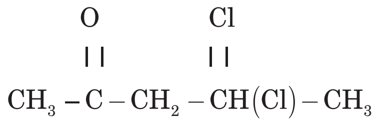
(*b*) An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolyse with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid also produced (B). On dehydration (C) gives but-1- ene. Write the equations for the reactions involved.

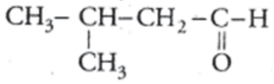
OR

(*a*) Given chemical tests to distinguish between the following pairs of compounds:
   (i) Ethanal and Propanal
   (ii) Phenol and Benzoic acid
(*b*) How will you bring about the following conversions?
   (i) Benzoic acid to benzaldehyde
   (ii) Ethanal to but-2-enal
   (iii) Propanone to propene

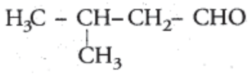
Give complete reaction in each case.

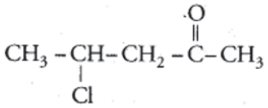
Solutions

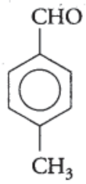
1. 
$CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{Cl}{\overset{||}{CH(Cl)}}-CH_3$ **[1]**

2. 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{||}{C}}-H$ **[1]**

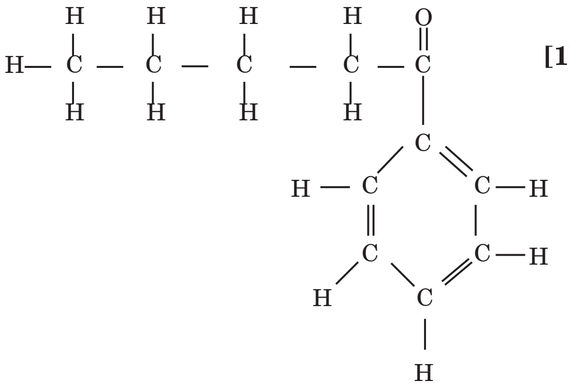
3. butanone<propanone<propanal< ethanol **[1]**

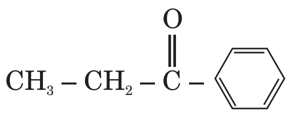
4. 
$H_3C-\underset{CH_3}{\underset{|}{CH}}-CH_2-CHO$ **[1]**

5. 
$CH_3-\underset{Cl}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{||}{C}}-CH_3$ **[1]**

6.  **[1]**

7. 4-hydroxypentan-2-one **[1]**

8.  **[1]**

9. 

1-pheny propan-1-one **[1]**

10. (i) $C_6H_5-CO-CH_3 \xrightarrow[\text{Clemensen's reaction/ Wolf Kishner reaction}]{Zn-Hg+HCl/N_2H_4+H_2O_2} C_6H_5-CH_2CH_3$

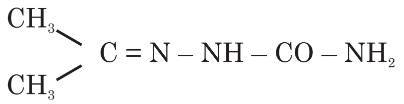
[1]

(ii) $CH_3-COOH \xrightarrow{K_2Cr_2O_7/HP} CH_3-COCl$ **[1]**

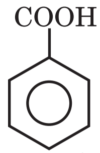
OR

. (i) $C_6H_5CHO < CH_3CHO < HCHO$ **[1]**

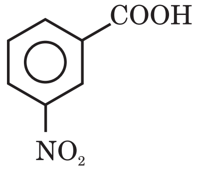
(ii) 4-methoxy benzoic acid < 4-nitrobenzoic acid < 2, 4-dinitro benzoic acid **[1]**

11. (i) 

Acetone semi carbazide **[1]**

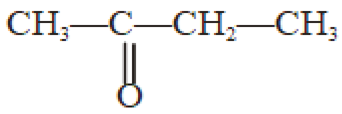
(ii) 

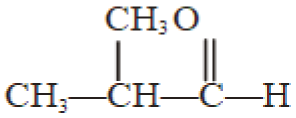
(Strong oxidation) **[1]**

(iii)  **[1]**

m-product is obtained due to deactivating nature of $-COOH$ group.

12. (a) ***A* is $CH_3CH_2CH_2CHO$** **[½]**

Ⓑ is 
$CH_3-\underset{O}{\underset{||}{C}}-CH_2-CH_3$

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

[½ + ½]

(d) $CH_3-CH_2-CH_2-CH_3$ **[½]**

(b) (B) will be least reactive as it contain ketone as functional group and ketones are less reactive than aldehyde towards nucleophilic addition reaction. **[1]**

13. (a) (i) Aldehydes respond to Fehling's test, but ketones do not.

Propanal being an aldehyde reduces Fehling's solution to a red-brown precipitate of Cu2O, but propanone being a ketone does notrespond to this test. **[1]**

$$CH_2CH_2CHO+2Cu^{2+}+5OH^- \longrightarrow CH_3CH_2COONa+Cu_2O\downarrow+3H_2O$$

[1]

(ii) Acetophenone on treatment with I_2^+NaOH undergoes iodoform test to give yellow ppt.

of iodoform that benzaldehyde does not. Methyl ketones are oxidized by sodium hypoiodite to give yellow ppt. of iodoform. Acetophenone being a methyl ketone responds to this test, but benzophenone does not

$$C_6H_5COCH_3 + 4NaOH + 3I_2 \longrightarrow C_6H_5COONa + CHI_3 \downarrow + 2H_2O + 3NaI$$

$$C_6H_5CHO \xrightarrow[NaOH+I_2]{} \text{No reaction}$$ **[1]**

(b) (i) $2CH_3CHO \xrightarrow[\text{(Aldol condensation)}]{\text{Dil. NaOH}}$

Ethanal

$$CH_3-CHOH-CH_2-CHO \xrightarrow[-H_2O]{\text{Heat}}$$

3-hydroxybutanal

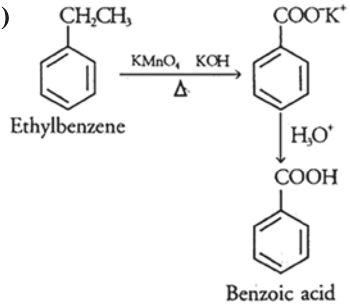
$$CH_3-CH=CH-CHO$$

But-2-enal

[1]

(ii) $CH_3CH_2CH_2CH_2OH \xrightarrow{alk.KMnO_4,\ dil.\ H_2SO_4} CH_3CH_2CH_2COOH + H_2O$

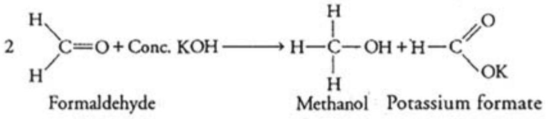
(iii)



[1]

OR

(a) (i) An aldehyde with no α-hydrogen atom undergoes self-reduction and oxidation in presence of conc. alkali to form alcohol and carboxylic acid salt. **[1]**

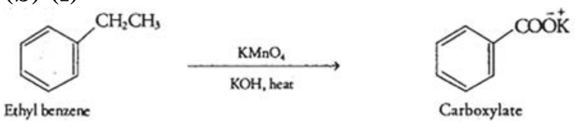


(ii) Sodium acetate undergoes decarboxylation (removal of CO_2) in presence of soda lime to give hydrocarbon.

$$CH_3COONa \xrightarrow{NaOH,\,CaO} CH_4 + Na_2CO_3$$

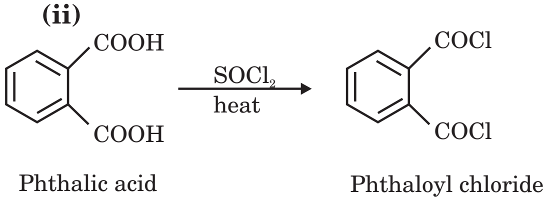
[1]

(b) (i)



[1]

(ii)



[1]

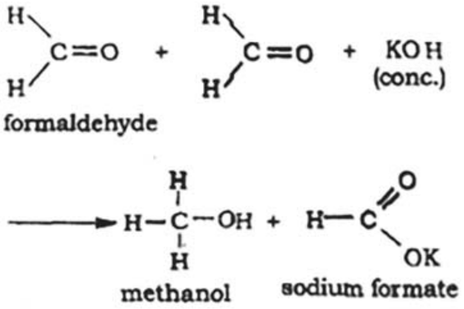
(iii) $C_6H_5CONH_2 \xrightarrow[heat]{H_3O^+} C_6H_5COOH$ **[1]**

Benzamide Benzoic acid

14.

(*a*)

(*i*) Cannizzaro reaction: Aldehydes which do not have an α-hydrogen atom, undergo self oxidation and reduction reaction on treatment with concentrated alkali **[1]**



(ii) Clemmensen reduction: The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc amalgam and concentrated HCl **[1]**

$$>C=O \xrightarrow[HCl]{Zn-Hg} >CH_2 + H_2O$$

(Clemmensen reduction)

(b)

(*i*) $2CH_3-CHO \xrightarrow{dil.NaOH} CH_3-CH(OH)-CH_2-CHO \xrightarrow{\Delta/-H_2O} CH_3-CH=CH-CHO$

[1]

(ii)

$$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow{CrO_3,H_2SO_4} CH_3-CH_2-CH_2-COOH$$

[1]

(*iii*)

$$C_6H_5-CH_2-CH_3 \xrightarrow{KMnO_4,KOH,H^+} C_6H_5-COOH$$

[1]

OR

(a)

(i) Benzoic acid and ethyl benzoate

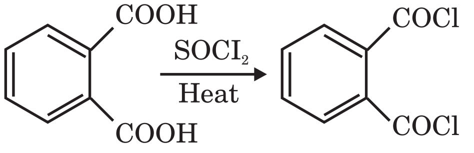
Sodium bicarbonate test- Warm each compound with $NaHCO_3$, Benzoic acid gives brisk effervescence of CO_2 gas whereas ethyl benzoate does not respond to this test. **[1]**

(ii) Benzaldehyde and Actophenone

Iodoform test- Warm each organic compound with I_2 and $NaOH$ solution. With Acetophenone $\left(C_6H_5COCH_3\right)$ Yellow precipitates of iodoform is formed, white Benzaldehyde does not respond to this test. **[1]**

(b)

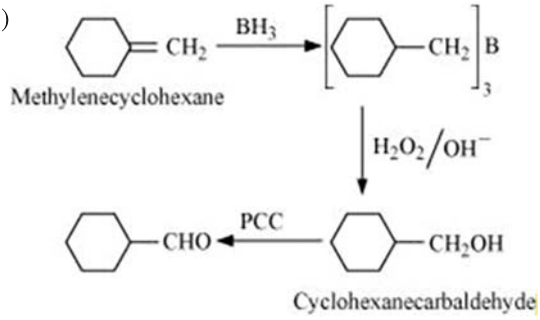
(i) **[1]**



Phathalic acid Phathaloyl chloide **[1]**

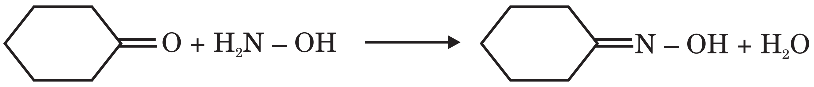
(ii) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2} C_6H_5CH = NHCONH_2$

(iii) **[1]**



15. (a)

(i)



Oxime **[1]**

(ii) $2C_6H_5CHO + NaOH(\text{conc.}) \longrightarrow C_6H_5COONa + C_6H_5CH_2OH$ **[1]**

Benzyl alcohol

(iii)

$$CH_3COOH \xrightarrow{Cl_2/\text{red P}} \underset{\displaystyle Cl}{\underset{|}{CH_2}} - COOH$$ **[1]**

α-chloroacetic acid

(b) (i) Benzoic acid reacts with $NaHCO_3$ to produce effervescence of CO_2 gas but benzaldehyde does not

$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2$ **[1]**

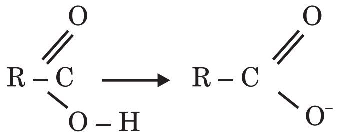
(*ii*) Propanone gives iodoform test but propanal does not because propanone has CH_3CO- group

$$CH_3COCH_3 + 3NaOH \xrightarrow{NaOH, I_2, \Delta} CH_3COONa + CHI_3$$ **[1]**

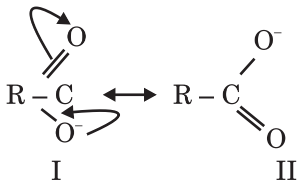
OR

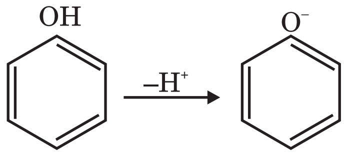
(a) (*i*) CH_3CHO is more reactive than CH_3COCH_3 because the reactivity of compound depends on the steric hindrance due to the groups present around the carbonyl group. More the steric hindrance, less will be the reactivity of the compound. Therefore, due to the presence of more electrophilic carbonyl carbon in CH_3CHO, it is more reactive than CH_3COCH_3. **[1]**

(*ii*) Carboxylic acid is stronger than phenol because of resonance, stabilization of more electronegative oxygen atom in carboxylate ion than carbon atom in phenoxide ion. **[1]**

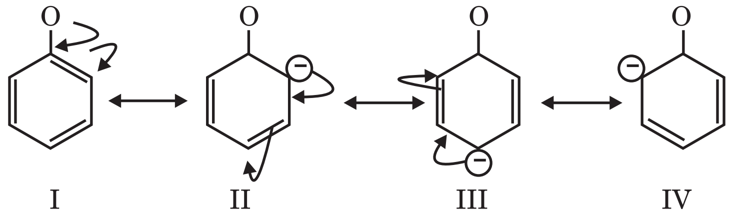


carboxylate ion



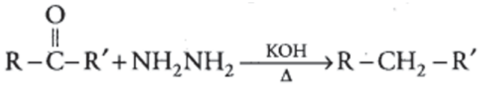


phenoxide ion



The, reason for greater stability of carboxylate ion is that it involves equivalent resonance in which negative charge is present on oxygen atom all the time whereas, in phenoxide ion, out of total four resonating structures, in three structures, negative charge is present on carbon atom which makes it less stable. **[1]**

(b) (i) Reduction of aldehyde or ketone to respective, hydrocarbon.

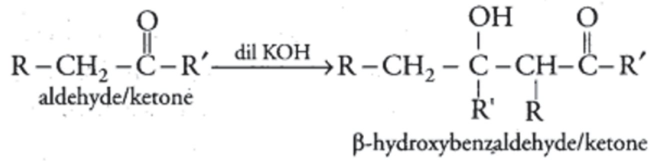


$$R-\overset{\overset{\large O}{\|}}{C}-R' + NH_2NH_2 \xrightarrow[\Delta]{KOH} R-CH_2-R'$$

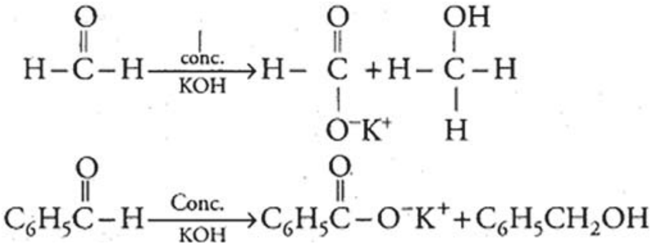
R = any alkyl group

R’ = -H or any alkyl group **[1]**

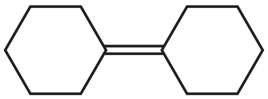
(ii) Formation of $\beta-$ hydroxyaldehyde or $\beta-$ hydroxy ketone from aldehydes and ketones respectively.



(iii) **[1]**



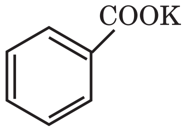
16. (a) (i) Cyclohexyldiene cyclohexane:



[1]

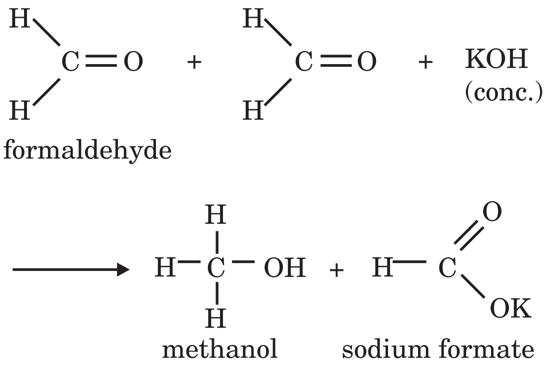
(ii) $\boldsymbol{BH_3, H_2O_2 / OH^-, PCC}$ **[1]**

(iii) Salt of benzoic acid:

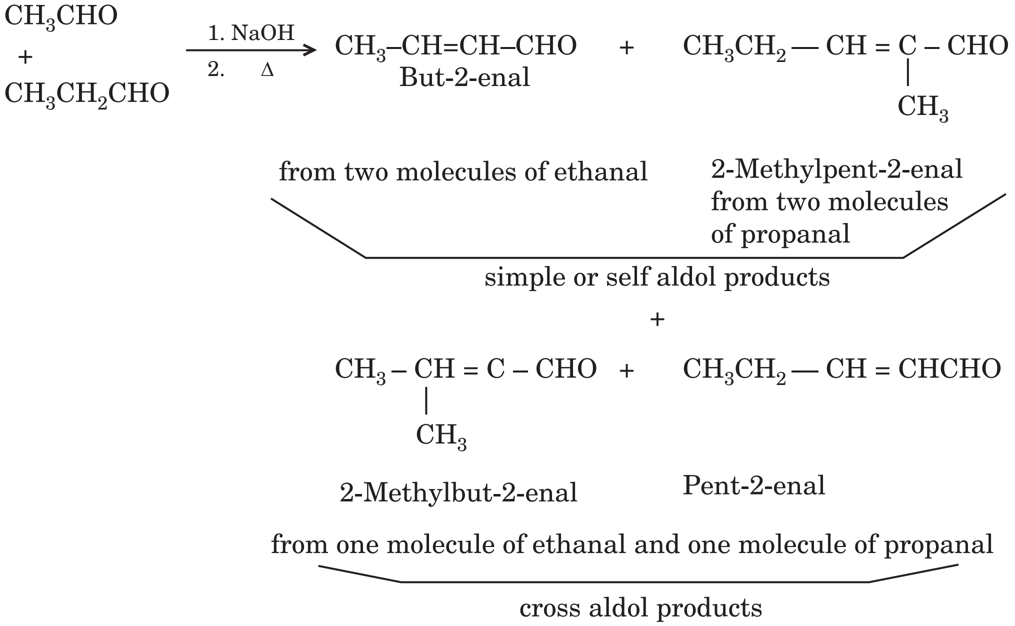


[1]

(b) (i) Cannizzaro reaction: Aldehydes which do not have α -hydrogen atom, undergo self-oxidation and reduction reaction on treatment with a concentrated alkali. **[1]**



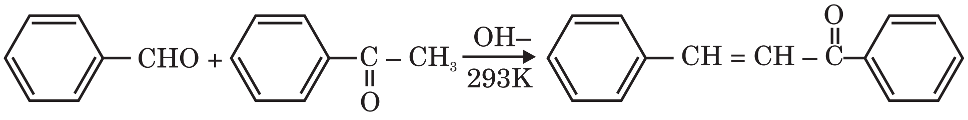
(ii) Cross aldol condensation: When aldol condensation is carried out between two different aldehydes and /or ketones, it is called Cross aldol condensation.



$$\begin{array}{c} CH_3CHO \\ + \\ CH_3CH_2CHO \end{array} \xrightarrow[2.\quad \Delta]{1.\ NaOH} \underbrace{\underset{\begin{array}{c}\text{But-2-enal}\\ \text{from two molecules of ethanal}\end{array}}{CH_3{-}CH{=}CH{-}CHO} + \underset{\begin{array}{c}\text{2-Methylpent-2-enal}\\ \text{from two molecules}\\ \text{of propanal}\end{array}}{CH_3CH_2{-}CH{=}\underset{\underset{CH_3}{|}}{C}{-}CHO}}_{\text{simple or self aldol products}}$$

$$+$$

$$\underbrace{\underset{\text{2-Methylbut-2-enal}}{CH_3{-}CH{=}\underset{\underset{CH_3}{|}}{C}{-}CHO} + \underset{\text{Pent-2-enal}}{CH_3CH_2{-}CH{=}CHCHO}}_{\begin{array}{c}\text{from one molecule of ethanal and one molecule of propanal}\\ \text{cross aldol products}\end{array}}$$



[1]

OR

(a)

(i) Two alkyl groups present in ketones reduce the positive charge on carbon atom of thec arbonyl group more effectively than in aldehydes, hence aldehydes are more reactive than ketones towards nucleophiles / or sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituents. **[1]**

(ii) Because of the absence of hydrogen bonding in aldehydes and ketones, their boiling points are lower than those of the corresponding acids and alcohols. **[1]**

(iii) Because of the presence of the sp^2 hybridised orbitals (or -bond) of carbonyl carbon, aldehydes and ketones undergo a number of addition reactions. **[1]**

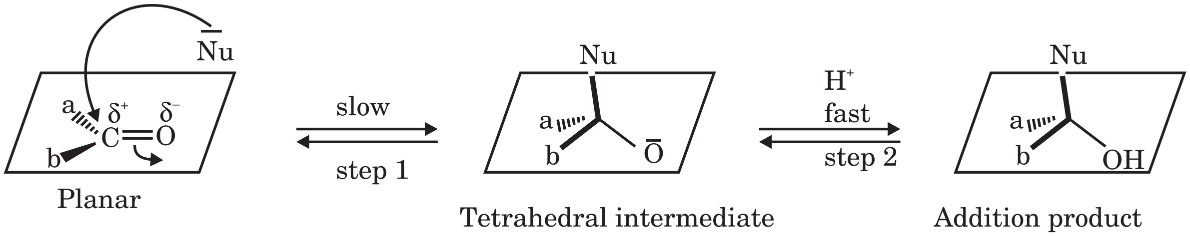
(b) (i) Acetaldehyde and benzaldehyde: Acetaldehyde gives yellow ppt of Iodoform(CHI_3) on addition of $NaOH\ /\ I_2$ whereas benzaldehyde does not give this test. **[1]**

(ii) Propanone and propanol: Propanone gives yellow ppt of Iodoform(CHI_3) on addition of $NaOH\ /\ I_2$ whereas propanol does not give this test. Or / Propanol gives brisk effervescence on adding a piece of Sodium metal whereas Propanone does not give this test. **[1]**

17. (a) Nucleophile attacks the electrophilic carbon atom of the polar carbonyl group of an aldehyde and a ketone from a direction approximately perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon. **[1]**

The hybridisation of carbon changes from sp^2 to sp^3 in this process, and a tetrahedral alkoxide intermediate is produced. **[1]**

This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is addition of Nu^- and H^+ across the carbon oxygen double bond.



[1]

(b) $$\underset{A\left(\text{butyl Butanoate}\right)}{CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3} \xrightarrow{dil.H_2SO_4} \underset{B\left(\text{Butanoic acid}\right)}{CH_3CH_2CH_2COOH} + \underset{C\left(\text{Butan-1-ol}\right)}{CH_3CH_2CH_2CH_2OH}$$

$\left(M.F. = C_8H_{16}O_2\right)$ **[1]**

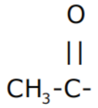
$$\underset{C}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{Oxidation}]{CrO_3\,/\,H_2SO_4} \underset{B}{CH_3CH_2CH_2COOH}$$

$$\underset{C}{CH_3CH_2CH_2CH_2OH} \xrightarrow[-H_2O,\text{Dehydration}]{conc.H_2SO_4} \underset{\text{But}-1-\text{ene}}{CH_3CH_2CH = CH_2}$$

[1]

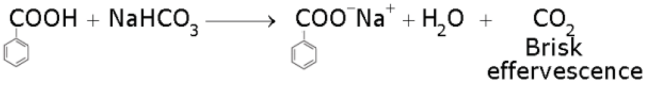
Or

(a) (i) Chemical test to distinguish between ethanal and propanal:

Ethanal $\left(CH_3CHO\right)$	Propanal $\left(CH_3CH_2CHO\right)$
Iodoform test: Ethanal gives yellow ppt. of iodoform with an alkaline solution of iodine sence it has the group  $CH_3-\overset{\overset{O}{\|}}{C}-$	Propanal does not give yellow ppt. of iodoform with an alkaline solution of iodine
$\underset{}{CH_3CHO + 3I_2 + 4NaOH \longrightarrow \underset{\left(Sodium\ formate\right)}{HCOONa} + \underset{Iodoform}{CHI_3} + 3NaI + 3H_2O}$	

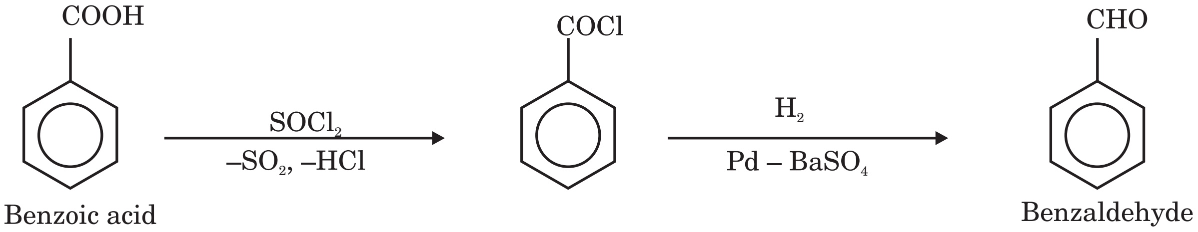
[1]

(ii) Chemical test to distinguish between phenol and benzoic acid

Phenol	**Benzoic acid**
On adding sodium bicarbonate to phenol, brisk effervescence of CO_2 is not produced.	On adding sodium bicarbonate to a benzoic acid, brisk effervescence of CO_2 is produced. 

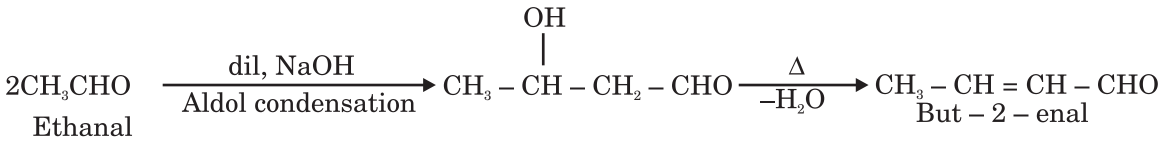
[1]

(b) (i) **Benzoic acid to benzaldehyde**



[1]

(ii) Ethanal to but-2-enal



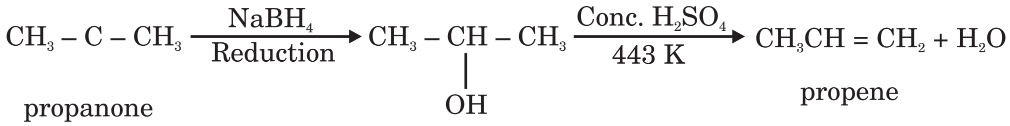
$$2CH_3CHO \xrightarrow[\text{Aldol condensation}]{\text{dil, NaOH}} CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-CHO \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$

Ethanal

But – 2 – enal

[1]

(iii) Propanone to propene



$$CH_3-C-CH_3 \xrightarrow[\text{Reduction}]{NaBH_4} CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[443\text{ K}]{\text{Conc. }H_2SO_4} CH_3CH=CH_2+H_2O$$

propanone

propene

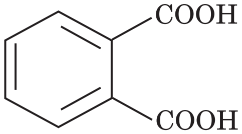
Topic 2: Carboxylic Acids

Summary

- These are the carbon compounds containing –*COOH* functional group.
- Carboxylic acids may be aliphatic (*RCOOH*)or aromatic (*ArCOOH*) depending on the group, alkyl or aryl, attached to carboxylic carbon.

Nomenclature

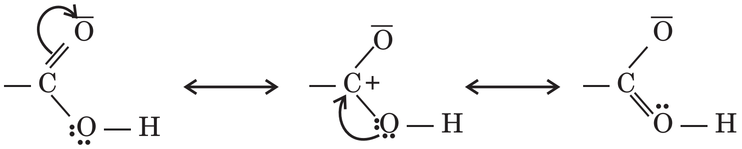
- Many of the carboxylic acids are known by their common names. Example: Ethanoic Acid is called as Acetic acid.
- In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending –e in the name of the corresponding alkane with – oic acid.
- In numbering the carbon chain, the carboxylic carbon is numbered one. Example: The IUPAC name of is



is Benzene-1, 2-dicarboxylic acid.

Structure of Carboxyl Group

- The bonds are in one plane and the angle between the bonds is 120°.
- Due to difference in electrophilic nature, resonance is present as shown below:



Preparation of Carboxylic Acids

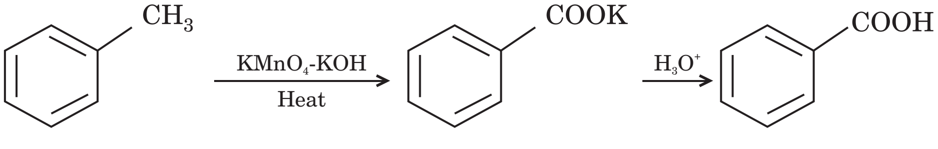
- **From primary alcohols and aldehydes**

  In the presence of oxidizing agents like potassium permanganate and potassium dichromate, primary alcohols are oxidized to carboxylic acids.

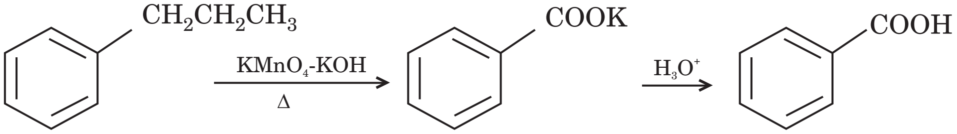
$$RCH_2OH \xrightarrow[2.\ H_3O^{\oplus}]{1.\ \text{alkaline } KMnO_4} RCOOH$$

$$\underset{\text{1-Decanol}}{CH_3(CH_2)_8CH_2OH} \xrightarrow{CrO_3-H_2SO_4} \underset{\text{Decanoic acid}}{CH_2(CH_2)_8COOH}$$

- **From alkylbenzenes:**



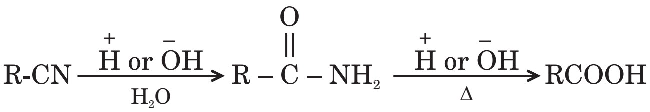
Benzoic acid



Benzoic acid

- **Using nitriles and amides**

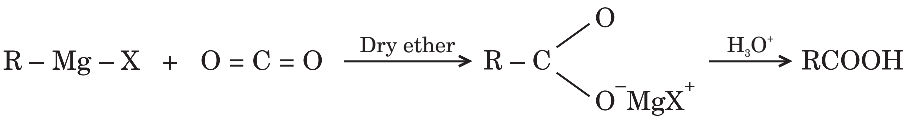
To stop the reaction at the amide stage, mild reaction conditions are used.



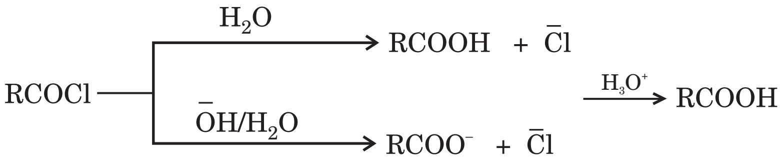
$$\text{R-CN} \xrightarrow[H_2O]{\overset{+}{H} \text{ or } \overset{-}{OH}} R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[\Delta]{\overset{+}{H} \text{ or } \overset{-}{OH}} RCOOH$$

- **Using Grignard Reagent**

Salts of carboxylic acids are formed when Grignard's reagent react with carbon dioxide(dry ice) which on acidification with mineral acid give carboxylic acids.



- **Using acyl halides and anhydrides**



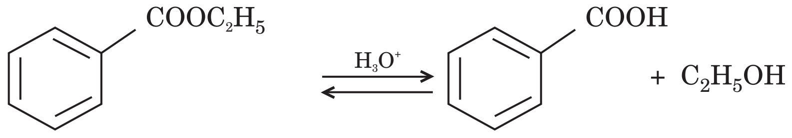
$$RCOCl \xrightarrow{H_2O} RCOOH + \bar{C}l$$

$$RCOCl \xrightarrow{\bar{O}H/H_2O} RCOO^- + \bar{C}l \xrightarrow{H_3O^+} RCOOH$$

$$\underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow{H_3O} \underset{\text{Benzoic acid}}{2C_6H_5COOH}$$

- **Using esters**

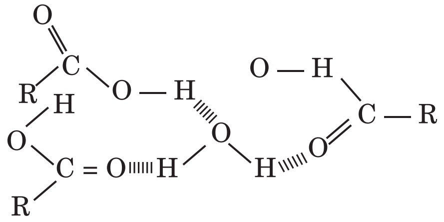
  Esters when subjected to acidic hydrolysis give carboxylic acids.



Ethyl benzoate Benzoic acid

Physical Properties

- Lower members are colorless liquid having pungent smell and the higher members are odourless waxy solid.
- The ability to form intermolecular hydrogen bonds causes carboxylic acids to have higher boiling point.



Hydrogen bonding of
RCOOH with H_2O

Chemical Reactions

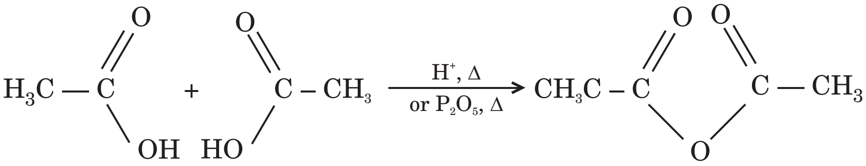
- **Reactions with metals and alkalies**

  On reacting with metals, the carboxylic acids evolve hydrogen.

$$2R-COOH+2Na \longrightarrow \underset{\text{Sodium carboxylate}}{2R-CO\bar{O}Na^+} + H_2$$

$$R-COOH+NaOH \longrightarrow R-CO\bar{O}Na^+ + H_2O$$

- **Formation of anhydride**



Ethanoic acid Ethanoic anhydride

- **Esterification:**

$$RCOOH + PCl_5 \longrightarrow RCOCl + PCl_3 + HCl$$

$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$

$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$

- **Reactions with** $PCl_5, PCl_3, SOCl_2$

  The hydroxyl group gets replaced by chlorine atom.

  $RCOOH + R'OH \xrightleftharpoons{H^+,\ \Delta} RCOOR' + H_2O$

- **Reaction with ammonia**

  Reaction of carboxylic acids with ammonia gives ammonium salts which when heated further gives amides.

$$CH_3COOH + NH_3 \rightleftharpoons \underset{\text{Ammonium acetate}}{CH_3CO\bar{O}\overset{+}{N}H_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}$$

Reactions involving –COOH group

- **Reduction**

  Carboxylic acids, when reduced by diborane give primary alcohols.

  $R-COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4\text{/ether or } B_2H_6} R-CH_2OH$

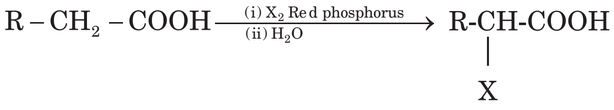
- Decarboxylation: The loss of carbon dioxide from carboxylic acids to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio 3 :1) is called decarboxylation.

  $R-COONa \xrightarrow[\text{Heat}]{\text{NaOH \& CaO}} R-H + Na_2CO_3$

Substitution Reactions

- **Halogenation (Hell Volhard-Zelinsky Reaction)**

  Carboxylic acids which have an -hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus which results in α halocarboxylic acids.

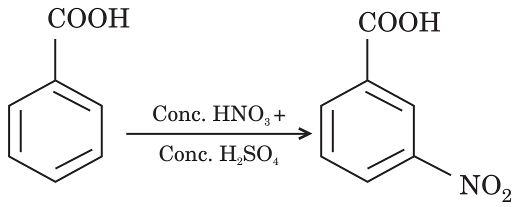


$$R-CH_2-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2 \text{ Red phosphorus}} R\text{-}\underset{X}{\underset{|}{C}}H\text{-}COOH$$

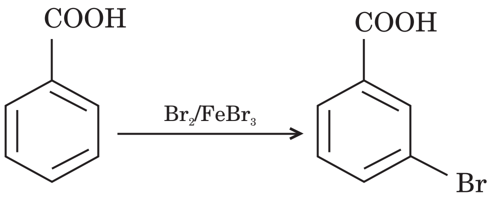
X = Cl, Br
α - Halocarboxvlic acid

- **Ring Substitution**

  In aromatic carboxylic acids, carboxyl group acts as a deactivating and meta-directing group.



m-Nitrobenzoic acid



m-Bromobenzoic acid

Applications of Carboxylic Acids

- Ethanoic acid is used as vinegar and as solvent.
- Methanoic acid is used in rubber, dyeing, leather,textile, and electroplating industries.
- Esters of benzoic acid are often used in perfume industry.
- For the manufacturing of soaps and detergents, higher fatty acids are used.

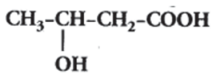
PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 2

1 Mark Questions

1. Write the IUPAC name of the compound. **[DELHI 2014]**



$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-COOH$$

2. Write the structure of 2-hydroxybenzoic acid. **[All INDIA 2014]**

3. Arrange the following compounds in an increasing order of their acid strengths:

$$(CH_3)_2\,CHCOOH, CH_3CH_2CH(Br)COOH, CH_3CH(Br)CH_2COOH$$

[DELHI 2016]

2 Marks Questions

4. How do you convert the following?
Toluene to benzoic acid **[All INDIA 2018]**

OR

Account for the following:
(a) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.
(b) pK_a value of 4-nitrobenzoic acid is lower than that of benzoic acid. **[All INDIA 2018]**

5. Write chemical equation for the following conversions:
(i) Nitrobenzene to benzoic acid.
(ii) Benzyl chloride to 2-phenylethanamine.
(iii)Aniline to benzyl alcohol. **[DELHI 2012]**

5 Marks Questions

6. (a) Illustrate the following name reactions giving suitable example in each case:
(i) Clemmensen reduction
(ii)Hell-Volhard-Zelinsky reaction
(b) How are the following conversions carried out?

(i) Ethyl cyanide to ethanoic acid
(ii)Butan-l-ol to butanoic acid
(iii)Benzoic acid to m-bromobenzoic acid

OR

(a) Illustrate the following reactions giving a suitable example for each:
(i) Cross aldol condensation
(ii) Decarboxylation

(b) Give simple tests to distinguish between the following pairs of compounds:
(i) Pentan-2-one and Pentan-3-one
(ii)Benzaldehyde and Acetophenone
(iii)Phenol and Benzoic acid

[DELHI 2012]

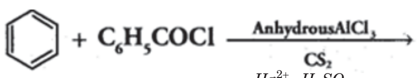
7. (a) Give a possible explanation for each one of the following:
(i) There are two $-NH_2$ groups in semicarbazide. However, only one such group is involved in the formation of semicarbazones.
(ii) Cyclohexanone forms cyanohydrin in good yield but 2, 4, 6-trimethylcyclohexanone does not.

(b) An organic compound with molecular formula $C_9H_{10}O$ forms 2, 4, -DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro's reaction. On vigorous oxidation it gives 1,2-benzene-di-carboxylic acid. Identify the compound.

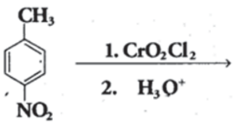
OR

(a) Give chemical tests to distinguish between
(i) Phenol and Benzoic acid
(ii)Acetophenone and Benzophenone

(b) Write the structures of the main products of following reactions:

(i) 

(ii) $H_3C-C\equiv C-H \xrightarrow{Hg^{2+},\ H_2SO_4}$

(iii) 

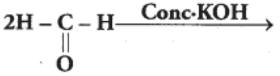
[DELHI 2012]

8. (a) Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Give two reasons.

(b) How will you bring about the following conversions?
(i) Propanone to propane
(ii) Benzoyl chloride to benzaldehyde
(iii) Ethanal to but-2-enal.

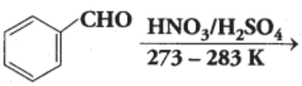
OR

(a) Complete the following reactions:

(i) 

$2H-\underset{\underset{O}{\|}}{C}-H \xrightarrow{\text{Conc·KOH}}$

(ii) $CH_3COOH \xrightarrow{Br_2/P}$

(iii) 

(b) Give simple chemical tests to distinguish between the following pairs of compounds:
(i) Ethanal and Propanal
(ii) Benzoic acid and Phenol.

[DELHI 2013]

9. (a) Illustrate the following name reaction giving suitable example in each case:
(i) Clemmensen reduction
(ii) Hell-Volhard-Zelinsky reaction

(b) How are the following conversions carried out?
(i) Ethylcyanide to ethanoic acid
(ii) Butan-1-ol to butanoic acid
(iii) Benzoic acid to m-bromobenzoic acid

OR

(a) Illustrate the following reactions giving a suitable example for each.
(i) Cross aldol condensation
(ii) Decarboxylation

(b) Give simple tests to distinguish between the following pairs of compounds
(i) Pentan-2-one and Pentan-3-one
(ii) Benzaldehyde and Acetophenone
(iii) Phenol and Benzoic acid

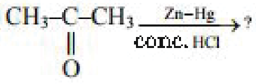
[DELHI 2013]

10. (a) How will you convert the following :
(i) Propanone to Propan-2-ol
(ii) Ethanal to 2-hydroxy propanoic acid
(iii) Toluene to benzoic acid

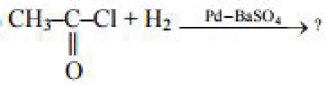
(b) Give simple chemical test to distinguish between :
(i) Pentan-2-one and Pentan-3-one
(ii) Ethanal and Propananl

OR

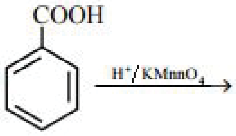
Write the products of the following reactions :

(i) 

$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[\text{conc. HCl}]{\text{Zn–Hg}} ?$

(ii) 

$CH_3-\underset{\underset{O}{\|}}{C}-Cl + H_2 \xrightarrow{\text{Pd–BaSO}_4} ?$

(iii) 

Which acid of each pair shown here would you expect to be stronger?

[All INDIA 2013]

11. (a) Write the products formed when CH_3CHO reacts with the following reagents:

(i) HCN

(ii) $H_2N - OH$

(iii) CH_3CHO in the presence of dilute $NaOH$

(b) Give simple chemical tests to distinguish between the following Pairs of compounds

(i) Benzoic acid and Phenol

(ii) Propanal and Propanone.

[All INDIA 2014]

OR

(a) Account for the following:

(i) $Cl - CH_2COOH$ is a stronger acid than CH_3COOH.

(ii) Carboxylic acids do not give reactions of carbonyl group.

(b) Write the chemical equations to illustrate the following name reactions:

(i) Rosenmund reduction

(ii) Cannizzaro's reaction

(c) Out of $CH_3CH_2 - CO - CH_2 - CH_3$ and $CH_3CH_2 - CH_2 - CO - CH_3$, which give iodoform test?

12. (*a*) Write the structures of A and B in the following reactions:

(*i*) $CH_3MgBr \xrightarrow[H_3O^+]{CO_2} A \xrightarrow{PCl_5} B$

(*ii*) $CH_3COCl \xrightarrow{H_2,\, Pd-BaSO_4} A \xrightarrow{H_2N-OH} B$

(b) Distinguish between:

(*i*) $C_6H_5 - COCH_3 \, and \, C_6H_5 - CHO$

(*ii*) $CH_3COOH \; and \; HCOOH$

(*c*) Arrange the following in the increasing order of their boiling points:

$CH_3CHO,\ CH_3COOH,\ CH_3CH_2OH$

OR

(*a*) Write the chemical reaction involved in Wolf-Kishner reduction.

(*b*) Arrange the following in the increasing order of their reactivity towards nuchleophilic addition reaction:

$C_6H_5COCH_3,\ CH_3 - CHO,\ CH_3COCH_3$

(*c*) Why carboxylic acid doesn't give reaction of carbonyl group?

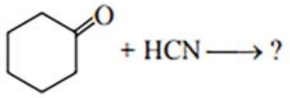
(*d*) Write the product in the following reaction:

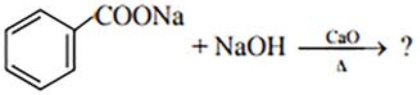
$CH_3CH_2CH = CH - CH_2CN \xrightarrow[H_2O]{(i-Bu)_2 AlH}$

(*e*) A and B are two functional isomers of compound C_3H_60. On heating with $NaOH$ and I_2, isomer B forms yellow precipitate of iodoform whereas isomer A does not form any precipitate. Write the formulae of A and B.

[DELHI 2016]

13. (*a*) Write the product(s) in the following reactions :

(i) 

(ii) 

(iii) $CH_3\text{–}CH\text{=}CH\text{–}CN \xrightarrow[\text{(b)}\, H_2O]{\text{(a) DIBAL} - H} ?$

(*b*) Give simple chemical tests to distinguish between the following pairs of compounds :

(*i*) Butanal and Butan-2-one

(*ii*) Benzoic acid and Phenol

OR

(*a*) Write the reactions involved in the following:

(*i*) Etard reaction

(*ii*) Stephen reduction

(*b*) How will you convert the following in not more than two steps :

(*i*) Benzoic acid to Benzaldehyde

(*ii*) Acetophenone to Benzoic acid

(*iii*) Ethanoic acid to 2-Hydroxyethanoic acid **[All INDIA 2017]**

14. (*a*) Write chemical equations of illustrate the following name bearing reactions:

(*i*) Cannizzaro's reaction

(*ii*) Hell- Volhard - Zelinskyreaction

(*b*) Give chemical tests to distinguish between the following pairs of compounds:

(i) Propanal and Propanone
(ii) Acetophenone and Benzophenone
(iii) Phenol and Benzoic acid

OR

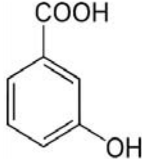
(*a*) How will you bring about the following conversions?
(i) Ethanol to 3 – hydroxybutanal
(ii) Benzaldehyde to Benzophenone

(*b*) An organic compound A has the molecular formula $C_8H_{16}O_2$. It gets hydrolysed with dilute sulphuric acid and gives a carboxylic acid B and an alcohol C. Oxidation of C with chromic acid also produced B. C on dehydration reaction gives but-1-ene. Write equations for the reactions involved.

Solutions

1. 3-hydroxybutan-1-oic acid **[1]**

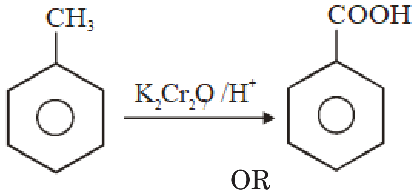
2. **[1]**



3. $(CH_3)_2CHCOOH < CH_3CH_2CH(Br)COOH < CH_3CH(Br)CH_2COOH$

$< CH_3CH_2CH(Br)COOH$ **[1]**

4.



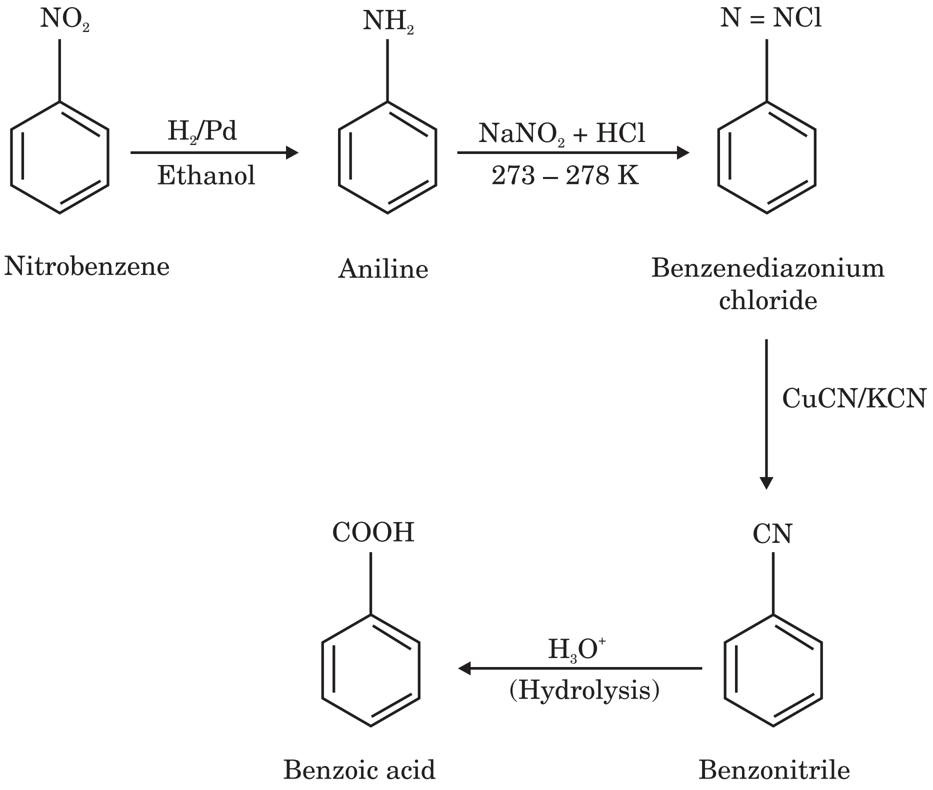
[1 + 1]

OR

(a) As –COOH group shows –m effect thus is electron withdrawing in nature and makes the aromatic ring deactivated toward selectrophilic substitution reaction. **[1]**

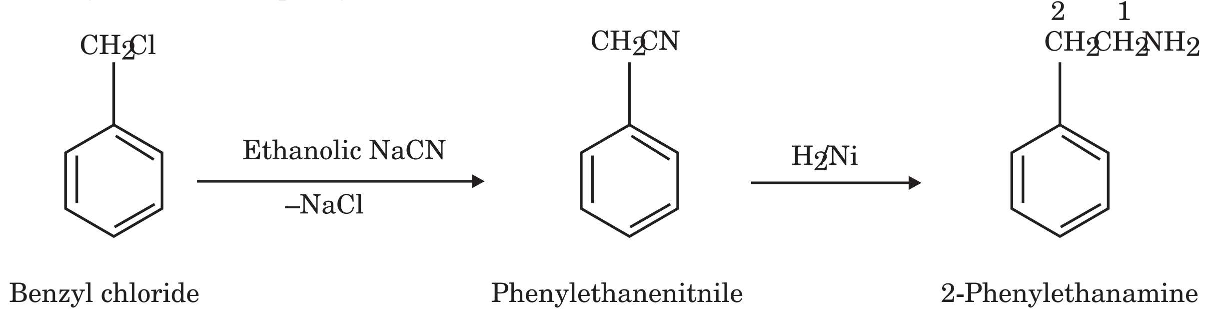
(b) Because of the presence of –NO2 group which is highly electron withdrawing in nature. The polarity of –OH bond in –COOH increases thus acidity increases and pK_a decreases. **[1]**

5. (i) Nitrobenzene to benzoic acid

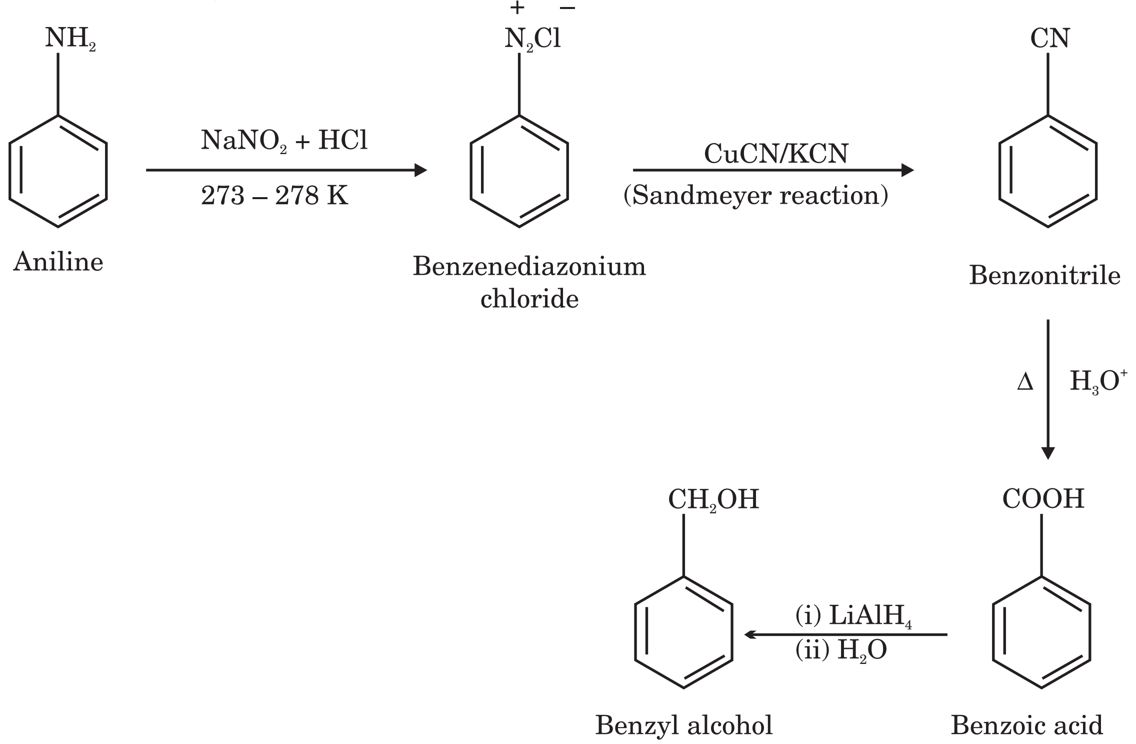


[1]

(ii) Benzyl chloride to 2-phenylethanamine.



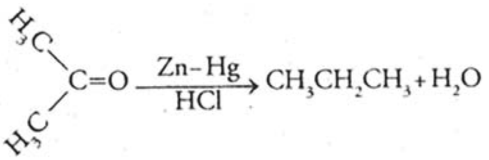
(iii)Aniline to benzyl alcohol.



[1]

6. (a)

(i) Aldehydes and ketones are reduced to CH_2 group on treatment with zinc-amalgam and cone. HCl. **[1]**



(*ii*) Carboxylic acids containing α-hydrogen atom gives halo carboxylic acids on treatment with halogens in the presence of red phosphorus. **[1]**

$CH_3COOH + Cl_2 \xrightarrow{\text{Red } P} ClCH_2COOH + HCl$

(*b*) (*i*) $C_2H_5CN \xrightarrow{H^+} C_2H_5COOH \xrightarrow{NH_3/\Delta^+}$ **[1]**

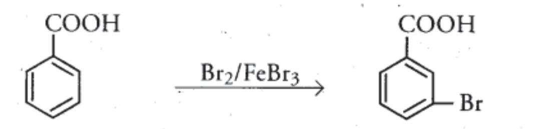
Ethylcyanide Propanoic acid

$$C_2H_5CONH_2 \xrightarrow{Br_2,\,KOH} \underset{\text{Ethylamine}}{C_2H_5NH_2} \xrightarrow{HNO_2}$$

$$\underset{\text{Ethylalcohol}}{C_2H_5OH} \xrightarrow{alk.KMnO_4} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

$$\underset{\text{Butanol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{K_2Cr_2O_7,\,[O]} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

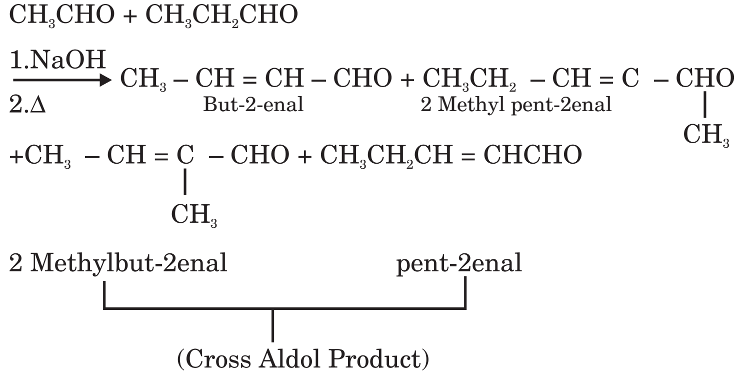
(*ii*) **[1]**



(*iii*) Benzoic acid m-Bromobenzoic acid **[1]**

OR

(*i*) Carboxylic acids containing α-hydrogen atom gives halo carboxylic acids on treatment with halogens in the presence of red phosphorous. **[1]**



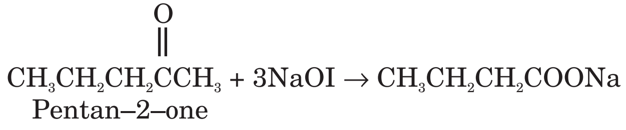
$$CH_3CHO + CH_3CH_2CHO \xrightarrow[2.\Delta]{1.NaOH} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO} + \underset{\text{2 Methyl pent-2enal}}{CH_3CH_2-CH=\underset{CH_3}{\underset{|}{C}}-CHO}$$

$$+\underset{\text{2 Methylbut-2enal}}{CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CHO} + \underset{\text{pent-2enal}}{CH_3CH_2CH=CHCHO}$$

(Cross Aldol Product)

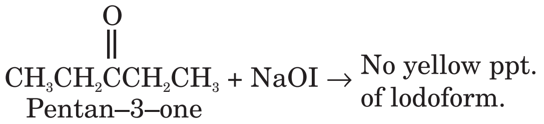
(ii) $R-COONa \xrightarrow[heat]{NaOH+CaO} R-H + Na_2CO_3$

(b) (*i*) Pentan-2-one gives iodoform test but pentan-3-one does not. **[1]**



$$\underset{\text{Pentan–2–one}}{CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3} + 3NaOI \rightarrow CH_3CH_2CH_2COONa$$

$$+\underset{\substack{\text{Iodoform}\\\text{(yellow ppt)}}}{CHI_3\downarrow} + 2NaOH$$



$$\underset{\text{Pentan–3–one}}{CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3} + NaOI \rightarrow \text{No yellow ppt. of Iodoform.}$$

(*ii*) Benzaldehyde does not give iodoform test but Acetophenone gives iodoform test.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 3NaOI \longrightarrow \underset{\text{Iodoform}}{CHI_3}\downarrow + C_6H_5COONa + 2NaOH$$

$$C_6H_5CHO + NaOI \longrightarrow \text{No yellow ppt of Iodoform}$$

(*iii*) Carboxylic acid lose carbon dioxide to form hydrocarbon, when their salts are heated with sodium. The reaction is known as decarboxylation reaction [1]

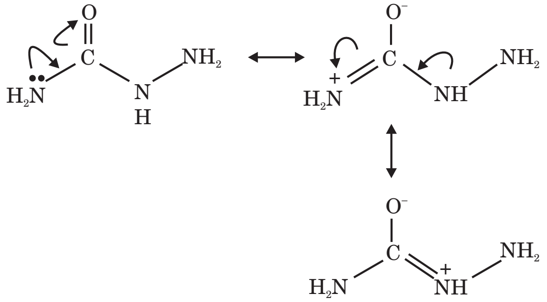
Phenol gives violet colour with neutral $FeCl_3$ solution but benzoic acid does not.

$$\underset{\text{Phenol}}{6C_6H_5OH} + FeCl_3 \longrightarrow \underset{\text{Violet colour}}{\left[Fe\left(OC_6H_5\right)_6\right]^{3-}} + 3H^+ + 3HCl$$ **[1]**

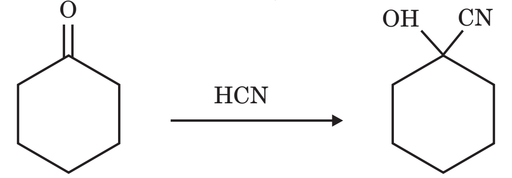
$$3C_6H_5COOH + FeCl_3 \longrightarrow \underset{\text{Buff color}}{\left(C_6H_5COO\right)_3Fe} + 3HCl$$ **[1]**

7. (a)

(i) Semicarbazide resonance involves one of the two $-NH_2$ groups, which is attached to the carboxyl carbon atom. Due to which electron density on $\boldsymbol{-NH_2}$ group involved in resonance decreases. So it cannot act as nucleophile. Other $-NH_2$ group can act as nucleophile to produce semicarbazones with aldehydes and ketones. **[1½]**



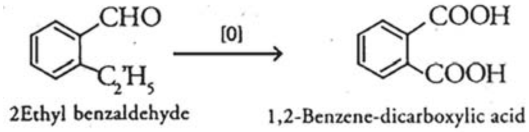
(ii) In cyclohexanone CN^- can easily attack without any steric hindrance. But in 2, 4, 6 — Trimethylcyclohexanone due to presence of methyl groups steric hindrance is produced and CN^- cannot attack effectively. **[1½]**



Cyclohexanone Cyanohydrin **[1]**

(b) $C_9H_{10}O$ is aldehyde because it reduces Tollen's reagent. It undergoes Cannizaro's reaction therefore

it is substituted benzaldehyde. It gives 1, 2, Benezene-di carboxylic acid. The compound is 2-Ethyl benzaldehyde. **[1 + 1]**



OR

(a)

(*i*) Phenol gives violet colour with neutral $FeCl_3$ solution but benzoic acid does not. **[1]**

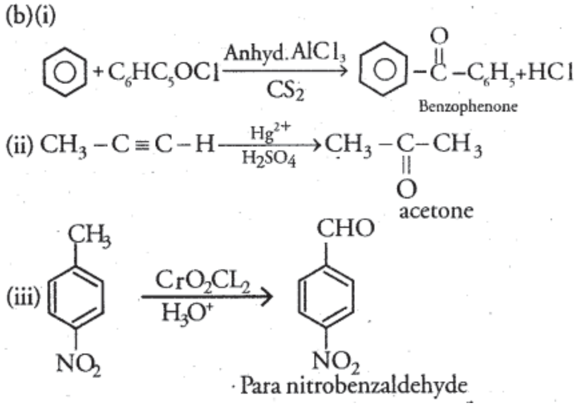
$$6C_6H_5OH + FeCl_3 \longrightarrow \left[Fe\left(OC_6H_5\right)\right]^{3-} + 3H^+ + HCl$$

$$3C_6H_5OH + FeCl_3 \longrightarrow \left[Fe\left(OC_6H_5\right)_3\right] + 3HCl$$

(*ii*) Acetophenone gives iodoform test but benzophenone does not **[1]**

$$C_6H_5COCH_3 + 3NaOI \xrightarrow{\Delta} C_6H_5COONa + CHI_3 + 2NaOI$$

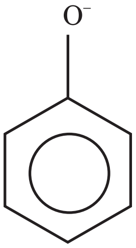
$$C_6H_5COC_6H_5 \xrightarrow{NaOI} \text{No yellow ppt of Iodoform}$$



[1 + 1 + 1]

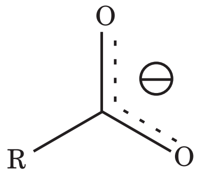
8. (a) On losing a proton, carboxylic acids forms carboxylate ion and phenol forms phenoxide ion as follows:

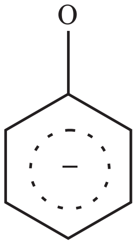
$RCOO^-$ (Carboxylate ion)



Phenoxide ion **[1]**

Now, the negative charge is delocalized in both molecules as follows:

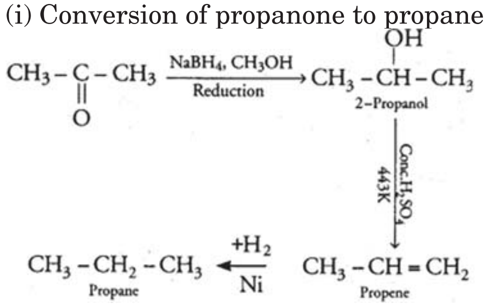




The conjugate base of carboxylic acid has two resonance structures in which negative charge is delocalized over two oxygen atoms which stabilizes the carboxylate ion. On the other hand, in phenoxide ion the charge is delocalized over entire molecule on the less electronegative atom, thus resonance of phenoxides is not important in comparison to resonance in carboxylate ion. **[1]**

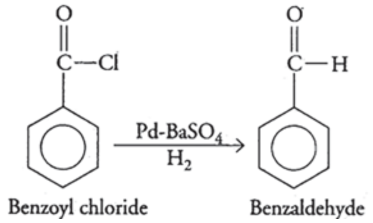
Further, in carboxylate ion the negative charge is effectively delocalized over two oxygen atoms whereas it is less effectively delocalized over one oxygen atom and less electronegative carbon atom. Thus, phenol is less acidic than carboxylic acids. In other words, carboxylic acids are stronger acids than phenol.

(b) (i) Conversion of propanone to propane:



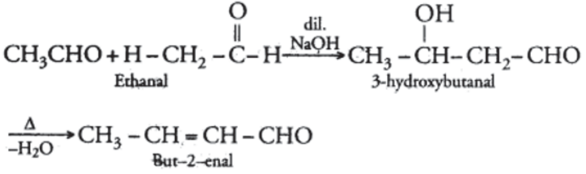
[1]

(ii) Conversion of benzoyl chloride to benzaldehyde:



[1]

(iii)On treatment with dilute alkali, ethanol produces 3-hydroxybutanal gives But-2-enal on heating.



$$CH_3CHO + H-CH_2-\overset{\overset{O}{\|}}{C}-H \xrightarrow[\text{NaOH}]{\text{dil.}} CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CHO$$

Ethanal 3-hydroxybutanal

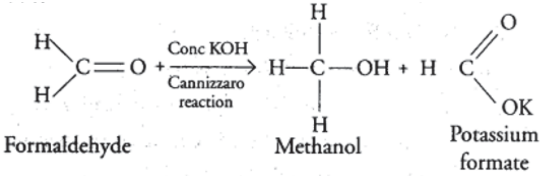
$$\xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$

But–2–enal

[1]

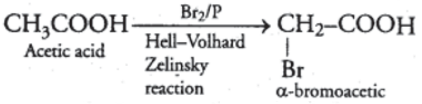
OR

(a) (i)



[1]

(ii)

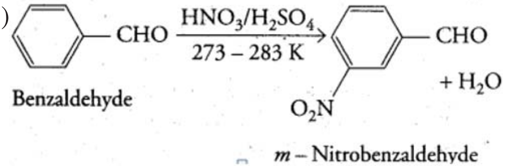


$$CH_3COOH \xrightarrow[\text{Hell–Volhard Zelinsky reaction}]{Br_2/P} \underset{\underset{Br}{|}}{CH_2}-COOH$$

Acetic acid α-bromoacetic

[1]

(iii)



[1]

(b) (i) Ethanal and Propanal:

Iodoform Test: When ethanal is treated with sodium liydroxide and ammonia, iodoform is obtained.

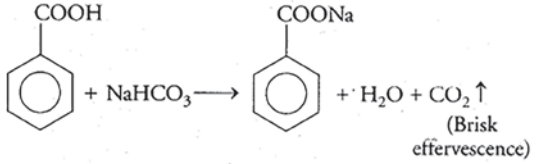
$$CH_3CHO + NaOH + 3I_2 \longrightarrow$$

$$\underset{\text{Iodoform(yellow ppt.)}}{CHI_3} + HCOONa + 4NaI + 3H_2O$$ **[1]**

Propanal does not give this test.

$CH_3CH_2CHO + 4NaOH + 3I_2 \rightarrow$ No reaction

(*ii*) Benzoic acid and phenol: When benzoic acid is treated with $NaHCO_3$ brisk effervescence of CO_2 gas is evolved.

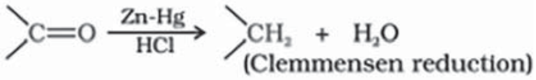


Phenol does not give this test:

$C_6H_5OH + NaHCO_3 \longrightarrow$ No reaction **[1]**

9. (a) (i) Clemmensen Reduction

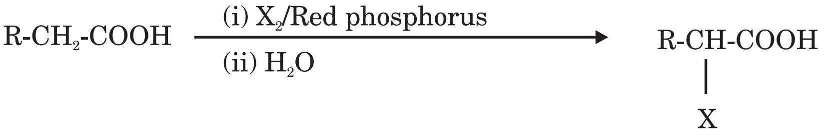
The carbonyl group of aldehydes and ketones is reduced to CH, on treatment with zinc-amalgam and concentrated hydrochloric acid. This is known as Clemmensen reduction.



[1]

(ii) HeII-Volhard-Zelinsky (HVZ)reaction Carboxylic acids having an α – hydrogen are halogenated at

the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.



$$R\text{-}CH_2\text{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/Red phosphorus}} R\text{-}\underset{\displaystyle X}{\underset{|}{CH}}\text{-}COOH$$

X = Cl. Br

α – Halcarboxylic acid

b (i)

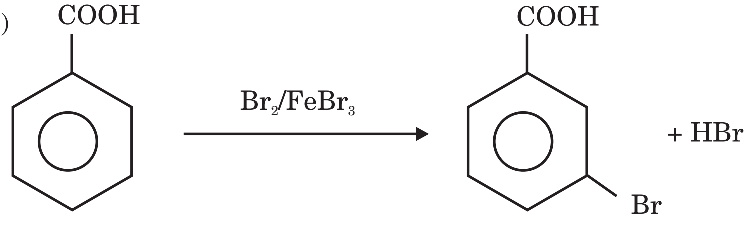
$$\begin{tikzcd}
\underset{\text{Ethyl cyanide}}{C_2H_5CN} \arrow[r, "H_2O/H^-"] & \underset{\text{Propanoic acid}}{C_2H_5COOH} \arrow[dr, "NH_3/\Delta"] & \\
C_2H_5OH \arrow[dr, "\text{alkaline } KMnO_4"'] & C_2H_5NH_2 \arrow[l, "HNO_2"'] & C_2H_5CONH_2 \arrow[l, "Br_2/KOH"'] \\
& \underset{\text{Ethanoic acid}}{CH_3COOH} &
\end{tikzcd}$$

[1 + 1]

(ii) $CH_3CH_2CH_2CH_2OH \xrightarrow[Dil.\ H_2SO_4]{K_2Cr_2O_7/H_2SO_4} CH_3CH_2CH_2COOH$

Butanol Butanoic acid

(iii) **[1 + 1]**



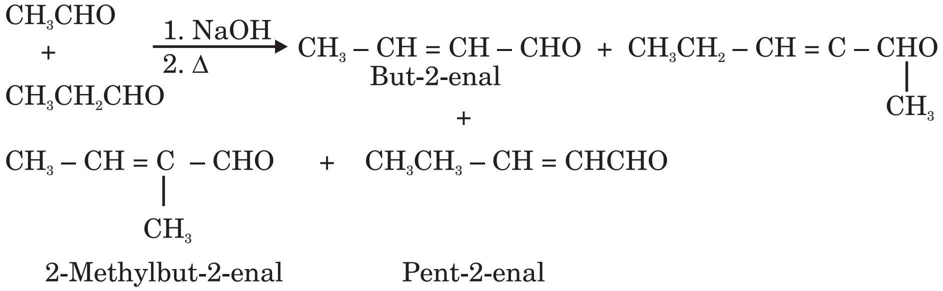
Benzoic acid

OR

m - bromo benzoic acid

(a) (i) Cross aldol condensation:

When aldol condensation is carried out between two different aldehydes and / or ketones, it is called cross aldol condensation. If both of them contain a-hydrogen atoms. it gives a mixture of four products. **[1]**



$$CH_3CHO + CH_3CH_2CHO \xrightarrow[2.\ \Delta]{1.\ NaOH} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO} + CH_3CH_2-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CHO + \underset{\text{2-Methylbut-2-enal}}{CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CHO} + \underset{\text{Pent-2-enal}}{CH_3CH_3-CH=CHCHO}$$

(ii) Decarboxylation refers to the reaction in which **carboxylic acids lose carbon dioxide to form hydrocarbons** when their sodium salts are heated with soda-lime.

$$CH_3-COONa \xrightarrow[\Delta]{Soda-lime(Mixture\ of\ NaOH\ and\ CaO\ in\ 3:1\ ratio)} CH_4+Na_2CO_3$$ **[1]**

(b) (i) **Ethanal gives positive iodoform test but not propanal** **[1]**

(ii) Benzaldehyde(C_6H_5CHO) and acetophenone$(C_6H_5COCH_3)$ can be distinguished by iodoform test.

Acetophenone, being a methyl ketone on treatment with I_2/NaOH undergoes iodoform reaction to give a yellow ppt. of iodoform. On the other hand, benzaldehyde does not give this test.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3}+3NaOI \longrightarrow C_6H_5COONa+\underset{\text{Iodoform}}{CHI_3}\downarrow+2NaOH$$

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{NaOI} \text{No yellow ppt of iodoform}$$ **[1]**

(iii)Phenol and benzoic acid can be distinguished by ferric chloride test.

Ferric chloride test:

Phenol reacts with neutral $FeCl_3$ to form ferric phenoxide complex giving violet colouration.

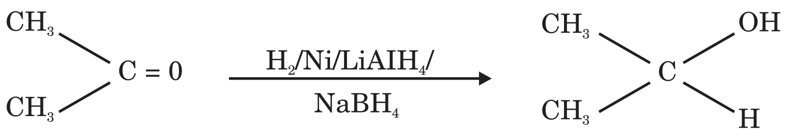
$$\underset{\text{Phenol}}{6C_6H_5OH}+FeCl_3 \longrightarrow \underset{\substack{\text{Iron phenol complex}\\ \text{(Voilet colour)}}}{\left[Fe(OC_6H_5)_6\right]^{3-}}+3H^++3Cl^-$$

But benzoic acid reacts with neutral $FeCl_3$ to give a buff-coloured precipitate of ferric benzoate.

$$\underset{\text{Benzoic acid}}{3C_6H_5COOH}+FeCl_3 \longrightarrow \underset{\substack{\text{Ferric benzoate}\\ \text{(Buff coloured ppt)}}}{(C_6H_5COO)_3Fe}+3HCl$$ **[1]**

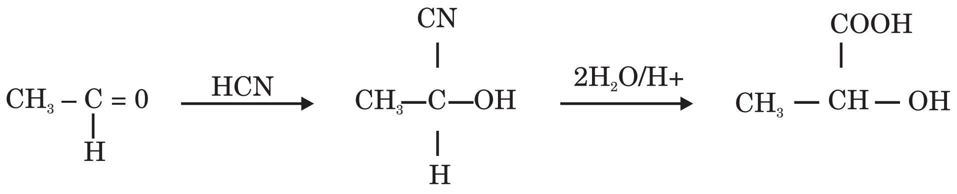
10. **(a)**

(i)



$$(CH_3)_2C=0 \xrightarrow[NaBH_4]{H_2/Ni/LiAlH_4/} (CH_3)_2C(OH)H$$ **[1]**

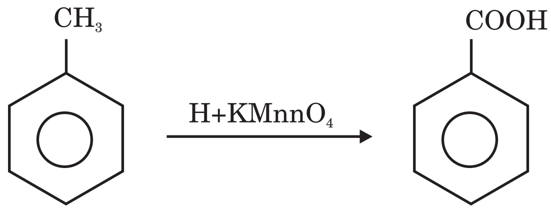
(ii)



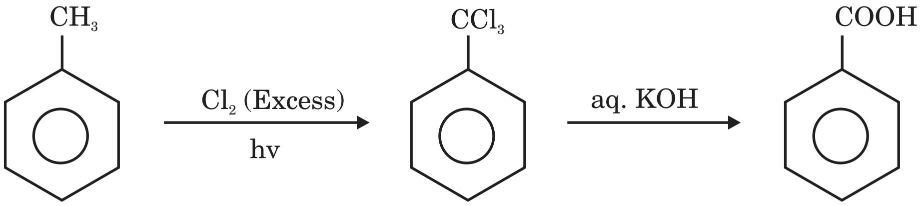
$$CH_3-\underset{\displaystyle H}{C}=0 \xrightarrow{HCN} CH_3-\underset{\displaystyle H}{\overset{\displaystyle CN}{C}}-OH \xrightarrow{2H_2O/H+} CH_3-\overset{\displaystyle COOH}{CH}-OH$$

[1]

(iii)



OR



[1]

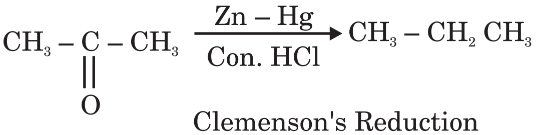
(b) (i) Pentane 2-one gives positive iodoform test but not pentane 3-one **[1]**

(ii) Ethanal gives positive iodoform test but not propanal **[1]**

OR

(a)

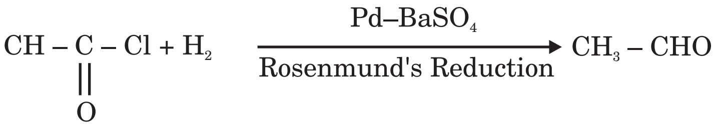
(i)



$$CH_3-\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}-CH_3 \xrightarrow[\text{Con. HCl}]{\text{Zn – Hg}} CH_3-CH_2\,CH_3$$

Clemenson's Reduction **[1]**

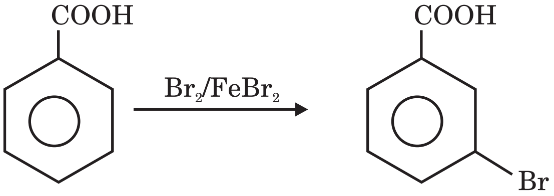
(ii)



$$CH-\underset{\displaystyle O}{\underset{\|}{C}}-Cl+H_2 \xrightarrow[\text{Rosenmund's Reduction}]{Pd–BaSO_4} CH_3-CHO$$

[1]

(iii)



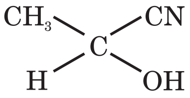
[1]

(b) (i) $F-CH_2-COOH$ is strong acid due to high -I power of F. **[1]**

(ii) CH_3-COOH , due to more stable conjugate base CH_{3-COO^-} **[1]**

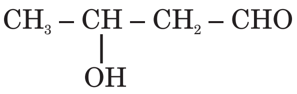
11.

(a) (i)



(ii) $CH_3-CH=N-OH$

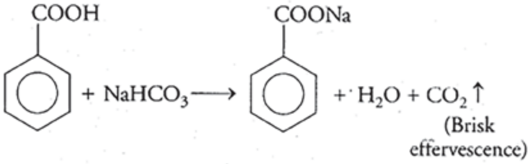
(iii)



$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CHO$$

[1 + 1 + 1]

(b) (*i*) Benzoic acid and phenol: When benzoic acid is treated with $NaHCO_3$ brisk effervescence of CO_2 gas is evolved. **[1]**



Phenol does not give this test:

$C_6H_5OH + NaHCO_3 \longrightarrow$ No reaction

(*ii*) Propanone gives iodoform test but propanal does not because propanone has $\boldsymbol{CH_3CO-}$ group

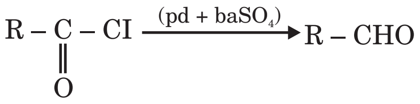
$$CH_3COCH_3 + 3NaOH \xrightarrow{NaOH, I_2, \Delta} CH_3COONa + CHI_3$$ **[1]**

OR

(a) (i) Due to presence of –Cl as an – I group **[1]**

(ii) The carbonyl group is involve in resonanced in –COOH group so the double bond character decreases here hence –COOH group does not give reaction of carbonyl group although it has $>C = O$. **[1]**

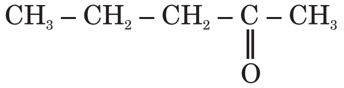
(b) (i) Rosenmund reduction



$$R-\underset{\underset{O}{\|}}{C}-CI \xrightarrow{(pd + baSO_4)} R-CHO$$

(ii) Cannizzaro's Reaction

$$2H-CHO \xrightarrow{50\%\ NaOH(conc.\ base)} CH_3-OH + H-COONa$$



$$CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

(methyl ketone) **[1 + 1 + 1]**

12. (a)

(i) $\underset{}{CH_3MgBr} \xrightarrow[H_3O^+]{CO_2} \underset{A}{CH_3COOH} \xrightarrow{PCl_5} \underset{B}{CH_3COCl}$ **[1]**

(ii) $CH_3COCl \xrightarrow{H_2, Pd-BaSO_4} \underset{A}{CH_3CHO} \xrightarrow{H_2N-OH} \underset{B}{CH_3CH = N-OH}$ **[1]**

(b) (i) $C_6H_5-COCH_3$ is a methyl ketone and therefore, gives a yellow precipitate when reacted with NaOH and I_2 . C_6H_5-CHO does not give this reaction.

$$C_6H_5-COCH_3 \xrightarrow{NaOH/I_2} C_6H_5COONa + CHI_3$$ **[1]**

(ii) As shown below, methanoic acid gives silver mirror test, while ethanoic acid will not give this test.

$$HCOOH + 2\left[Ag\left(NH_3\right)_2\right]NO_3 \longrightarrow 2Ag + CO_2 + 2NH_4NO_3 + 2NH_3$$ **[1]**

(c) The boiling points of the given compounds can be compared on the basis of intermolecular hydrogen bond formation. Hydrogen bonding is most extensive in acetic acid, followed by ethanol. It is least in acetaldehyde. Hence, the increasing order of boiling points of given compounds is as follows:

$$CH_3CHO < CH_3CH_2OH < CH_3COOH$$ **[1]**

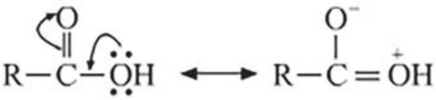
OR

(a) $\underset{\text{Acetaldehyde}}{CH_3CHO} + NH_2NH_2 \xrightarrow{-H_2O} \underset{\text{Hydrazone}}{CH_3CH = NNH_2} \xrightarrow{KOH,\ 453-473K} CH_3 - CH_3 + N_2$ **[1]**

(b) Aldehydes are more reactive than ketones towards the nucleophilic addition reaction. Among the all ketones, aromatic ketones are more susceptible to nucleophilic attack than an aliphatic one. Hence, the increasing order of reactivity towards nucleophilic addition reaction for the given compounds is as follows:

$$CH_3COCH_3 < C_6H_5COCH_3 < CH_3 - CHO$$ **[1]**

(c) The carbon of carboxylic acid is much less electrophilic as compared to aldehydes and ketones because the lone pair of oxygen attached to hydrogen is involved in resonance, as shown below:



$$R-\overset{\overset{O}{\|}}{C}-\ddot{O}H \longleftrightarrow R-\overset{\overset{O^-}{|}}{C}=\overset{+}{O}H$$

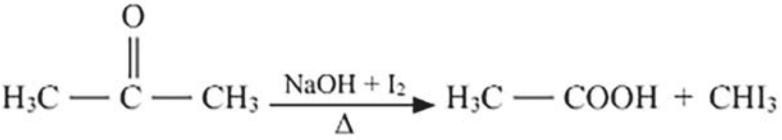
[1]

(d) $CH_3CH_2CH = CH - CH_2CN \xrightarrow[H_2O]{(i-Bu)_2AlH} CH_3CH_2CH = CH - CH - CHO$ **[1]**

(e) The possible functiona e $CH_3 - CH_2 - CHO$ and

$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3$$

Out of these, methyl ketone can give iodoform test as shown:

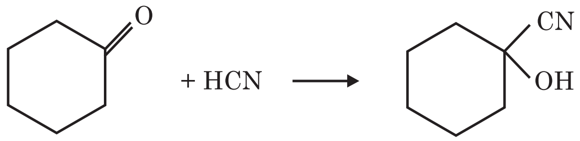


$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\Delta]{NaOH + I_2} H_3C - COOH + CHI_3$$

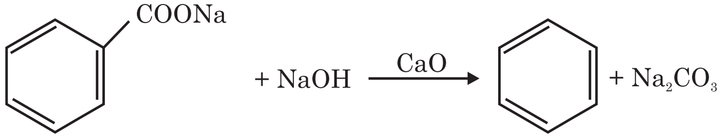
[1]

13. (a)

(i)



(ii)



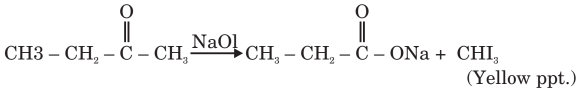
[1 + 1]

(iii)

$$CH_3 - CH = CH - CN \xrightarrow[\text{(b) } H_2O]{\text{(a) DIBAL-H}} CH_3 - CH = CH - CHO$$

[1]

(b) (i) Difference between butanal and butan-2-one

Test	Butanal	Butan-2-one
Tollen's test	Positive test Reaction: $CH_3-CH_2-CH_2-CHO+2\left[Ag\left(NH_3\right)_2\right]^{+}+3OH^{-}$ $\downarrow$ $RCOO^{-}+2Ag+2H_2O+4NH_3$ (Bright Silver Mirror)	Negative test
Iodoform test	Negative test	Positive test Reaction:  $CH3-CH_2-\overset{O}{\overset{\Vert}{C}}-CH_3 \xrightarrow{NaOI} CH_3-CH_2-\overset{O}{\overset{\Vert}{C}}-ONa+\ CHI_3$ (Yellow ppt.)

[1]

(ii) Distinguish test between phenol and benzoic acid

Ferric chloride test:

Phenol reacts with neutral $FeCl_3$ to form an iron-phenol complex giving violet colouration.

$$\underset{\text{Phenol}}{6C_6H_5OH} + FeCl_3 \longrightarrow \underset{\substack{\text{Iron-phenol complex}\\ \text{(Violet colour)}}}{\left[Fe\left(OC_6H_5\right)_6\right]^{3-}} + 3H^{+} + 3Cl^{-}$$

[1]

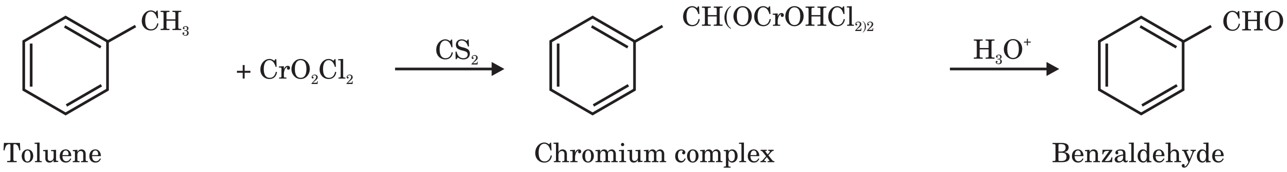
But benzoic acid reacts with neutral $FeCl_3$ to give a buff coloured ppt. of ferric benzoate.

$$\underset{\text{Benzoic acid}}{3C_6H_5COOH} + FeCl_3 \longrightarrow \underset{\substack{\text{Ferric benzoate}\\ \text{(Buff coloured ppt.)}}}{\left(C_6H_5COO\right)_3 Fe} + 3HCl$$

[1]

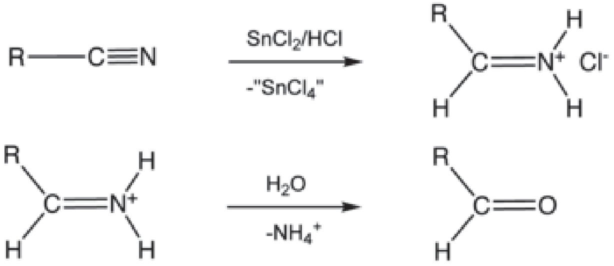
OR

(a) (i)



[1]

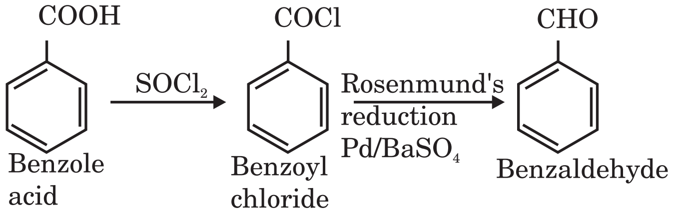
(ii)



[1]

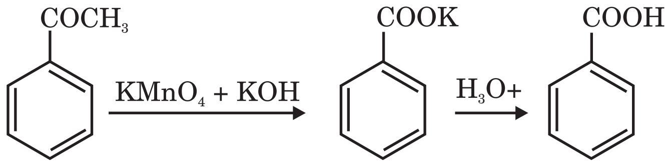
(b)

(i)



[1]

(ii)



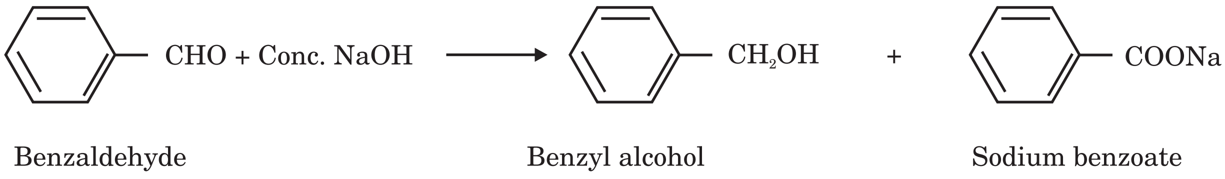
[1]

(iii) Ethanoic acid to 2-hydroxyethanoic acid

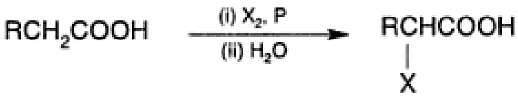
$$CH_3-COOH \xrightarrow[-HCl]{Cl_2} CH_2(Cl)-COOH \xrightarrow[-KCl]{KOH} CH_2(OH)-COOH$$

Ethanoic acid 2-hydroxyethanoic acid **[1]**

14. (a) (i) Cannizzaro reaction: Aldehydes which do not have α-hydrogen atom undergo self oxidation and reduction on treatment with concentrated alkali. **[1]**



(ii) Hell- Volhard - Zelinsky reaction: Carboxylic acids having α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give - halocarboxylic acids. **[1]**



$$RCH_2COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2,\ P} \underset{\displaystyle X}{\underset{|}{RCHCOOH}}$$

(b) (i) Propanal and propanone

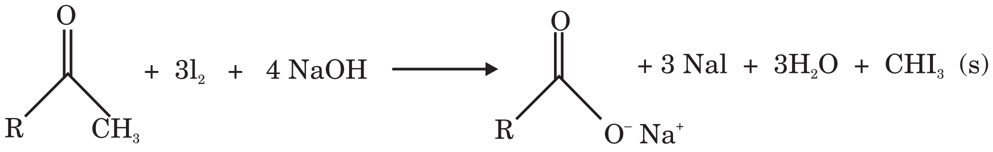
Fehling's test:

$$CH_3CH_3CHO + 2Cu^{2+} + 5OH^- \longrightarrow CH_3CH_2COO^- + \underset{(\text{Red ppt})}{Cu_2O} + 3H_2O$$

Propanone being a ketone will not give this test. **[1]**

(ii) Acetophenone and benzophenone

Iodoform test



Benzophenone does not give this test. **[1]**

(iii) Phenol and Benzoic acid

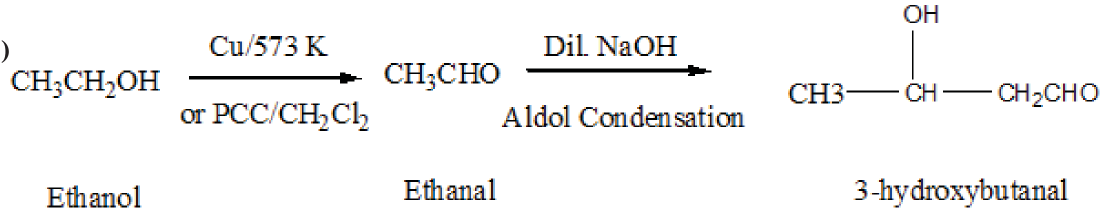
$FeCl_3$ test

$$C_6H_5OH + FeCl_3 \longrightarrow \underset{(\text{Blue Violet Colour})}{\left[\left(C_6H_5O^-\right)_6 Fe\right]^{3-}} + 3HCl$$

Benzoic acid does not give this test. **[1]**

OR

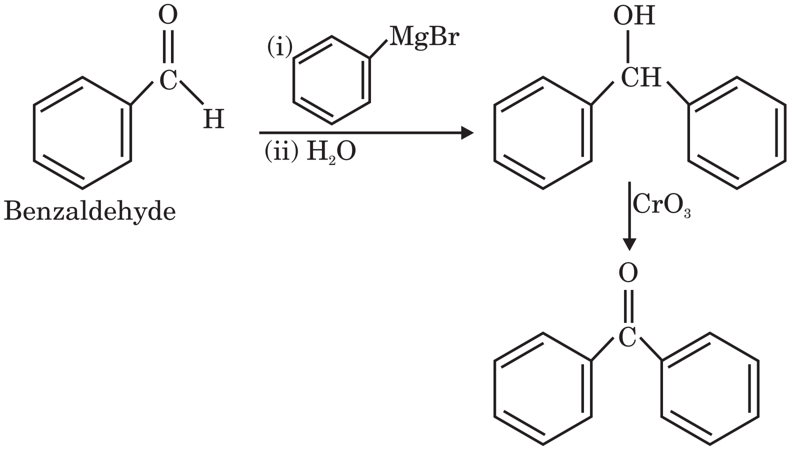
(a) (i)



$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{or } PCC/CH_2Cl_2]{Cu/573\ K} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[\text{Aldol Condensation}]{\text{Dil. NaOH}} \underset{\text{3-hydroxybutanal}}{CH3-\overset{\displaystyle OH}{\overset{|}{CH}}-CH_2CHO}$$

[1]

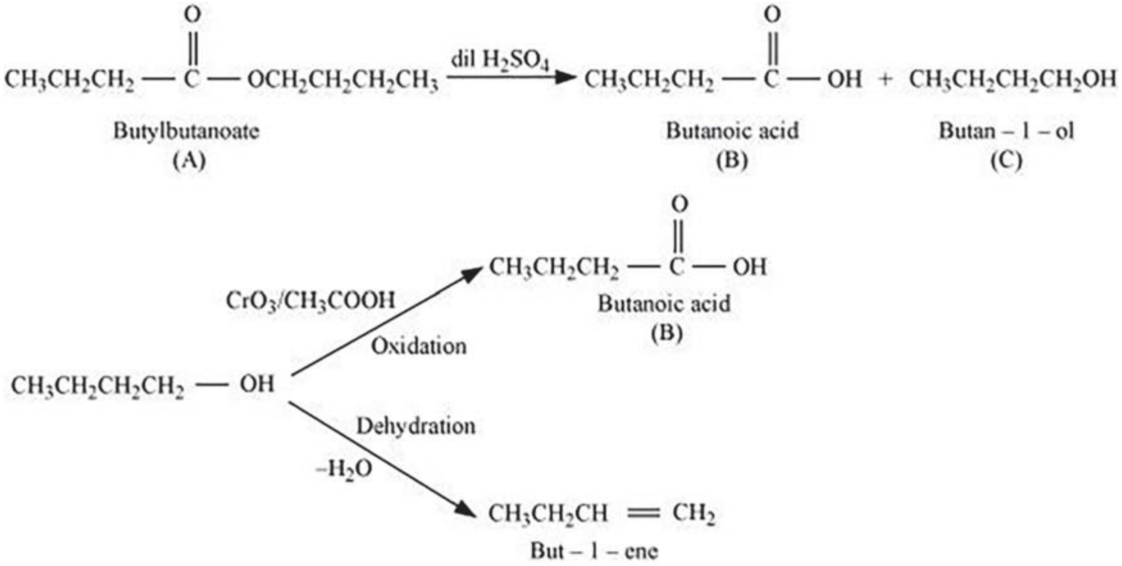
(ii)



Benzophenone

[1]

(b)



[1]

$$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow{CrO_3} CH_3-CH_2-CH_2-COOH$$

C B [1]

$$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow{Dehydration} CH_3-CH_2-CH=CH_2$$

But-1-ene [1]

Smart Notes ....

Smart Notes ....

CHAPTER 13

Amines

Chapter Analysis with respect to Last 3 Years' Board Exams

List of Topics	2016		2017		2018	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Amines: Nomenclature, classification, structure, methods of preparation				(2 marks)		
Physical and chemical properties, uses	(3 marks)	(2, 3 marks)	(3 marks)	(3 marks)		
Identification of primary, secondary and tertiary amines						
Cyanides and Isocyanides						
Diazonium salts: Preparation, chemical reactions and importance in synthetic organic chemistry.					(5 marks)	(5 marks)

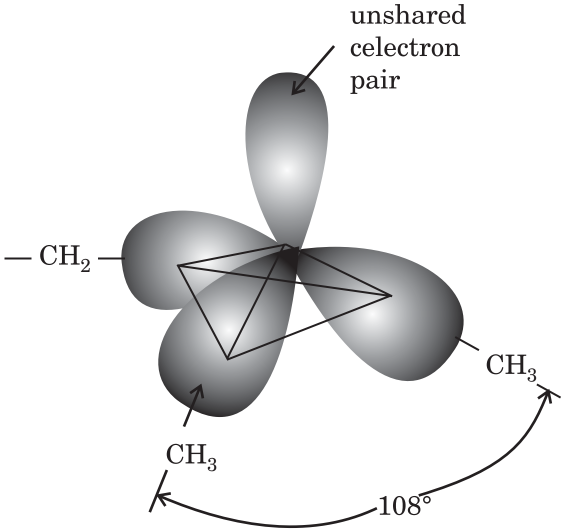
Topic 1: Introduction, Methods of Preparation and Physical Properties

Summary

- Amines: Amines can be considered as the amino derivatives of hydrocarbons or alkyl derivatives of ammonia. Amines are obtained by replacing one, two or three hydrogen atoms by alkyl and/or aryl groups. For example, $CH_3NH_2, C_2\,\mathrm{H_5NH_2}, C_6\,\mathrm{H_5NH_2}$ *etc.*
- Classification of amines:

$$\underset{\begin{array}{c}\mathrm{Pr}\,imary\\(1^o)\end{array}}{-NH_2}\qquad \underset{\begin{array}{c}Secondary\\(2^o)\end{array}}{-\overset{|}{N}H}\qquad \underset{\begin{array}{c}Tertiary\\(3^o)\end{array}}{-\overset{|}{N}-}$$

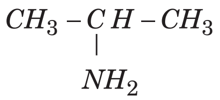
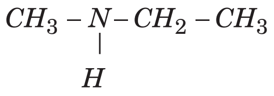
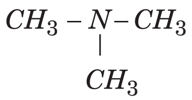
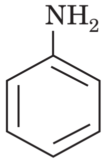
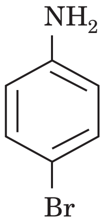
- Structure of amines:



Pyramidal shape of trimethylamine

Nitrogen orbitals in amines are sp^3 hybridised and the geometry of amines is pyramidal. The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. Due to the presence of unshared pair of electrons, the angle $C-N-E$ is less than 109.5°.

- **Nomenclature of some alkylamines and arylamines:**

Amines	**Common Names**	**IUPAC name**
$CH_3-CH_2-NH_2$	Ethylamine	Ethanamine
$CH_3-CH_2-CH_2-NH_2$	n-Propylamine	Propan-1-amine
 $CH_3-\underset{\underset{\displaystyle NH_2}{\mid}}{C}H-CH_3$	Isopropylamine	Propane-2-amine
 $CH_3-\underset{\underset{\displaystyle H}{\mid}}{N}-CH_2-CH_3$	Ethylmethylamine	N-Methylethanamine
 $CH_3-\underset{\underset{\displaystyle CH_3}{\mid}}{N}-CH_3$	Trimethylamine	N,N-Dimethylmethaneamane
	Aniline	Aniline or benzenamine
	*p*-Bromoanaline	4-Bromobenzylamine Or 4-Bromoaniline

- Preparation of Amines:

  - By reduction of nitro compounds:

$$\underset{}{R-NO_2+3H_2}\xrightarrow{Ni}\underset{1^o\,amine}{R-NH_2}+2H_2O$$

  - By ammonolysis of alkyl halides:

$$R-X+NH_3\rightarrow \underset{(1^o)}{RNH_2}\xrightarrow{RX}\underset{(2^o)}{R_2NH}\xrightarrow{RX}\underset{(3^o)}{R_3N}\xrightarrow{RX}\underset{\substack{Quaternary\\ammonium\,salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

The free amine can be obtained from the ammonium salt by treatment with a strong base:

$$R-\overset{+}{N}H_3\overset{-}{X}+NaOH\rightarrow R-NH_2+H_2O+\overset{+}{Na}\overset{-}{X}$$

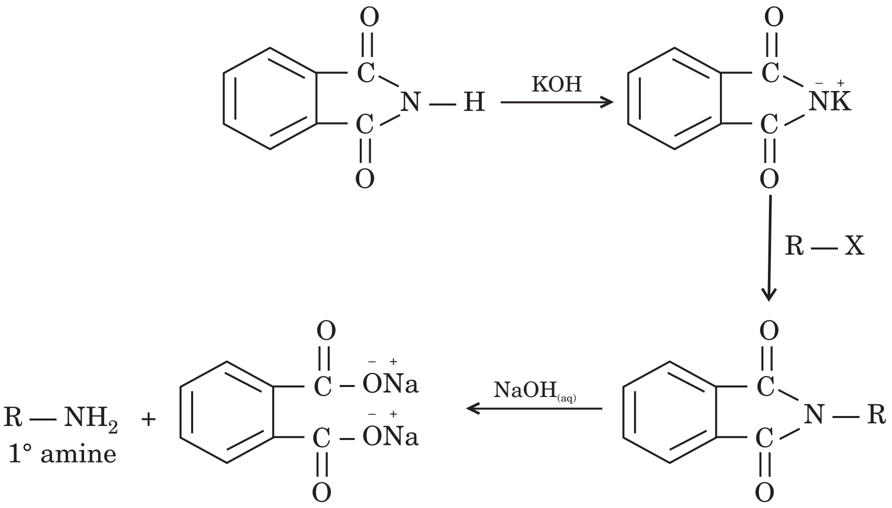
  - By reduction of nitriles:

$$2H_2+R-C\equiv N\xrightarrow{Ni}R-CH_2-NH_2$$

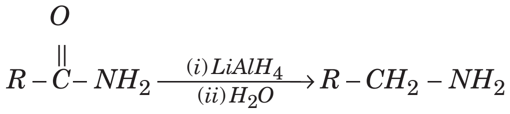
$$R-C\equiv N+4[H]\xrightarrow[\text{or LiAlH}_4]{Na(Hg)/C_2H_5OH}R-CH_2-NH_2$$

1^{o} amine

- Gabriel phthalmide synthesis:

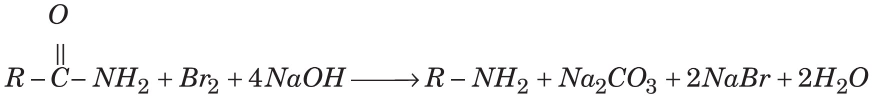


- By reduction of amides:



$$R-\overset{\overset{\displaystyle O}{||}}{C}-NH_2\xrightarrow[(ii)H_2O]{(i)LiAlH_4}R-CH_2-NH_2$$

- By Hoffmann Bromamide degradation reaction:



$$R-\overset{\overset{\displaystyle O}{||}}{C}-NH_2+Br_2+4NaOH\longrightarrow R-NH_2+Na_2CO_3+2NaBr+2H_2O$$

- Physical properties:
    - Lower members are combustible gases, members from C_3 to C_1 are volatile liquids and C_{12} onwards are gaseous. Lower aromatic amines are liquids.
    - Pure amines are colourless, although they develop colour on keeping in air for a long time.
    - With increase in molecular weight, the boiling point also increases. The order of boiling points of isomeric amines is, Primary > Secondary > Tertiary.
    - Lower members of amine are readily soluble in water. They decrease in water and increase in organic solvents with an increase in molecular weight.

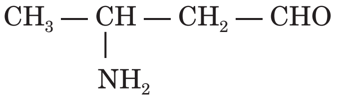
PREVIOUS YEARS'
EXAMINATION QUESTIONS
TOPIC 1

1 Mark Questions

1. Arrange the following compounds in an increasing order of their solubility in water:
$C_6H_5NH_2, (C_2H_5)_2NH, C_2H_5NH_2$
[DELHI 2011]

2. Write the structure of 2-aminotoluene.
[DELHI 2013]

3. Write the IUPAC name of the compound:



$$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_2-CHO$$

[DELHI 2014]

3 Mark Questions

4. Account for the following:
(i) Primary amines $(R-NH_2)$ have higher boiling point than tertiary amines (R_3N)
(ii) Aniline does not undergo Friedel-Crafts reaction.
(iii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. **[All INDIA 2014]**

5. State reasons for the following:
(i) pK_b value for aniline is more than that for methylamine.
(ii) Ethylamine is soluble in water whereas aniline is not soluble in water.
(iii) Primary amines have higher boiling points than tertiary amines. **[All INDIA 2011]**

6. Account for the following observations:
(i) pk_b for aniline is more than that for methylamine.
(ii) Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.
(iii) Aniline does not undergo Friedel-Crafts reaction. **CBSE 2016]**

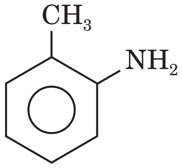
7. Give reasons for the following:
(i) Aniline does not undergo Friedel-Crafts reaction.
(ii) $(CH_3)_2$ NH is more basic than $(CH_3)_3$N in an aqueous solution.
(iii) Primary amines have higher boiling point than tertiary amines. **[All INDIA 20146**

8. In the following cases rearrange the compounds as directed:
(i) In an increasing order of basic strength:
$C_6H_5NH_2,\ C_6H_5N(CH_3)_2,\ (C_2H_5)_2NH$ and CH_3NH_2
(ii) In a decreasing order of basic strength:
Aniline, p-nitroaniline and p-toluidine
(iii) In an increasing order of pk_b values:
$C_2H_5NH_2,\ C_6H_5NHCH_3,\ (C_2H_5)_2NH$ and $C_6H_5NH_2$

Solutions

1. The more extensive the H-bonding, the higher is the solubility. $C_2H_5NH_2$ contains two H-atoms whereas $(C_2H_6)_2NH$ contains only one H-atom. Thus $C_2H_5NH_2$ undergoes more extensive H-bonding than $(C_2H_6)_2NH$. Hence, the solubility in water of $C_2H_5NH_2$ is more than that of $(C_2H_5)_2NH$.
$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$ **[1]**

2. 2-Amino toluene

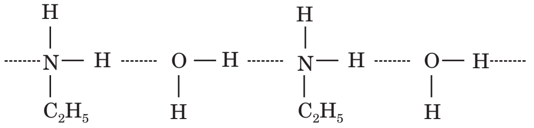


[1]

3. 3-aminebutan-1-al **[1]**

4. (i) Due to higher intermolecular hydrogen bonding in primary amines (due to presence of more number of H-atoms) primary amines have high BP in comparison to tertiary amines. **[1]**
(ii) Aniline doesn't undergo Friedel Craft Reaction because the reagent AlCl3, being e- deficient acts as lew is base and attacks on the lone pair of nitrogen present in aniline to form an insoluble complex which precipitates out and the reaction doesnt proceed. **[1]**
(iii) In $(CH_3)_3$ N there is maximum steric hindrance and least solvation but in $(CH_3)_2NH$ the solvation is more and the steric hindrance is less than in $(CH_3)_3N$; Although +I effect is less, since there are two methyl groups; di-methyl amine is still a stronger base than tri-methyl amine.

5. (i) Due to resonance in aniline, N acquires partial +ve charge which increases its pK_b whereas due to electron donating methyl group electron density increases on N which decreases its pK_b. **[1]**
(ii) Ethylamine when added to water forms intermolecular H-bonds with water. And therefore it is soluble in water.
But aniline does not form H-bond with water to a very large extent due to the presence of a large hydrophobic –C6H5 group. Hence, aniline is insoluble in water.



Ethylamine **[1]**

(iii) Due to hydrogen bonding in primary amines, they have higher boiling points whereas there is no hydrogen bonding in tertiary amines. Amines have high boiling point due to presence of hydrogen bonding between amine molecules. But the boiling point decreases with increase in alkyl groups attached to the N atom, because the number of H atoms present for hydrogen bonding decreases. **[1]**

6. (i) pk_b for aniline is more than that for methylamine because in aniline, the $–NH_2$ group is attached directly to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation and hence aniline is a weaker base than methylamine. **[1]**

(ii) Methyl amine in water gives OH ions which react with $FeCl_3$ to give precipitate of ferric hydroxide/ or

$$CH_3NH_2 + H_2O \longrightarrow CH_3NH_3^+OH^-$$

$$Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3$$

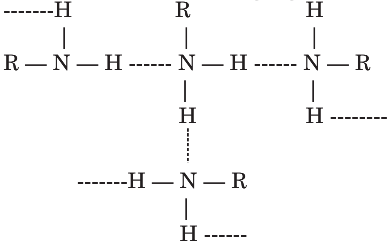
[1]

(i) Aniline forms salt with aluminium chloride, the catalyst of the Friedel—Crafts reaction. As a result, the nitrogen atom in aniline acquires a positive charge, which deactivates the group towards the reaction. Thus, aniline does not undergo the Friedel-Crafts reaction. **[1]**

7. (i) Aniline forms salt with aluminium chloride, the catalyst of the Friedel—Crafts reaction. As a result, the nitrogen atom in aniline acquires a positive charge, which deactivates the group towards the reaction. Thus, aniline does not undergo the Friedel-Crafts reaction. **[1]**

(ii) There are two factors that affect the basicity of the amines in an aqueous solution: solvation of ammonium ions and inductive effect. Inductive effect of the alkyl group is greater in $(CH_3)_3N$ than in $(CH_3)_2NH$. However, due to greater stabilisation by increased hydrogen bonding in $(CH_3)_2NH$ on solvation with water molecules, $(CH_3)_2NH$ is more basic than $(CH_3)_3N$. **[1]**

(iii) Primary amines are engaged in intermolecular association because of hydrogen bonding between nitrogen of one molecule and hydrogen of another molecule, as shown in the image given below:



On the other hand, no such interaction is possible in tertiary amines because of absence of the hydrogen atom directly attached to nitrogen. Therefore, due to stronger intermolecular forces, the boiling point of primary amines is higher than that of secondary amines. **[1]**

8. (i) In an increasing order of basic strength:

$$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$$

This is because $–C_6H_5$ group has an electron withdrawing inductive effect or -I effect and $–CH_3$ and $–C_2H_5$ group has electron releasing inductive effect or +I effect. Groups with –I effect decreases the electron density on the nitrogen of amino group and hence decreases the basic strength. Groups with +I effect increases the electron density on the nitrogen of amino group and hence increases the basic strength. **[1]**

(ii) Decreasing order of basic strength:

p- Toluidine > aniline > p- nitroaniline

This is because $–NO_2$ group has an electron withdrawing inductive effect or -I effect and $–CH_3$ group has electron releasing inductive effect or +I effect. Groups with –I effect decreases the electron density on the nitrogen of amino group and hence decreases the basic strength. Groups with +I effect increases the electron density on the nitrogen of amino group and hence increases the basic strength. **[1]**

(iii) Increasing order of pK_b value:

$$(C_2H_5)_2NH < C_2H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2$$

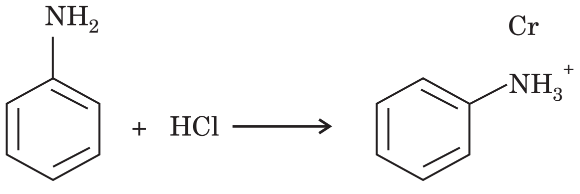
This is because $–C_6H_5$ group has an electron withdrawing inductive effect or -I effect and $–C_2H_5$ group has electron releasing inductive effect. Groups with –I effect decreases the electron density on the nitrogen of amino group and hence decreases the basic strength. Groups with +I effect increases the electron density on the nitrogen of amino group and hence increases the basic strength. Greater the basic strength the smaller is the pK_b value. **[1]**

Topic 2: Chemical Reaction of Amines and Diazonium Salts

Summary

- **Chemical properties:**
  - **Reactions due to alkyl group:**

$$R-\overset{\bullet\bullet}{N}H_2+HX \rightleftharpoons R-\overset{+}{N}H_3\,\overset{-}{X}\,(Salt)$$



Aniline Anilinium chloride

Amines, being basic in nature, react with acids to form salts. When these amine salts are treated with a base such as $NaOH$, they regenerate the parent amine.

$$\underset{\text{Amine Salts}}{R\overset{+}{N}H_3\,\overset{-}{X}}+\underset{\text{base}}{\overset{-}{O}H}\longrightarrow \underset{\text{parent amine}}{R\overset{\bullet\bullet}{N}H_2}+\ H_2O\ +\ \overset{-}{X}$$

Amine salts are soluble in water but insoluble in organic compounds like ether. This reaction helps in separating the amines from the non basic organic compounds insoluble in water.

The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. The order of basic strength in case of methyl Substituted amines and ethyl substituted amines in aqueous solution is as follows:

$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$$

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

The $-NH_2$ group is attached directly to the benzene ring in aryl amines, which results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation.

In case of substituted aniline, it is observed that electron releasing groups increase basic strength whereas electron withdrawing groups decrease it.

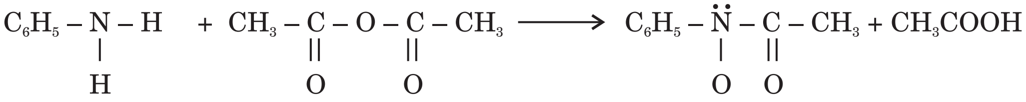
Alkylation:

$$CH_3-CH_2-NH_2\xrightarrow[-HBr]{+CH_3-CH_2-Br}(CH_3-CH_2)_2NH\xrightarrow[-HBr]{+CH_3-CH_2-Br}\underset{Triethylamine}{(CH_3-CH_2)_3}$$

$$(CH_3-CH_2)_3N\xrightarrow[-HBr]{+CH_3-CH_2-Br}\underset{\text{Tetraethyl ammonium bromide}}{(CH_3-CH_2)_4\overset{+}{N}\overset{-}{Br}}$$

Acylation:

Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophillic substitution reaction. This reaction is known acylation.



$$\underset{\text{Benzenamine}}{C_6H_5-\underset{\underset{H}{|}}{N}-H}+\underset{\text{Ethanoic anhydride}}{CH_3-\underset{\underset{O}{||}}{C}-O-\underset{\underset{O}{||}}{C}-CH_3}\longrightarrow\underset{\text{N-Phenylethanamide or Acetanilide}}{C_6H_5-\underset{\underset{O}{|}}{\overset{\bullet\bullet}{N}}-\underset{\underset{O}{||}}{C}-CH_3}+CH_3COOH$$

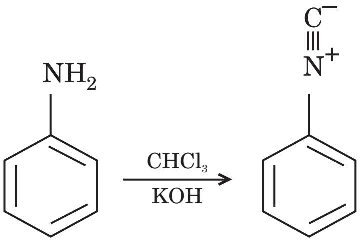
Benzenamine Ethanoic anhydride N-Phenylethanamide or Acetanilide

Benzoylation:

$$\underset{Methlamine}{CH_3NH_2}+\underset{\text{Benzoyl Chloride}}{C_6H_5COCl}\longrightarrow\underset{N-Methylbenzamide}{CH_3NHCOC_6H_5}+HCl$$

Carbylamine reaction: Secondary and tertiary amines do not give this reaction. This reaction is used as a test for primary amines.

$$R-NH_2+CHCl_3+3KOH\xrightarrow{Heat}R-NC+3KCl+3H_2O$$



Reaction with nitrous acid:

$$\underset{1^o\ amine}{R-NH_2}+HNO_2\xrightarrow{NaNO_2+HCl}\left[R-\overset{+}{N_2}\overset{-}{Cl}\right]\xrightarrow{H_2O}ROH+N_2+HCl$$

$$\underset{2^o\ amine}{R_2NH}+HNO_2\longrightarrow\underset{\text{N-Nitrosamine}}{R_2N-N=O}+H_2O$$

$$R_3N + HNO_2 \longrightarrow R_3NHNO_2$$

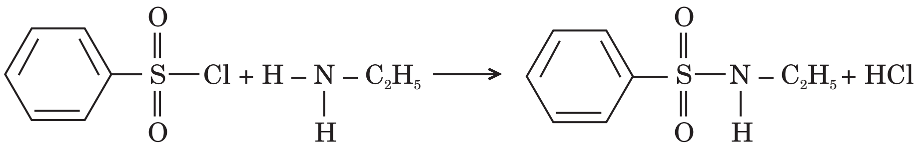
3^o amine Trialkyl ammonium nitrite

$$C_6H_5 - NH_2 \xrightarrow[273\text{–}278k]{NaNO_2+2HCl} C_6H_5 - \overset{+}{N_2}\overset{-}{Cl} + NaCl + 2H_2O$$

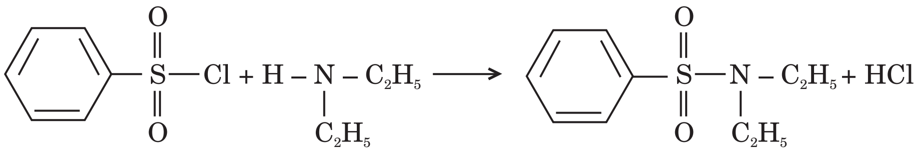
Aromatic amine Benzenediazonium chloride

Secondary and tertiary amines react with nitrous acid in a different manner.

Reaction with arylsulphonyl chloride:



N-Ethylbenzenesulphonamide
(soluble in alkali)

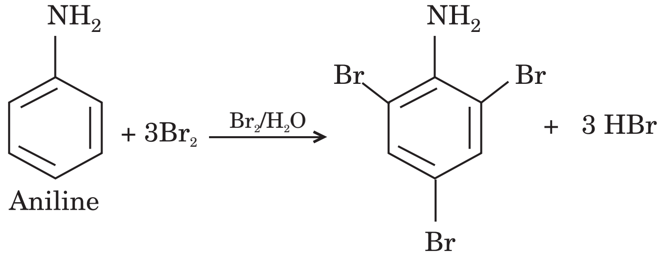


N, N-Diethylbenzenesulphonamide

Tertiary amines do not react with benzenesulphonyl chloride and therefore, benzenesulphonyl chloride is used to differentiate between primary, secondary and tertiary amines.

Bromination:

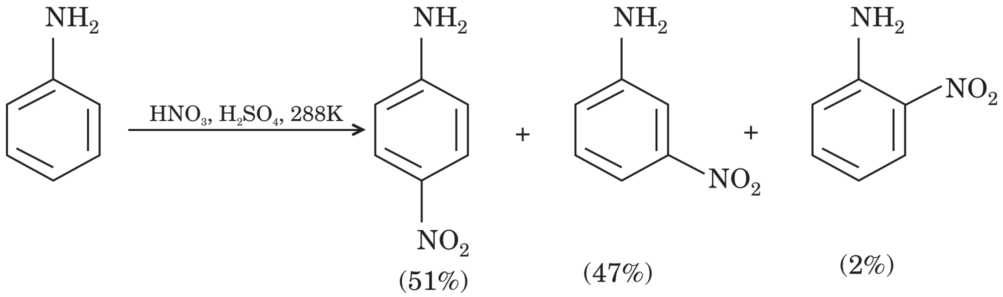
Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoanaline.



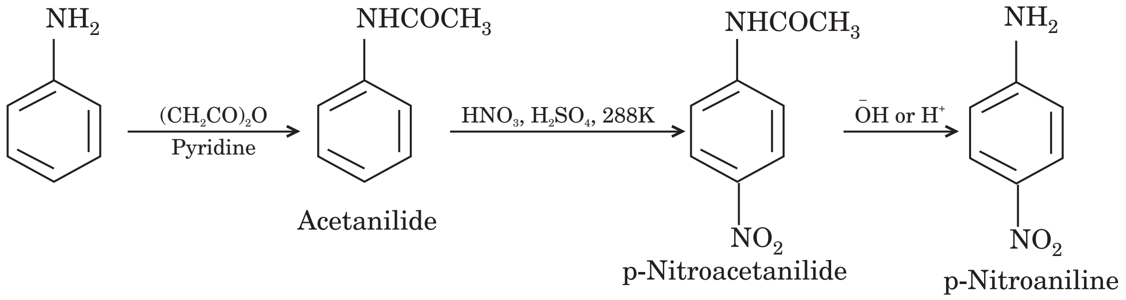
2, 4, 6- Tribromoaniline

Nitration:

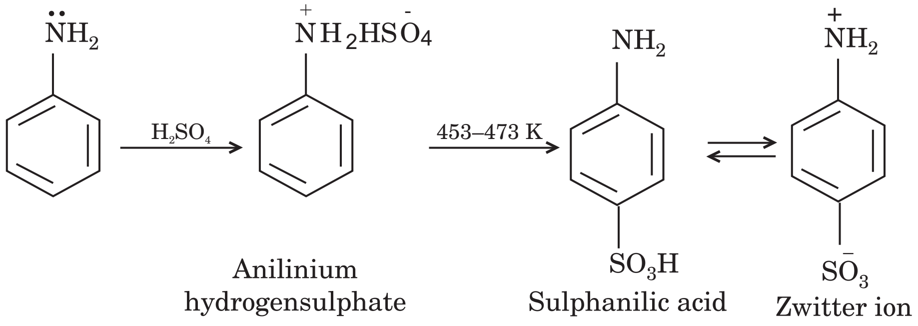
Direct nitration of aniline yields nitro derivatives.



Preparation of monosubstituted aniline derivative by acetylation of group:



Sulphonation:



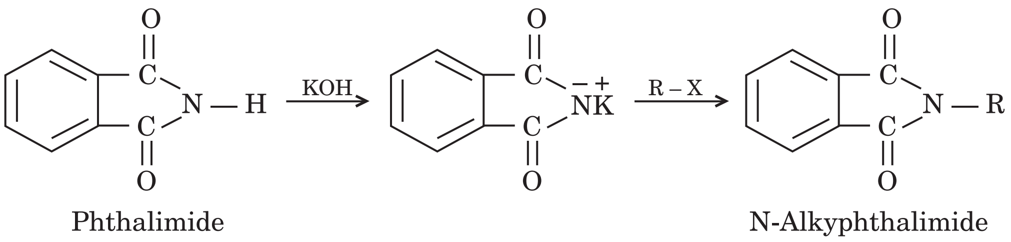
Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride.

Ammonolysis:

Alkyl halide reacts with ammonia to form primary amine. The reaction of ammonia with alkyl halide is known as ammonolysis.

$$C_2H_5I \xrightarrow{NH_3/343K} C_2H_5NH_2 \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_2 NH \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_3 N \xrightarrow[-HI]{C_2H_5I} \left[(C_2H_5)_4 \overset{+}{N}\right]\overset{-}{I}$$

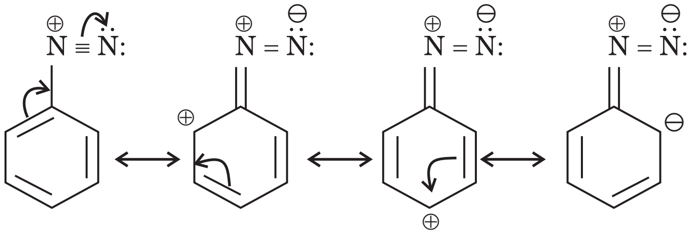
Gabriel Phthalimide Synthesis: In Gabriel phthalimide synthesis, phthalimide reacts with alcoholic KOH to get potassium phthalimide which reacts with alkyl halide to form N-alkyl phthalimide which on basic hydrolysis gives primary amine and phthalic acid.



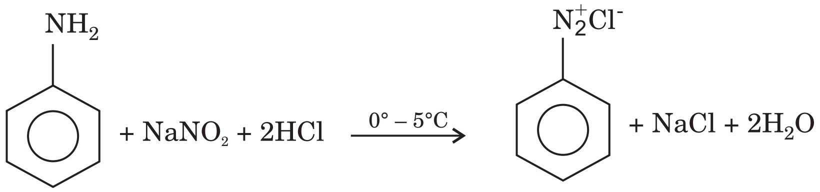
Friedel-Crafts reaction: Aniline does not undergo Friedel-Crafts reaction as it forms a salt with $AlCl_3$ which is a Lewis acid.

- **Diazonium salts:**

  - **General formula:** $R\overset{+}{N_2}\overset{-}{X}$, where R stands for an aryl group and $\overset{-}{X}$ ion may be for halides
  - **Stability of diazonium salts:** Primary aliphatic amines are highly unstable alkyldiazonium salts. Arenediazonium salts, made up of primary aromatic amines are more stable than alkyl diazonium slts due to the dispersal of the positive charge over the benzene ring.



  - **Preparation of diazonium salts:**



Benzene diazonium

  - **Chemical properties:**

Reactions involving displacement of nitrogen:

Replacement by halide or cyanide ion-

$$\mathrm{Ar\overset{+}{N}_2\overset{-}{X}}\;\begin{array}{l}\xrightarrow{\mathrm{CuCl/HCl}} \mathrm{ArCl + N_2}\\ \xrightarrow{\mathrm{CuBr/HBr}} \mathrm{ArBr + N_2}\\ \xrightarrow{\mathrm{CuCN/KCN}} \mathrm{ArCN + N_2}\end{array}$$

Sandmeyer reaction

$$\mathrm{Ar\overset{+}{N}_2\overset{-}{X}}\;\begin{array}{l}\xrightarrow{\mathrm{Cu/HCl}} \mathrm{ArCl + N_2 + CuX}\\ \xrightarrow{\mathrm{Cu/HBr}} \mathrm{ArBr + N_2 + CuX}\end{array}$$

Gatterman's reaction

Replacement by iodide ion-

$$\underset{\substack{\text{Benzene}\\ \text{diazonium}\\ \text{chloride}}}{Ar\overset{+}{N_2}\overset{-}{Cl}} + KI \longrightarrow \underset{\text{Iodobenzene}}{ArI} + KCI + N_2$$

Replacement by fluoride ion-

$$Ar\overset{+}{N_2}\overset{-}{Cl} + HBF_4 \longrightarrow Ar\overset{+}{N_2}\overset{-}{BF_4}$$

$$Ar\overset{+}{N_2}\overset{-}{BF_4} \xrightarrow{\Delta} Ar-F+BF_3+N_2$$

Replacement by H-

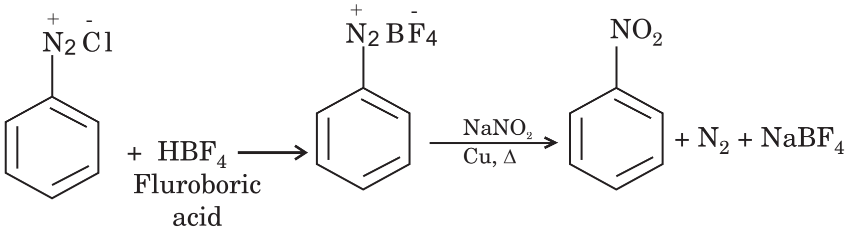
$$Ar\overset{+}{N_2}\overset{-}{Cl}+H_3PO_2+H_2O \longrightarrow ArH+N_2+H_3PO_3+HCl$$

$$Ar\overset{+}{N_2}\overset{-}{Cl}+CH_3CH_2OH \longrightarrow ArH+N_2+CH_3CHO+HCl$$

Replacement by hydroxyl group-

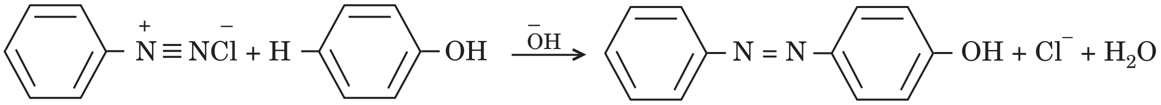
$$Ar\overset{+}{N_2}\overset{-}{Cl}+H_2O \xrightarrow{\Delta} \underset{Phenol}{ArOH}+N_2+HCl$$

Replacement by $-NO_2$ group-

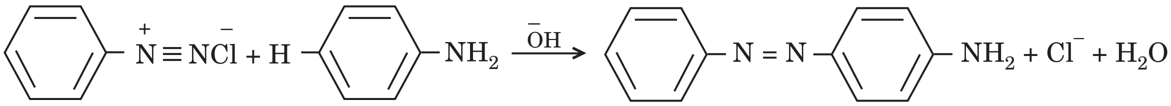


Reactions involving retention of diazo group:

Coupling reaction: The reaction of diazonium salts with phenols and aromatic amines to form azo compounds with the general formula, $Ar-N=N\,Ar$ is known as coupling reaction.



p-Hydroxyazobenzene (orange dye)



p-Aminoazobenzene (yellow dye)

- Importance of Diazonium salts: They are very good intermediates for the introduction of *–F, –Cl, Br, – I, – CN, OH, OH, NO*$_2$ groups into aromatic ring. Cyanobenzene can be prepared from diazonium salts.

- **Synthesis of organic compounds from diazonium salts:**

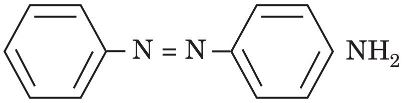
$$C_6H_5N_2Cl \xrightarrow{CH_3CH_2OH} C_6H_6$$

$$C_6H_5N_2Cl \xrightarrow{H_2O} C_6H_5OH$$

$$C_6H_5N_2Cl \xrightarrow{HBF_4} C_6H_5F$$

$$C_6H_5N_2Cl \xrightarrow{C_6H_6 / NaOH} C_6H_5C_6H_5$$

$$C_6H_5N_2Cl \xrightarrow{C_6H_5NH_2 / acid}$$



- Identification of primary, secondary and tertiary amines:

Test	Primary amine	Secondary amine	Tertiary amine
Reaction with nitrous acid.	Gives alcohol with effervescence of N_2 gas.	Gives only nitrosoamine which gives Liebermann's nitrosoamine test.	Forms nitrite in cold soluble in water and on heating gives nitrosoamine.
Recation with benzene sulphonyl chloride (Hiesenberg's reagent).	Gives N-alkyl benzene-sulphonamide which is soluble in alkali.	Gives N, N-dialkyl benzene sulphonamide which is insoluble in alkali.	No reaction.
Carbylamine test: Reaction with chloroform and alcoholic KOH.	Forms carbylamines or isocyanide (RNC) with characteristic unpleasant odour.	No reaction.	No reaction.
Hoffman's Mustard oil reaction: Recation with CS_2 and $HgCl_2$.	Forms N-substituted isotiocyanate with characteristic unpleasant smell of mustard oil.	No reaction.	No reaction.

PREVIOUS YEARS'
EXAMINATION QUESTIONS
TOPIC 2

1 Mark Questions

1. Rearrange the following in an increasing order of their basic strength
$C_6H_5NH_2, C_6H_5N\left(CH_3\right)_2, \left(C_6H_5\right)_2NH$ and CH_3NH_2. **[All INDIA 2011]**

2. Arrange the following in the decreasing order of their basic strength in aqueous solution. **[All INDIA 2012]**

3. Question: Arrange the following in increasing order of their basic strength in aqueous solution:

$CH_3NH_2,\ \left(CH_3\right)_3N,\ \left(CH_3\right)_2NH$

[DELHI 2013]

4. The conversion of primary aromatic amines into diazonium salts is known as________ **[All INDIA 2014]**

2 Marks Questions

5. Write the chemical equation involved in the following reactions:
(i) Hoffmann-bromamide degradation reaction
(ii) Carbylamine reaction **[All INDIA 2016]**

3 Marks Questions

6. Write the structures of compounds A, B and C in the following reactions :

(a) $CH_3-COOH \xrightarrow{NH_3/\Delta} A \xrightarrow{Br_2/KOH(aq)} B \xrightarrow{CHCl_3+alc.KOH} C$

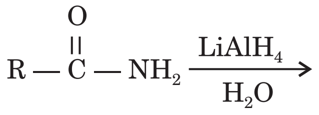
(b) $C_6H_5N_2{}^+BF_4{}^- \xrightarrow{NaNO_2/Cu/\Delta} A \xrightarrow{Fe/HCL} B \xrightarrow{CH_3COCl/Pyridine} C$

[DELHI 2017]

7. Complete the following chemical equations:

(i) $CH_3CH_2Cl \xrightarrow{NaCN} (A) \xrightarrow{reduction,\ Ni/H_2} (B)$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(iii)

$R-\overset{\overset{\large O}{||}}{C}-NH_2 \xrightarrow[H_2O]{LiAlH_4}$ **[DELHI 2011]**

8. (a) Explain why an alkylamine is more basic than ammonia?
(b) How would you convert?
(i) Aniline to nitrobenzene
(ii)Aniline to iodobenzene **[DELHI 2011]**

9. Write chemical equations for the following conversions:
(i) Nitrobenzene to benzoic acid.
(ii) Benzyl chloride to 2-phenylethanamine
(iii)Aniline to benzyl alcohol **[All INDIA 2012]**

10. Give the structures of products A, B and C in the following reactions:

(i) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_3,0°C} C$

(ii) $CH_3COOH \xrightarrow{NH_3} A \xrightarrow{NaOH+Br_2} B \xrightarrow{CHCl_3+Alc.KOH} C$ [DELHI 2013]

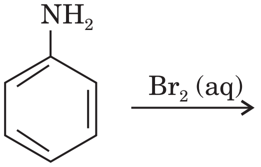
11. Give the structures of A, B and C in the following reactions:

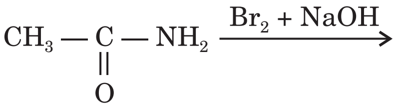
(i) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(ii) $C_6H_5NO_2 \xrightarrow{Sn+HCl} A \xrightarrow[273K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$ **[All INDIA 2014]**

12. Write the main products of the following reaction?

(i) $C_6H_5N_2^+Cl^- \xrightarrow{H_3PO_2+H_2O}$

(ii)


(iii)

$CH_3-\underset{\underset{\large O}{||}}{C}-NH_2 \xrightarrow{Br_2+NaOH}$

[All INDIA 2013]

13. Give the structures of A, B and C in the following reactions:

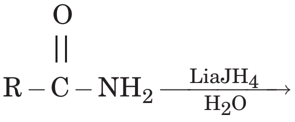
(i) $CH_3Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_2,273K} C$

(ii) $CH_3COOH \xrightarrow{NH_2,\Delta} A \xrightarrow{Br_2+KOH} B \xrightarrow{CHCl_3+NaOH} C$

OR

How will you convert the following?
(i) Nitrobezene into aniline.
(ii) Ethanoic acid into methanamine.
(iii)Aniline into N-phenylethanamide.
(Write the chemical equations involved.)
[DELHI 2014]

14. Complete the following reaction equations:

(i)

$R-\overset{\overset{\large O}{||}}{C}-NH_2 \xrightarrow[H_2O]{LiaJH_4}$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(iii) $C_6H_5NH_2 + Br_2(aq) \longrightarrow$ **[DELHI 2017]**

15. Give reasons for the following:

(a) Acetylation of aniline reduces its activation effect.

(b) CH_3NH_2 is more basic than $C_6H_5NH_2$.

(c) Although $-NH_2$ is o/p directing group, yet aniline on nitration gives a significant amount of m-nitroaniline.

[All INDIA 2017]

5 Mark Questions

16. An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions.

$$\begin{tikzcd}(C_7H_7ON)A \arrow[r, "Br_2/KOH"] & C_6H_5NH_2 \arrow[r, "NaNO_2 + HCl", "273\ K"'] \arrow[d, "CHCl_3 + NaOH"] & H \arrow[r, "CH_3CH_2OH"] \arrow[d, "KI"] & C \\ & D & E & \end{tikzcd}$$

OR

(a) Write the structures of main products when aniline reacts with the following reagents:

(i) Br_2 water

(ii) HCl

(iii) $(CH_3CO)_2O$ /pyridine.

(b) Arrange the following in the increasing order of their boiling point:

$C_2H_5NH_2,\ C_2H_5OH,\ (CH_3)_3N$

(c) Give a simple chemical test to distinguish between the following pair of compounds:

$(CH_3)_2NH$ and $(CH_3)_3N$. **[DELHI 2015]**

17. (a) Write the reactions involved in the following:

(i) Hofmann bromamide degradation reaction

(ii) Diazotisation

(iii) Gabriel phthalamide synthesis

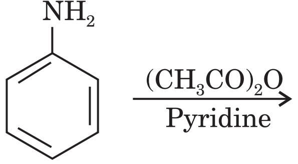
(b) Give reasons:

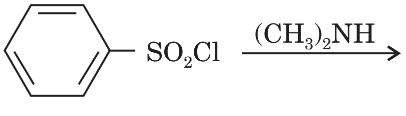
(i) $(CH_6)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.

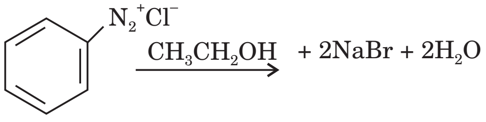
(ii) Aromatic diazonium salts are more stable than aliphatic diazonium salts.

OR

(a) Write the structures of the main products of the following reactions:

(i) 

(ii) 

(iii) 

(b) Give a simple chemical test to distinguish between Aniline and N,N-dimethylaniline.

(c) Arrange the following in the increasing order of their pK_b values:

$C_6H_5NH_2, C_2H_5NH_2, C_6H_5NHCH_3$

[All INDIA 2018]

Solutions

1. $(C_6H_5)_2NH < C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2$ **[1]**

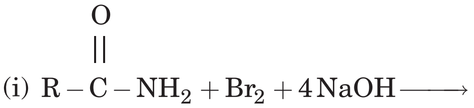
2. Better the solvation by hydrogen bonding, higher will be the basic strength.

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ **[1]**

3. $(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$ **[1]**

3°amine 1°amine 2°amine

4. Diazotisation Reaction **[1]**

5. (i) 

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow$$

$R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$ **[1]**

(ii) $R-NH_2 + CHCl_3 + 3KOH(Alc.) \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$

[1]

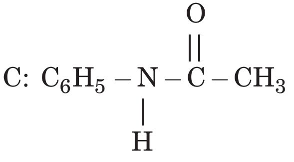
6. (a) A: CH_3CONH_2 (Ethanamide) **[½]**

B: CH_3NH_2(Methenamine) **[½]**

C: CH_3NC (Methyl isocyanide)

(b) A: $C_6H_5NO_2$ (Nitrobenzene) **[½]**

B: $C_6H_5NH_2$ (Aniline)

C: 

$$C_6H_5-\underset{\underset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$ **[½]**

N-Phenylethanamide

7. (i) $CH_3CH_2Cl \xrightarrow{NaCN} CH_3-CH_2-C\equiv N$

Chloroethane Propanenitrile

$\xrightarrow{Reduction} CH_3-CH_2-CH_2-NH_2$

Propan-1-amine

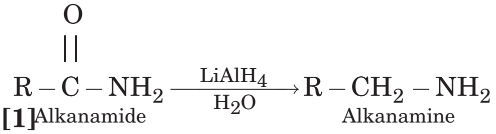
(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$ **[1]**

Benzene diazonium chloride

$C_6H_6 + N_2 + H_3PO_3 + HCl$

Benzene

[1]

(iii) 

$$R-\overset{\overset{\large O}{||}}{C}-NH_2 \xrightarrow[H_2O]{LiAlH_4} R-CH_2-NH_2$$

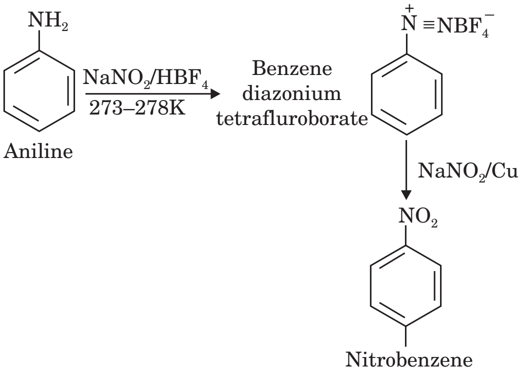
Alkanamide Alkanamine

[1]

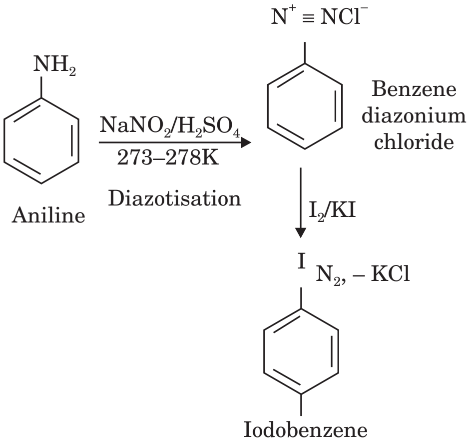
8. (a) Alkyl groups are electron donating groups and increase the electron density on nitrogen in alkylamine making them more basic than ammonia. **[1]**

(b) (i) $C_6H_5^-NH_2 \xrightarrow[HCl]{NaNO_2} C_6H_5N_2^+Cl^-$

$\xrightarrow{NaNO_2} C_6H_5NO_2$



[1]

(ii) 

[1]

9. (i) $(C_6H_5NO_2) \xrightarrow[BaSO_4]{H_2/Pd} C_6H_5^-NH_2 \xrightarrow[HCl]{NaNO_2}$

(Nitobenzene) Aniline

$C_6H_5^-N_2^+Cl^- \xrightarrow{CuCN} C_6H_5-CN$

Benzenediazonium chloride Benzonitrile

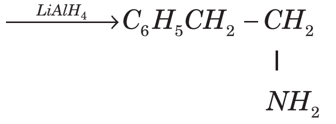
$\xrightarrow[H^+]{H_2O} C_6H_5COOH$

Benzoic acid

[1]

(ii) $C_6H_5-CH_2Cl+KCN \longrightarrow C_6H_5-CH_2-CN$

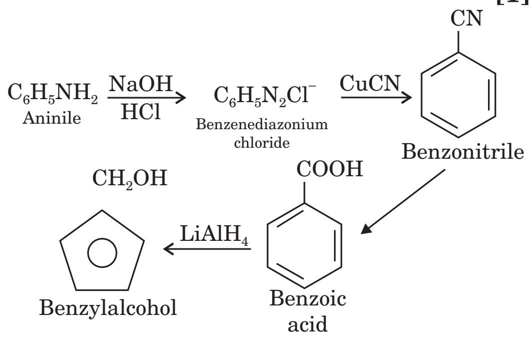
Benzylchloride Phenylethanenitrile



$$\xrightarrow{LiAlH_4} \underset{\underset{\displaystyle NH_2}{|}}{C_6H_5CH_2-CH_2}$$

2-phenylethanamine

[1]

(iii) 

[1]

10. (i) $CH_3CH_2Br \xrightarrow{KCN} CH_3CH_2CN \xrightarrow{LiAlH_4}$

$CH_3CH_2CH_2NH_2 \xrightarrow{HNO_3,0°C} CH_3CH_2CH_2OH$

[1½]

(ii) $CH_3COOH \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow{NaOH+Br_2}$

$CH_3NH_2 \xrightarrow{CHCl_3+Alc.KOH} CH_3NC$

[1½]

11. (i) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} C_6H_5CN \xrightarrow{H_2O/H^+}$

Benzene diazonium chloride (A) Benzonitrile

[1½]

$C_6H_5COOH \xrightarrow[\Delta]{NH_3} C_6H_5COO^-NH_4^+$

(B) Benzoic acid Ammonium benzoate

$\xrightarrow{\Delta} C_6H_5CONH_2$

(C)

Benzamide

[1]

(ii) $C_6H_5NO_2 \xrightarrow{Sn+HCl} C_6H_5NH_2 \xrightarrow[273K]{NaNO_2+HCl}$

(A)

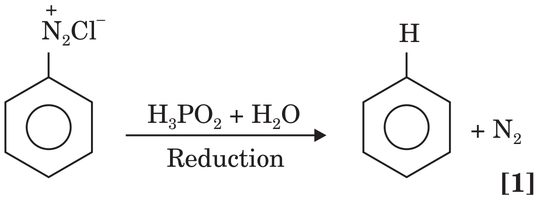
Aniline

$C_6H_5N^+ \equiv NCl^- \xrightarrow[\Delta]{H_2O/H^+} C_6H_5OH$

(B) Benzene diazonium chloride (C) Phenol

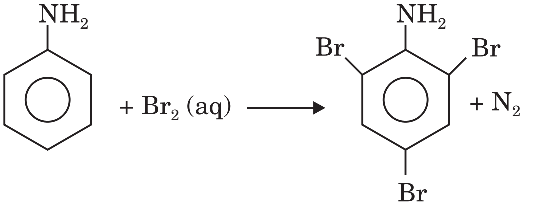
[1½]

12. (i)



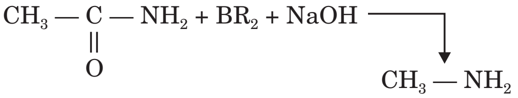
[1]

(ii)



[1]

(iii)



$$CH_3 - \underset{\underset{O}{\parallel}}{C} - NH_2 + BR_2 + NaOH \longrightarrow CH_3 - NH_2$$

[1]

13. (i)

$$CH_3Br \xrightarrow{KCN} \underset{\text{(A)}}{CH_3CN} \xrightarrow{LiAlH_4} \underset{\text{(B)}}{CH_3CH_2NH_2}$$

Ethanenitrile Ethaneamine

$$\xrightarrow[273K]{HNO_2} \underset{\text{(C)}}{C_2H_5OH} + N_2 + HCl$$

Ethanol

[1½]

(ii)

$$CH_3COOH \xrightarrow{NH_3} \underset{\text{(A)}}{CH_3CONH_2} \xrightarrow{Br+KOH}$$

Ethanamide

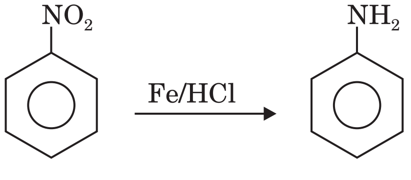
$$\underset{\text{(B)}}{CH_3NH_2} \xrightarrow{CHCl_3+NaOH} \underset{\text{(C)}}{CH_3NC}$$

Methanamine Methyl isonitrite

[1½]

OR

(i) Nitobenzene to Aniline



[1]

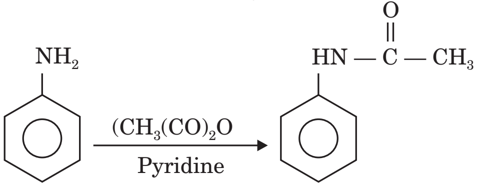
(ii) Ethanoic acid into methanamine

$$CH_3COOH \xrightarrow[\Delta]{NH_3} CH_3CONH_2$$

$$\xrightarrow[NaOH]{Br_2} CH_3NH_2$$

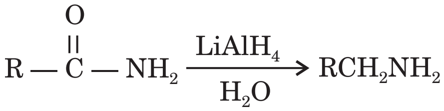
[1]

(iii)Aniline into N-Phenylethanamide



[1]

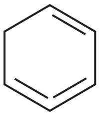
14. (a)



$$R - \overset{\overset{O}{\parallel}}{C} - NH_2 \xrightarrow[H_2O]{LiAlH_4} RCH_2NH_2$$

[1]

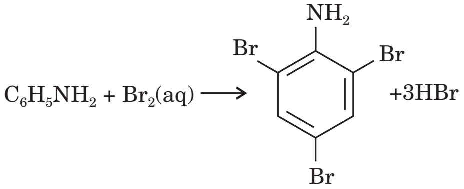
(b) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$



$+ N_2 + H_3PO_3 + HCl$

[1]

(c)



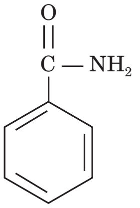
[1]

15. (a) Because acetylation of aniline is result in decrease of electron density on nitrogen so activation effect reduces. **[1]**

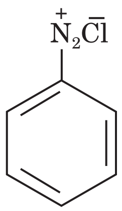
(b) CH_3NH_2 is more basic than $C_6H_5NH_2$ because of positive I effect. **[1]**

(c) Although amino group is o, p- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing). For this reason, aniline on nitration gives a substantial amount of m-nitroaniline. **[1]**

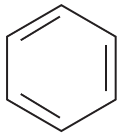
16. (A) **[1]**



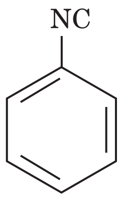
Benzamide



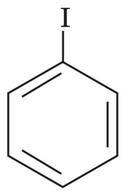
(B) Benzene diazonium chloride **[1]**



(C) Benzene **[1]**



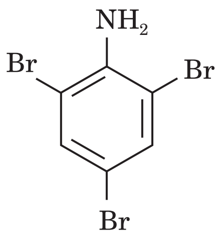
(D) Phenylisocyanide **[1]**



(E) Iodobenzene **[1]**

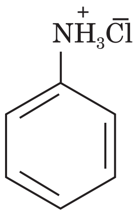
OR

(a) (i) **[1]**



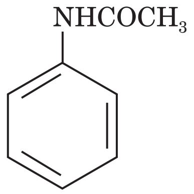
2, 4, 6-Tribromo aniline

(ii) **[1]**



Anilinium Chloride

(iii) **[1]**



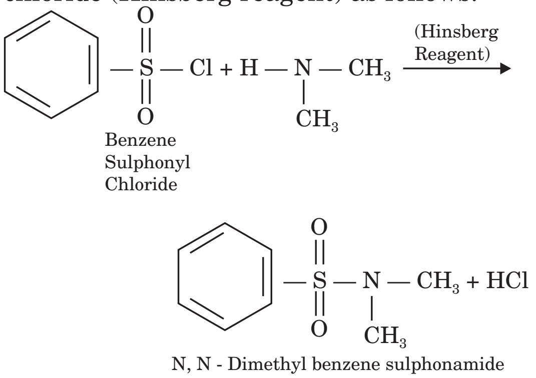
Acetanilide

(b) Ethanol has high boiling point than ethylamine because oxygen being more electronegative forms strong extensive hydrogen bond as compared to that of nitrogen. In trimethylamine there is no hydrogen and hence has the lowest boiling point.

Increasing order of boiling point:

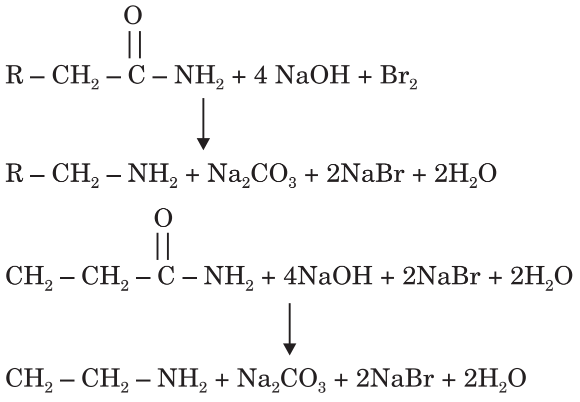
$(CH_3)_3 N < C_2H_5NH_2 < C_2H_5OH$ **[1]**

(c) $(CH_3)_2NH$ reacts with benzene sulphonyl chloride (Hinsberg reagent) as follows:



$(CH_3)_3N$ does not react with benzene sulphonyl chloride. **[1]**

17. (a) (i)

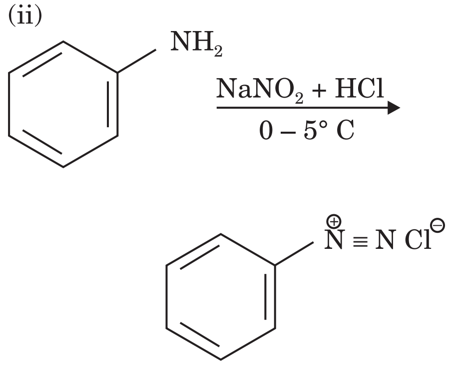


$$R-CH_2-\overset{O}{\overset{||}{C}}-NH_2 + 4\,NaOH + Br_2 \downarrow R-CH_2-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

$$CH_2-CH_2-\overset{O}{\overset{||}{C}}-NH_2 + 4NaOH + 2NaBr + 2H_2O \downarrow CH_2-CH_2-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

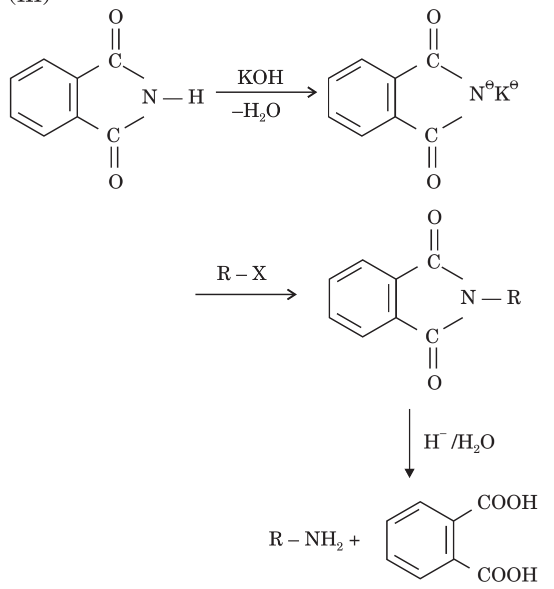
[1]

(ii)



[1]

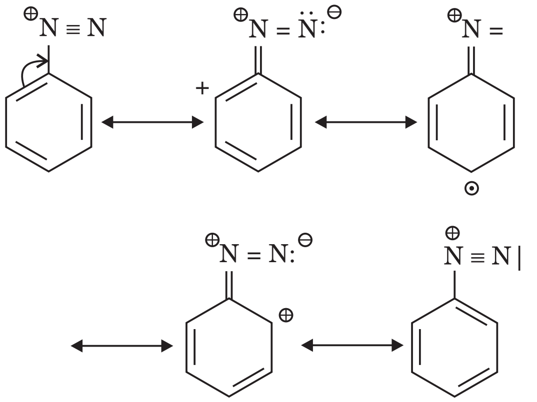
(iii)



[1]

(b) (i) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution because Amine will accept a proton and form cation. This cation will be stabilized in water by salvation (by hydrogen bonding). Better the salvation by hydrogen bonding, higher will be the basic strength. Thus with increase in methyl group, hydrogen bonding and stabilization by salvation decreases. The net effect is when we move from secondary to tertiary amine basic strength actually decreases. **[1]**

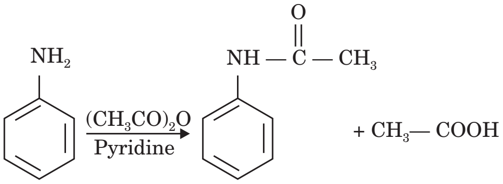
(ii) **Aromatic** diazonium salt sares table due to the dispersed of positive charge over the benzenering. The diazonium ion undergoes resonance.This resonance accounts for the stability of the diazoniumion.Hence,diazonium salts of aromatic amines are more stable than those of aliphatic amines.



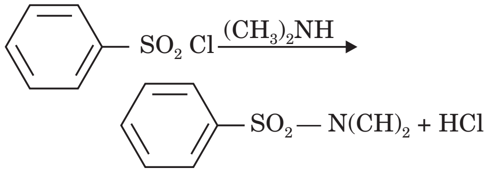
Dispersal of charge is not possible in aliphatic diazonium salts. **[1]**

OR

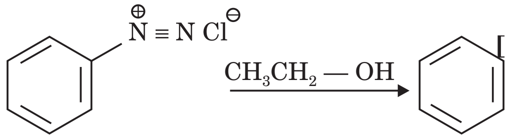
(a) (i)



(ii)

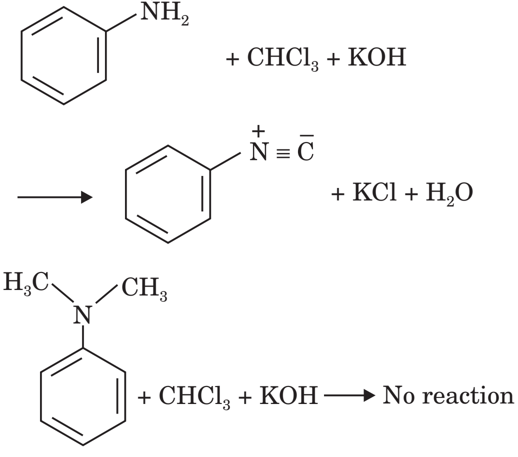


(iii)



[1]

(b) Aniline and N,N-dimethylaniline can be distinguished using the Carbylamine test. Primary amines, on heating with chloroform and ethanolic potassium hydroxide, form foul-smelling isocyanides or carbylamines. Aniline, being an aromatic primary amine, gives positive carbylamine test. However, N,N-dimethylaniline, does not react. **[1]**



[1 + 1]

(c) $C_2H_5NH_2 < C_6H_5NH_2 < C_6H_5NHCH_3$ **[1]**

Smart Notes ....

CHAPTER 14

Biomolecules

Chapter Analysis with respect to Last 3 Years' Board Exams

List of Topics	**2016**		**2017**		**2018**	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Carbohydrates - Classification (aldoses and ketoses), monosaccahrides (glucose and fructose)						
D-L configuration oligosaccharides (sucrose, lactose, maltose)						
Polysaccharides (starch, cellulose, glycogen) importance				(3 marks)	(3 marks)	(3 marks)
Proteins - Elementary idea of α - amino acids, peptide bond, polypeptides, proteins			(3 marks)	(4 marks)	(3 marks)	(3 marks)
Structure of proteins - primary, secondary, tertiary structure and quaternary structures (qualitative idea only)						
Denaturation of proteins; enzymes. Hormones - Elementary idea excluding structure.						
Vitamins - Classification and functions						
Nucleic Acids: DNA and RNA			(2 marks)			

Topic 1: Carbohydrates

Summary

- There are various complex biomolecules of which living systems are made up of. These biomolecules include carbohydrates, proteins, nucleic acids, lipids etc.
- Carbohydrates are primarily produced by plants and most of them have general formula, $C_x(H_2O)_y$. Example: the molecular formula of glucose is ($C_6H_{12}O_6$). Carbohydrates are classified into three groups on the basis of their behaviour on hydrolysis:
  - ➢ **Monosaccharides:** A carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone. Example: glucose, fructose etc.
  - ➢ **Oligosaccharides:** A carbohydrate that yields two to ten units of monosaccharide units on hydrolysis. The most common oligosaccharides are disaccharides. The two monosaccharides units obtained on hydrolysis of a disaccharide may be same or different. Example: Sucrose of hydrolysis gives one molecule of glucose and one molecule of fructose whereas maltose of hydrolysis gives two molecules of glucose only.
  - ➢ **Polysaccharides :** These are the carbohydrates which yield a large number of monosaccharide units on hydrolysis. Example: Starch, cellulose etc. They are also called non-sugars.
- The carbohydrates which reduce Fehling's solution and Tollen's reagent are called **reducing sugars.** Example: Maltose.
- If the reducing group of monosaccharides i.e. aldehydic or ketonic groups are bonded they are called **non-reducing sugars.** Example: Sucrose.
- **Glucose:**

Preparation of glucose:

- From Sucrose: WhenSucrose is boiled with dilute HCl or H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equal amounts.

$$\underset{\text{Sucrose}}{C_2H_{22}0_{11}} + H_20 \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_20_6} + \underset{\text{Fructose}}{C_6H_20_6}$$

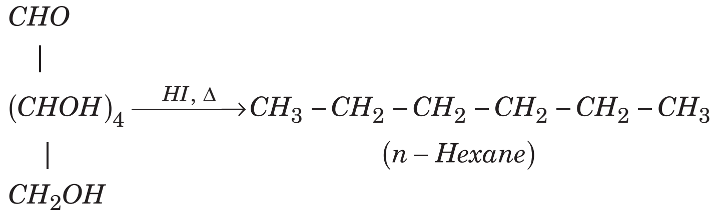
- **From starch:** Hydrolysis of starch by boiling it with dilute H_2SO_4 at 393 K under pressure.

$$\underset{\text{Satch or cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[393K;\ 2\text{–}3\ atm]{H^+} \underset{\text{Glucose}}{\mathrm{n}C_6H_{12}O_6}$$

Structure of Glucose:

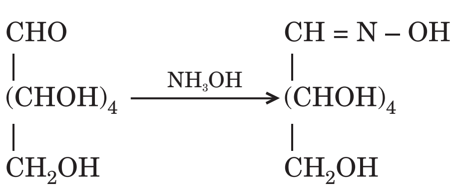
Glucose is also called dextrose. It is a monomer of many larger carbohydrates. The structure of glucose was assigned on the basis of the following facts:

- ➢ The molecular formula was found to be $C_6H_{12}O_6$.
- ➢ Prolonged heating of glucose with HI forms n-Hexane.

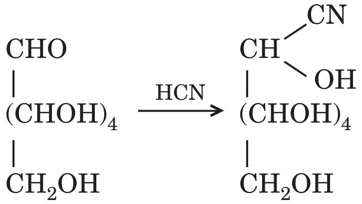


$$\begin{array}{l} CHO \\ \mid \\ (CHOH)_4 \\ \mid \\ CH_2OH \end{array} \xrightarrow{HI,\ \Delta} \underset{(n-Hexane)}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_3}$$

- ➢ Glucose on reacting with hydroxylamine forms an oxime and adds molecule of hydrogen cyanide to give cyanohydrin. This confirms the presence of carbonyl group in glucose.

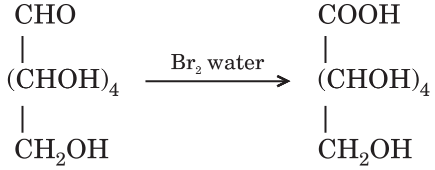


$$\begin{array}{l} \mathrm{CHO} \\ \mid \\ \mathrm{(CHOH)_4} \\ \mid \\ \mathrm{CH_2OH} \end{array} \xrightarrow{\mathrm{NH_3OH}} \begin{array}{l} \mathrm{CH=N-OH} \\ \mid \\ \mathrm{(CHOH)_4} \\ \mid \\ \mathrm{CH_2OH} \end{array}$$



$$\begin{array}{l} \mathrm{CHO} \\ \mid \\ \mathrm{(CHOH)_4} \\ \mid \\ \mathrm{CH_2OH} \end{array} \xrightarrow{\mathrm{HCN}} \begin{array}{l} \mathrm{CH}\begin{smallmatrix} \diagup \mathrm{CN} \\ \diagdown \mathrm{OH} \end{smallmatrix} \\ \mid \\ \mathrm{(CHOH)_4} \\ \mid \\ \mathrm{CH_2OH} \end{array}$$

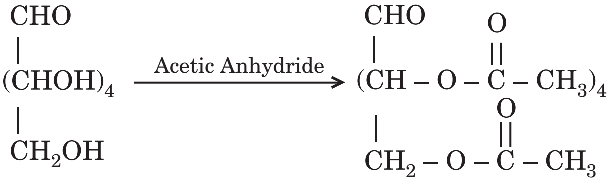
- ➢ On reacting with mild oxidizing agent like bromine water it oxidise to six carbon carboxylic acid. This indicates the presence of carbonyl group as an aldehydic group.



$$\begin{array}{l} \mathrm{CHO} \\ \mid \\ \mathrm{(CHOH)_4} \\ \mid \\ \mathrm{CH_2OH} \end{array} \xrightarrow{\mathrm{Br_2\ water}} \begin{array}{l} \mathrm{COOH} \\ \mid \\ \mathrm{(CHOH)_4} \\ \mid \\ \mathrm{CH_2OH} \end{array}$$

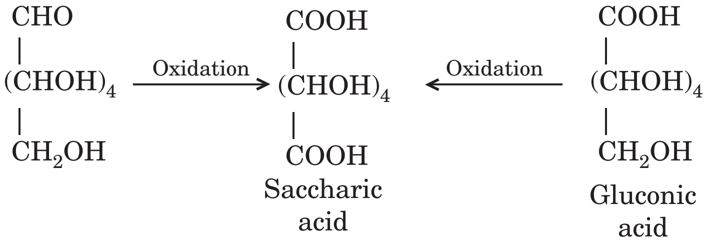
Gluconic acid

- ➢ To confirm the presence of five –OH groups glucose is acetylated with acetic anhydride to give glucose pentaacetate.



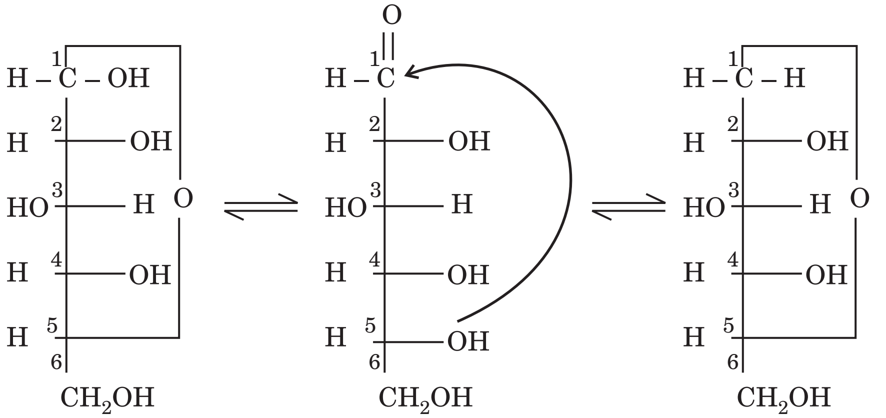
$$\begin{array}{l} \mathrm{CHO} \\ \mid \\ \mathrm{(CHOH)_4} \\ \mid \\ \mathrm{CH_2OH} \end{array} \xrightarrow{\text{Acetic Anhydride}} \begin{array}{l} \mathrm{CHO} \\ \mid \\ \mathrm{(CH-O-\overset{\overset{\displaystyle O}{\parallel}}{C}-CH_3)_4} \\ \mid \\ \mathrm{CH_2-O-\overset{\overset{\displaystyle O}{\parallel}}{C}-CH_3} \end{array}$$

- To indicate the presence of a primary alcoholic (-OH) group in glucose, glucose as well as gluconic acid are both oxidized with nitric acid to yield dicarboxylic acid, saccharic acid.



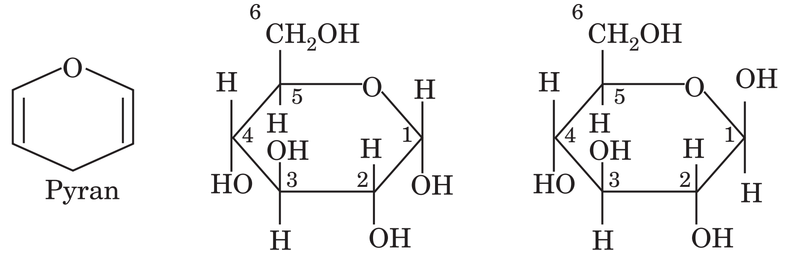
Cyclic Structure of Glucose:

- Glucose does not give 2, 4-DNP test, Schiff's test and does not form the hydrogensulphite addition product with $NaHSO_3$.
- The absence of free-CHO group is indicated as the pentaacetate of glucose does not react with hydroxylamine.
- Glucose exist in two different crystalline forms which are named as α and β. It was found that glucose forms a six-membered ring in which –OH at C5 in involved in ring formation.
- The cyclic structure is given below:



α – D – (+) – Glucose β – D – (+) – Glucose

- Haworth structure of glucose is given below:



α – D – (+) – Glucose β – D – (+) – Glucose

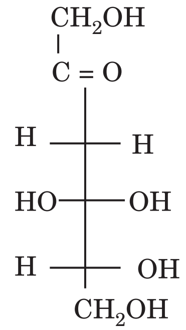
- **Fructose**

It is obtained along with glucose by the hydrolysis of sucrose.

➢ Structure of Fructose:

Fructose has the molecular formula $C_6H_{12}O_6$. It is found to have a ketonic functional group at carbon 2 and six carbons which are in straight chain.

➢ The open chain structure of fructose is:

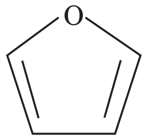


D – (–) – Fructose

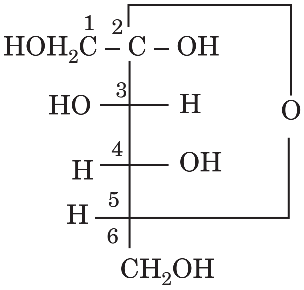
➢ **Cyclic structure of fructose:**

Fructose exists in two cyclic forms and they are obtained by adding –OH at C5 to the ketonic group. The ring is a five membered ring.

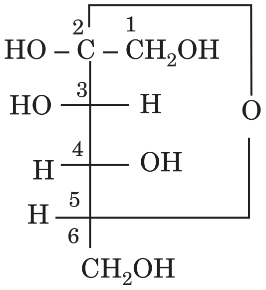
➢ **The structures are given below**



Furan

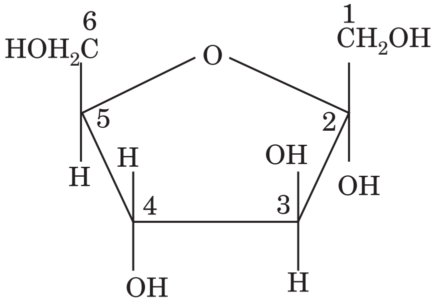


α – D – (–) – Fructofuranose

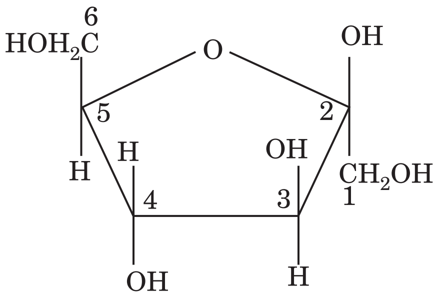


β – D – (–) – Fructofuranose

➢ **The Haworth structures of fructose are given below:**



α – D – (–) – Fructofuranose



β – D – (–) – Fructofuranose

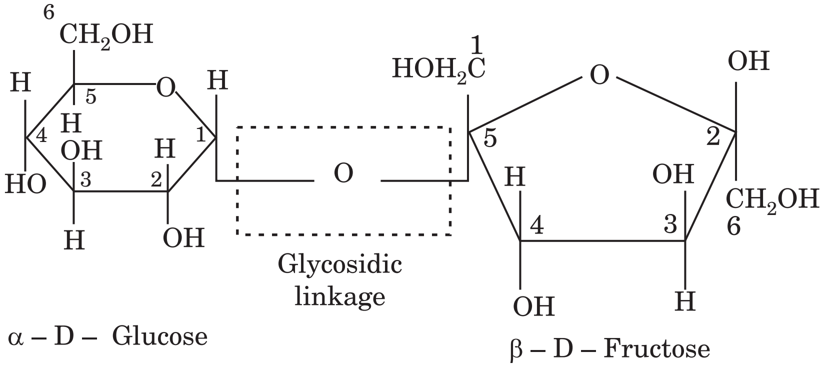
- Sucrose

  ➢ Sucrose on hydrolysis gives equimolar mixture of D-(+)-glucose and D-(-) fructose.

$$C_2H_{22}0_{11}+H_20 \xrightarrow{H^+} C_6H_20_6+C_6H_20_6$$

Sucrose D-(+)-Glucose D-(−)-Fructose

  ➢ The structure of sucrose is given below:



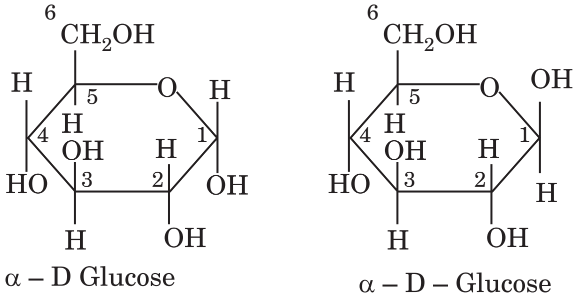
Sucrose

  ➢ The two monosaccharides in sucrose are held together by a glycosidic linkage. The product obtained on hydrolysis of sucrose is called invert sugar as the hydrolysis brings about a change in the sign of rotation from dextro (+) to laevo (-).

- Maltose:

  ➢ Maltose has two α-*D*-glucose units. In maltose the C 1 of one glucose (I) is linked to C4 of another glucose unit (II).

  ➢ **Structure of Maltose:**

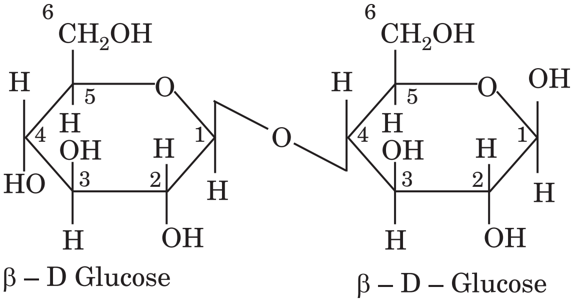


Maltose

- Lactose:

  ➢ It is commonly known as milk sugar as it is found in milk.

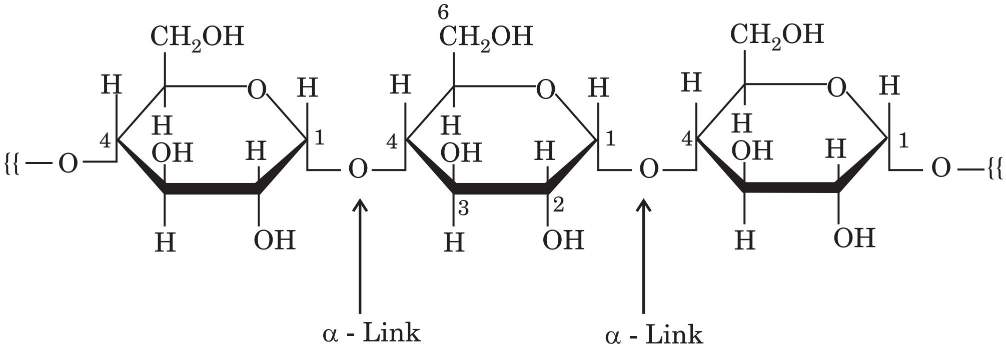
- **Structure of lactose:**



Lactose

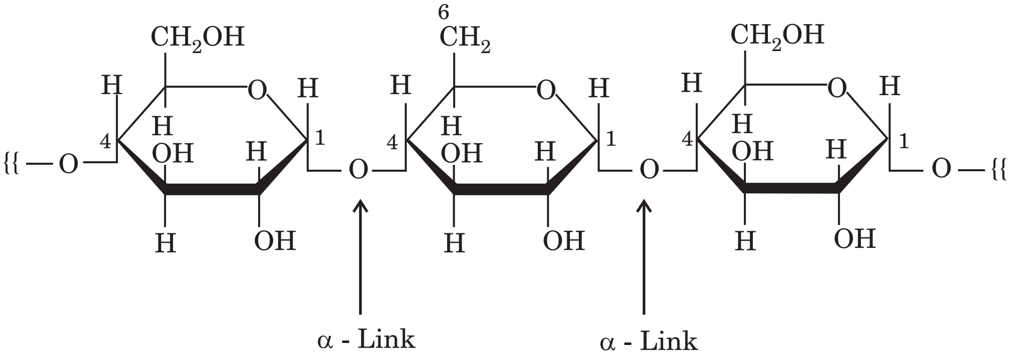
- **Polysaccharides:** They contain a large number of monosaccharide units joined together by glycosidic linkage.

- Starch
  - It is the main storage polysaccharide of plants and important dietary source for human beings. It consists of two components namely Amylose and Amylopectin.
  - Amylose: It is water soluble component and constitutes 15-20% of starch. It is a long unbranched chain with 200-1000 α-*D*-(+)-glucose units held by C1-C4 glycosidic linkage.
  - **Structure of Amylose is given below:**

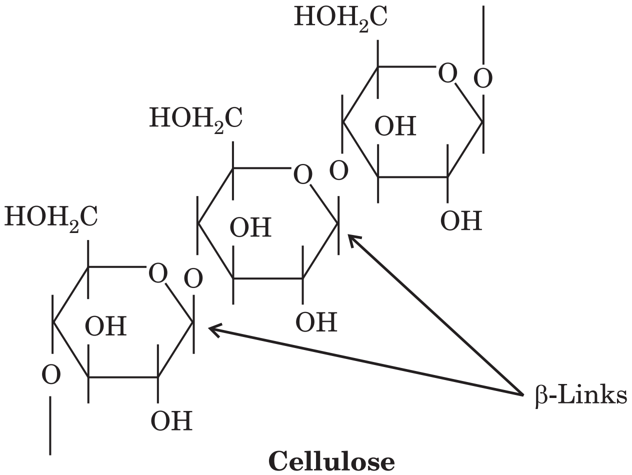


Amylose

  - Amylopectin: It is insoluble in water and constitutes 80-85% of starch. It is a branched chain polymer of units in which chain is formed by C1-C4 glycosidic linkage whereas branching occurs by C1-C6 glycosidic linkage.
  - **Structure of Amylopectin is given below:**



- **Cellulose:**
  - It occurs exclusively in plants. It is an important constituent of cell wall of plant cells. Its fundamental unit is β-*D*-glucose which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.
  - **Structure of cellulose is:**



Cellulose

- **Glycogen:**
  - Carbohydrates are stored in animals as glycogen. Its structure is similar to amylopectin and is rather more branched therefore it is also known as animal starch. It is present in liver, muscles and brain.
- **Importance of carbohydrates:**
  - They are essential for both plants and animals as they are the source of energy.
  - They are used as storage molecules.
  - Cell wall of plants and bacteria is made of cellulose.
  - They also act as raw materials for many important industries like textiles, paper etc.

PREVIOUS YEARS'

EXAMINATION QUESTIONS

TOPIC 1

1 Mark Questions

1. Write the products of hydrolysis of lactose. **[All INDIA 2014]**

2. Name the products of hydrolysis of sucrose. **[DELHI 2014]**

3. Which of the two components of starch is water soluble? **[DELHI 2015]**

4. Which component of starch is a branched polymer of α-glucose and insoluble in water? **[DELHI 2015]**

2 Marks Questions

5. What is essentially the difference between a-form of glucose and p-form of glucose? Explain. **[DELHI 2011]**

6. Write any two reactions of glucose which cannot be explained by the open chain structure of glucose molecule. **[DELHI 2011]**

7. Write any two reactions of glucose which cannot be explained by the open chain structure of glucose molecule. **[All INDIA 2012]**

8. List the reactions of glucose which cannot be explained by its open chain structure. **[DELHI 2015]**

4 Marks Questions

9. After watching a programme on TV about the presence of carcinogens (cancer causing agents) Potassium bromate and Potassium iodate in bread and other bakery products, Rupali a class XII student decided to make others aware about adverse affect of these carcinogens in foods. She consulted the school principal and requested him to instruct canteen contactor to stop selling sandwiches, pizzas, burgers and other bakery products to the students. The Principal took an immediate action and instructed to canteen contractor to replace the bakery products with some protein and vitamin rich food like fruit, salads, sprout setc. The decision was welcomed by the parents and the students.

After reading the above passage, answer the following questions:

(a) What are the values (at least two) displayed by Rupali?

(b) Which Polysaccharide component of carbohydrates is commonly present in bread?

(c) Write the two types of secondary structures of proteins.

(d) Give two examples of water soluble vitamins. **[All INDIA 2017]**

Solutions

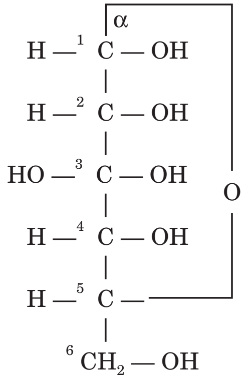
1. β-D-Glucose and β-D-Galactose **[1]**

2. Glucose and fructose. **[1]**

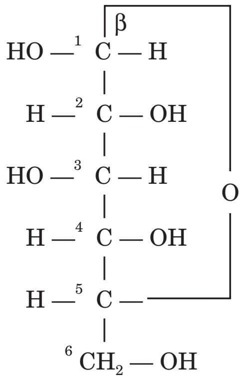
3. Amylose is the water soluble content of starch between Amylose and Amylopectin. **[1]**

4. Amylopectin is a branched polymer of α-glucose and in insoluble in water. **[1]**

5. In α-form of glucose –OH group lies at C1 towards right but in β-form of glucose it is towards left. This is because –OH group at C1 in glucose is chiral.



α–D–(+)-Glucose



β–D–(+)-Glucose

[1 + 1]

6. The following two reactions of glucose cannot be explained by the open chain structure of glucose.

(i) Despite having the aldehyde group glucose does not give 2, 4-DNP test. **[1]**

(ii) The pentacetate of glucose does not react with hydroxylamine indicating the absence of free –CHO group. **[1]**

7. The following two reactions of glucose cannot be explained by the open chain structure of glucose.

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8. The following two reactions of glucose cannot be explained by the open chain structure of glucose.

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(ii) The pentacetate of glucose does not react with hydroxylamine indicating the absence of free –CHO group. **[1]**

9. (a) Value of being aware and informed. **[1]**

1. To be aware about adverse effect of carcinogen present in bread and bakery products. **[½]**
2. To replace the bakery product with some protein and vitamin rich food like fruits, salads etc. value of Taking Initiative. **[½]**

(b) Starch, Glycogen **[1]**

(c) Alpha helix, Beta pleated sheet **[1]**

(d) Riboflavin, Thiamine **[1]**

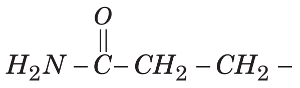
Topic 2: Protein, Vitamins and Nucleic Acids

Summary

- **Proteins:** They are the most abundant biomolecules of the living system. They form the fundamental basis of structure and functions of life.
- **Amino acids:** Amino acids contain amino $(-NH_2)$ and carboxyl $(-COOH)$ function groups.
- α-**Amino acids:** These are formed by the hydrolysis of proteins. In this the amino and the carboxyl function groups are attached to the same carbon.
- **Classification of amino acids:**

  Acidic, Basic and Neutral Amino Acids: Amino acids are classified as acidic, basic and neutral depending upon the relative number of amino and carboxyl groups in their molecules. If there are equal number of amino and carboxyl groups it makes it neutral; if there are more number of amino groups than carboxyl groups it makes it basic and if there are more number of carboxyl groups than amino groups it makes it acidic.
- **Non-Essential amino acids:** Those which can be generated in the body. Example: Gylycine.
- **Essential amino acids:** Those which cannot be generated in the body and must be obtained through diet. Example: Valine

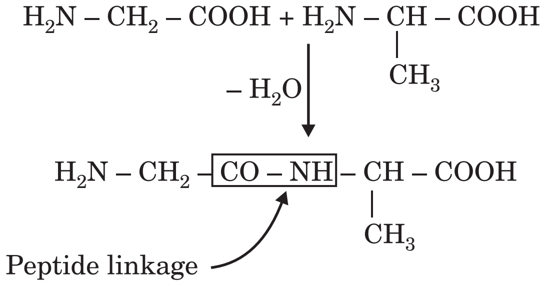
- **Some amino acids are given below in the table:**

Name of amino acids	Characteristic feature of side chain, R	Three letter symbol	One letter code
1. Glycine	H	Gly	G
2. Alanine	$-CH_3$	Ala	A
3. Valine	$(H_3C)_2\,CH-$	Val	V
4. Leucine	$(H_3C)_2\,CH-CH_2-$	Leu	L
5. Glutamine	 $H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-$	Gln	Q
6. Phenylalanine	$C_6H_5-CH_2-$	Phe	F

- **Properties of amino acids:**
  - They are colourless, crystalline solids.
  - They are water soluble, have high melting point and behave like salts.
- **Structure of proteins:**

They are the polymers of α-amino acids and are connected to each other by peptide bond or peptide linkage.

Example: Formation of Glyclalanine



$$H_2N-CH_2-COOH + H_2N-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH \xrightarrow{-H_2O} H_2N-CH_2-\boxed{CO-NH}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$$

Peptide linkage

Glycylalanine (Gly-Ala)

- **Classification of proteins on the basis of molecular shape:**
  - **Fibrous proteins:** They are fibre like structure which is formed when the polypeptide chains run parallel and are held together by hydrogen disulphide bonds. They are insoluble in water. Example: Keratin
  - **Globular proteins:** This shape of protein is formed when the chains of polypeptides coil around to give a spherical shape. Such proteins are soluble in water. Example: Insulin.
- **Classification of proteins on the basis of structure and shape:**
  - **Primary structure of proteins:** Each polypeptide in a protein has amino acids linked with each other in a specific sequence and this sequence of amino acids is called primary structure of proteins.

- **Secondary structure of proteins:** It is the shape in which a long polypeptide chain can exist. They exist in two different types of structure:

  (i) *a – Helix*: In this polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw with the –NH group of each amino acid residue hydrogen bonded to the > C = O of an adjacent turn of the helix. Example: Keratin.

  (ii) β-structure : In this all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as β– pleated sheet .

- **Tertiary structure of proteins:** It shows the overall folding of the polypeptide chains. The forces which stabilize the 2 and 3 structures of proteins are hydrogen bonds, disulphide linkages, van der Walls and electrostatic forces of attraction.

- **Quaternary structure of proteins:** The spatial arrangement of the two or more polypeptide chains with respect to each other is known as quaternary structure.

- **Denaturation of Proteins:**

  When protein in its native form is given any physical change like change in temperature or chemical changes like change in pH, the hydrogen bonds are disturbed. Due to this, globules gets unfolded and helix gets uncoiled and protein loses its biological activity. The complete process is called denaturation of proteins. Example: coagulation of egg white on boiling.

- **Enzymes:** They are essential biocatalysts which are needed to catalyse biochemical reactions. Example: The enzyme that cataylses hydrolysis of maltose into glucose is maltase.

- **Vitamins:** These are the organic compounds that are required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism.

  - **Classification of vitamins:**

    (i) **Fat soluble vitamins:** Vitamins which are soluble in fat and oils but insoluble in water. They are stored in liver and adipose tissues. Vitamin A, D, E and K are fat soluble.

    (ii) **Water soluble vitamins:** Vitamins such as B group vitamins and vitamin C are soluble in water. These vitamins are readily excreted in urine and cannot be stored (except vitamin B12) in our body so they must be supplied regularly in diet.

- **Some important Vitamins, their sources and their deficiency diseases are shown below in the table:**

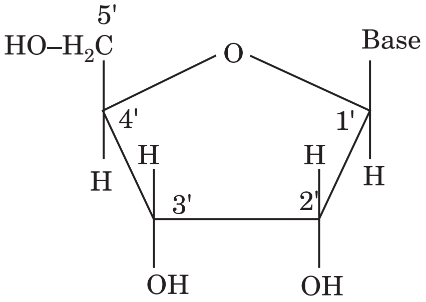
Name of Vitamins	Sources	Deficiency diseases
Vitamin A	Fish liver oil, butter and milk	Xerophthalmia, night blindness
Vitamin B_1 (Thiamine)	Yeast, milk, green vegetables and cereals	beriberi
Vitamin B_2 (Riboflavin)	Milk, egg white, liver, kidney	Cheilosis, digestive disorders
Vitamin B_6 (Pyridoxine)	Yeast, milk, egg york	Convulsions
Vitamin B_{12}	Meat, fish, egg and curd	Pernicious anaemia
Vitamin C	Citrus fruits, amla and green leafy vegetables	Scurvy
Vitamin D	Exposure to sunlight, fish and egg yolk	Rickets and osteomalacia
Vitamin E	Vegetable oils like wheat germ oil, sunflower oil etc.	Increased fragility of RBCs and muscular weakness
Vitamin K	Green leafy vegetables	Increased blood clotting time

- **Nucleic Acids:**
  - These are the long chain polymers of nucleotides which help in synthesis of protein and transfer of genetic traits.
  - There are two types of nucleic acids:

    (i) Deoxyribonucleic acid (DNA)

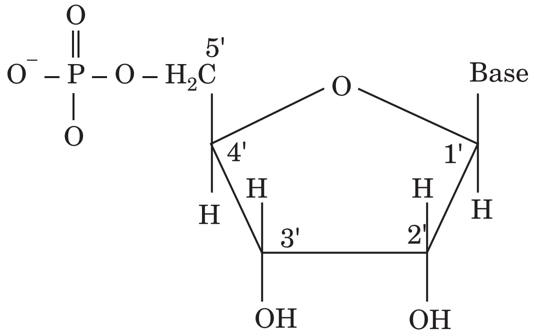
    (ii) Ribonucleic acid (RNA)
- **Chemical composition of Nucleic Acids:**
  - Complete hydrolysis of DNA (or RNA) gives a pentose sugar, phosphoric acid and nitrogenous bases.
  - DNA contains four bases, which are adenine, guanine, cytosine and thymine.
  - In RNA also there are four bases. The first three bases (adenine, guanine and cytosine) are same as in DNA, but the fourth one is uracil.
- **Structure of Nucleic Acids:**
  - **Nucleoside:** The unit which is formed by the attachment of a base to position of sugar is known as nucleoside.

    Structure of nucleoside is given below:

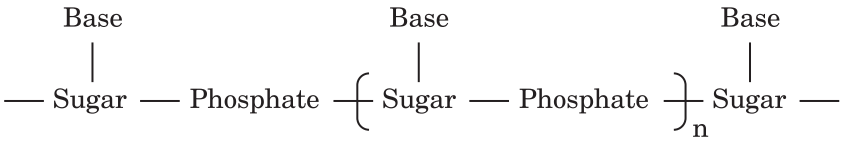


- **Nucleotide:** When nucleoside is linked to phosphoric acid at -position of sugar moiety.

  Structure of nucleotide is given below:



- The simplified version of nucleic acid chain is given below:



$$-\overset{\overset{\text{Base}}{|}}{\text{Sugar}}-\text{Phosphate}-\left(\overset{\overset{\text{Base}}{|}}{\text{Sugar}}-\text{Phosphate}\right)_n-\overset{\overset{\text{Base}}{|}}{\text{Sugar}}-$$

- **DNA:**
  - James Watson and Francis Crick gave a double strand helix structure for DNA.
  - There are two nucleic acid chains which are turned around each other and are held together by hydrogen bonds between pairs of bases.
  - The two strands in the DNA structure are complementary to each other due to the hydrogen bonding between specific pairs of bases.
- **RNA:**
  - In RNA helices are only single stranded which sometimes fold on themselves to form a double helix structure.
  - The three types of RNA molecules are given which perform different function.

    (i) Messenger RNA (m-RNA)

    (ii) Ribosomal RNA (r-RNA)

    (iii) Transfer RNA (t-RNA)
- **Biological functions of Nucleic Acids:**
  - DNA is responsible for maintaining the identity of different species of organisms.
  - Nucleic Acid helps in protein synthesis.
  - DNA is chemical basis for heredity.
  - DNA is regarded as reserve of genetic information.

PREVIOUS YEARS'
EXAMINATION QUESTIONS
TOPIC 2

▶ 1 Mark Questions

1. Write the name of linkage joining two amino acids. **[ALL INDIA 2013]**

2. What are the types of RNA molecule which perform different functions? **[DELHI 2013]**

3. What is a glycosidic linkage? **[DELHI 2013]**

▶ 2 Marks Questions

4. Explain what is meant by the following:
(i) peptide linkage
(ii) pyranose structure of glucose
[ALL INDIA 2011]

5. Write the main structural difference between DNA and RNA. Of the four bases, name those which are common to both DNA and RNA.
[ALL INDIA 2011]

6. What is meant by
(i) peptide linkage
(ii) biocatalysts **[ALL INDIA 2011]**

7. Describe what you understand by primary structure and secondary structure of proteins.
[DELHI 2011]

8. Explain what is meant by
1. a peptide linkage,
2. aglycosidic linkage **[DELHI 2011]**

9. Name the bases present in RNA. Which one of these is not present in DNA. **[DELHI 2011]**

10. What is meant by
1. peptide linkage,
2. biocatalysts? **[DELHI 2012]**

11. Write the main structural difference between DNA and RNA. Out of the two bases, thymine and uracil, which one is present in DNA?
[DELHI 2012]

12. Name the four bases present in DNA. Which one of these is not present in RNA?
[DELHI 2017]

13. What are essential and non-essential amino acids in human food? Give one example of each type.

14. Define the following terms in relation to proteins:
(*i*) Peptide linkage
(*ii*) Denaturation **[DELHI 2015]**

▶ 3 Marks Questions

15. Define the following terms:
(i) Nucleotide
(ii) Anomers
(iii) Essential amino acids **[ALL INDIA 2014]**

16. **(i)** Deficiency of which vitamin causes rickets?
(ii) Give an example for each of fibrous protein and globular protein.
(iii) Write the product formed on reaction of D-Glucose With Br_2 water. **[DELHI 2014]**

17. (i) Deficiency of which vitamin causes scurvy?
(ii) What type of linkage is responsible for the formation of proteins?
(iii) Write the product formed when glucose is treated with HI. **[DELHI 2014]**

18. (*i*) Which one of the following is a disaccharide: Starch, Maltose, Fructose, Glucose?
(*ii*) What is the difference between fibrous protein and globular protein?
(*iii*) Write the name of vitamin whose deficiency causes bone deformities in children.
[DELHI 2015]

19. (*i*) Which one of the following is a disaccharide: Starch, maltose, fructose, glucose
(*ii*) What is the difference between acidic amino acid and basic amino acid?
(*iii*) Write the name of the linkage joining two nucleotides **[ALL INDIA 2015]**

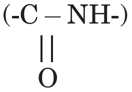
20. (*i*) Write the structural difference between starch and cellulose.
(*ii*) What type of linkage is present in Nucleic acids?
(*iii*) Give one example of each for fibrous protein and protein. **[ALL INDIA 2016]**

21. Define the following with an example of each:
(a) Polysaccharides
(b) Denatured protein
(c) Essential protein

OR

(a) Write the product when D-glucose reacts with conc. HNO_3.
(b) Amino acids show amphoteric behaviour. Why?
(c) Write one difference between α - helix and β - pleated structures of proteins.
[DELHI 2016]

Solutions

1. Peptide bond  $(-\underset{\underset{O}{||}}{C}-NH-)$ **[1]**

2. Three types of RNA molecules which perform different functions are: **[1]**
(i) Messenger RNA (m-RNA)
(ii) Transfer RNA (t-RNA)
(iii)Ribosomal RNA (r-RNA)

3. The linkage between the two monosaccharide units through oxygen atom accompanied by the loss of a water molecule is called glycosidic linkage.This type of chemical linkage is between the monosaccharide units of disaccharides, oligosaccharides, and polysaccharides, which is formed by the removal of a molecule of water (i.e. a condensation reaction) **[1]**

4. (i) Peptide linkage: Peptide linkage is an amide formed between –COOH group and $-NH_2$ group of two amino acids. i.e. A link between two amino acids with loss of water (–CO – NH–) **[1]**
(ii) The six membered cyclic structure of glucose is called pyranose structure in analogy with pyran heterocyclic compound / or structure **[1]**

5. In DNA, sugar is Deoxyribose while in RNA, it is ribose. DNA is double stranded while RNA is single stranded. The common bases present in both are adenine, cytosine & guanine. **[1 + 1]**

6. (i) Peptide linkage: Peptide linkage is an amide formed between –COOH group and $-NH_2$ group of two amino acids. Peptide linkage is responsible for the primary structure of proteins. **[1]**
(ii) Biocatalyst: A biocatalyst is a substance, especially an enzyme that initiates or modifies the rate of a chemical reaction in a living body. Example, amylase **[1]**

7. Primary structure of proteins refer to the sequence in which amino acids are joined together by peptide linkage. The sequence of amino acids in primary structure is very specific. Any change in the sequence of amino acids creates a different protein with different biological activity. **[1]**

Secondary structure of proteins refers to the conformation which arises due to the coiling of polypeptide chain due to intramolecular hydrogen bonding between carbonyl ($>C = O$) and —NH groups. Depending upon the size of -R group, there are two secondary structures of protein, i.e. α-Helix and β-Pleated sheet like structure. **[1]**

8. 1. Peptide linkage is present in proteins to bind together amino acids. The linkage involves the carboxyl group of one amino acid and amine group of another amino acid. **[1]**
2. Glycosidic linkage is the (–C–O–C–) linkage present between two molecules of a monosaccharide to form a disaccharide. **[1]**

9. Four bases present in RNA are adenine, guanine, Cytosine and Uracil. Ucil is not present in DNA. **[2]**

10. 1. Peptides linkage is the amide bond that helps to connect amino acids to form proteins. It is formed between – COOH and $-NH_2$ group of two amino acids with the loss of water molecule. **[1]**
2. Biocatalysts are enzymes that catalyses the biochemical reactions in the bodies of living organisms, e.g. Amylase. **[1]**

11.

DNA	RNA
1. DNA has deoxyribose sugar.	1. RNA has ribose sugar.
2. It has double helical structure.	2. It is single stranded.
3. It is less reactive due to presence of C-H bonds.	3. It has larger grooves so it is more reactive.

[2]

DNA contains thymine base and uracil base is present in RNA.

12. Four bases in DNA are Adenine, Guanine, Thymine and Cytosine. **[1]**
Thymine is not present in RNA. **[1]**

13. Essential amino acids are those amino acids which are not produced in our body and they must be a part of our diet. **[1]**
Example: Valine Non- essential amino acids are those amino acids which are produced by our body Examples: Glycine **[1]**

14. (i) Peptide linkage: Peptide linkage is an amide (– CO – NH –) bond formed between –COOH and $-NH_2$ group in protein formation. **[1]**
(ii) Denaturation: When a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH, protein loses its biological activity. This is called denaturation of protein. **[1]**

15. (i) Nucleotide : It is the monomer unit of DNA which is formed by nitrogenous base, Deoxyribose sugar and Phosphoric acid. **[1]**
(ii) Anomer: Anomers are cyclic monosaccaride which differ from each other in the configuration of C-1. If they are aldose or in the configuration at C-2, they are ketoses. **[1]**

(iii) Essential amino acid: The Amino acid which cannot be synthesised by body and essential for body. **[1]**

16. (i) Deficiency of vitamin D causes rickets **[1]**

(ii) Fibrous protein: Keratin or myosin Globular Protein: Insulin or albumin. **[1]**

(iii) Gluconic acid i.e. $HOOC(CH_2OH)_4CH_2OH$. **[1]**

17. (i) Vitamin-C **[1]**

(ii) Peptide linkage **[1]**

(ii) n-hexane: $CH_3CH_2CH_2CH_2CH_2CH_3$ **[1]**

18. (i) Maltose is a disaccharide, as it contains α-D- glucose units. **[1]**

(ii)

Fibrous Proteins	**Globular Proteins**
1. In fibrous proteins, the polypeptide chains run parallel and are held together by strong hydrogen and disulphide bonds.	In globular proteins, the polypeptide chains are folded, looped or twisted around themselves, giving these proteins a spherical structure.
2. They are usually insoluble in water.	They are usually soluble in water.
3. They are structural proteins. For example: keratin is present in nails and hair, collagen is present in tendons and myosin is present in muscles.	They are functional proteins. For example: most enzymes and some hormones like insulin.

[1]

(*iii*) The deficiency that causes bone deformities in children is vitamin D. **[1]**

19. (*i*) Maltose **[1]**

(*ii*) The difference is in their side chains. The acidic ones have acidic side chain and the basic ones have a basic side chain at neutral pH. **[1]**

Arginine, lysine, and histidine are the basic ones. Aspartate and glutamate are the acidic ones.

(*iii*) Phosphodiester linkage **[1]**

20. (*i*) Cellulose is a linear polymer made up of β-glucose having the C1-C4 glycosidic linkage, whereas starch is a polymer of α-glucose having two components: amylose and amylopectin. Amylose is a long, unbranched chain with 200-1,000 α-D-(+)-glucose units held by the C1-C4 glycosidic linkage. Amylopectin is a branched-chain polymer of α-D-glucose unit in which the chain is formed by the C1—C4 glycosidic linkage and branching occurs at the C1—C6 glycosidic linkage. **[1]**

(*ii*) A phosphodiester bond is a linkage present in nucleic acids. **[1]**

(*iii*) Fibrous protein: Keratin; Globular protein: Egg albumin **[1]**

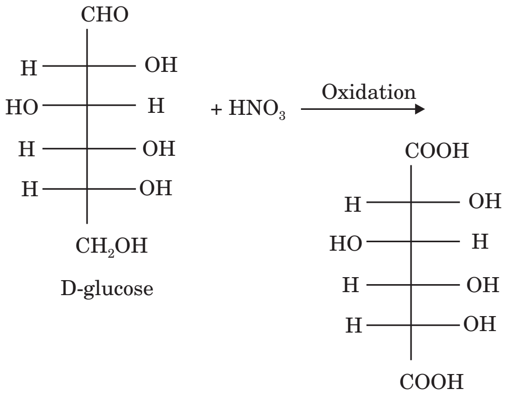
21. (*a*) Polysaccharides: These are the carbohydrates containing large number mono saccharides units joined together by glycosidic linkage upon hydrolysis. eg:-starch, cellulose. **[1]**

(*b*) Denatured protein: When a protein is subjected to physical change like change in temperature or chemical change like pH, the hydrogen bonds are disturbed and the protein loses its biological activity. This is denaturated protein eg:- The coagulation of egg on boiling, curding of milk **[1]**

(*c*) Essential amino acids: The amino acids which cannot be synthesised in the body and must be obtained from diet are known asessential amino acids. eg:- Histidine, Valineetc. **[1]**

OR

(*a*)

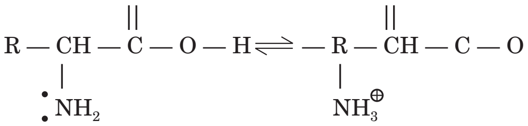


D-glucose

(Saccharic acid)

[1]

(b) As amino acid contains both acidic and basic group present in them, i.e. COOH and NH_2 in the same molecule can lose a proton and amino can accept a proton, giving rise to dipolar ion known as zwitter ion. **[1]**



$$R-\underset{\underset{NH_2}{|}}{CH}-\overset{\overset{O}{||}}{C}-O-H \rightleftharpoons R-\underset{\underset{NH_3^{\oplus}}{|}}{CH}-\overset{\overset{O}{||}}{C}-O$$

(Zwitter ion)

Hence, shows amphoteric nature. **[1]**

(c) α-helix: It has a polypeptide chain which forms all possible hydrogen bonds twisting it into a right handed screw. (helix) **[1]**

β-pleated: It has peptide chain which are stretched out to nearly maximum extension and then laid side by side which are held by inter molecular hydrogen bonds. **[1]**

Smart Notes

CHAPTER 15

Polymers

Chapter Analysis with respect to Last 3 Years' Board Exams

List of Topics	**2016**		**2017**		**2018**	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Classification - natural and synthetic						
Methods of polymerization (addition and condensation)			(2 marks)			
Copolymerization, some important polymers: natural and synthetic like polythene nylon polyesters, bakelite, rubber	(3 marks)	(3 marks)	(1 mark)	(3 marks)	(4 marks)	(4 marks)
Biodegradable and non-biodegradable polymers.						

Summary

The word polymer means having many parts. It is built of very large molecules having high molecular masses which can be called as Macromolecules. This means that they are formed by joining same structural units on a large scale. This process which requires joining these molecules by covalent bonds is called **Polymerisation.** The structural unit derived from simple molecules is called a **monomer**.

Classification of polymers

- **Classification based on Sources**

➢ **Natural polymers:** They are found in animals and plants. For example, starch, cellulose, proteins and rubber.

➢ **Semi-synthetic polymers:** These are derived from cellulose. For example, cellulose nitrate.

➢ **Synthetic polymers:** These are produced from chemical reactions. For example, Buna-S which is a synthetic rubber.

- **Classification Based on Structure of Polymers**

➢ **Linear polymers:** They comprise of straight and long chains. For example, high density polythene, polyvinyl chloride, etc.

➢ **Branched chain polymers:** They also comprise of long chains but with some branches. For example, low density polythene.

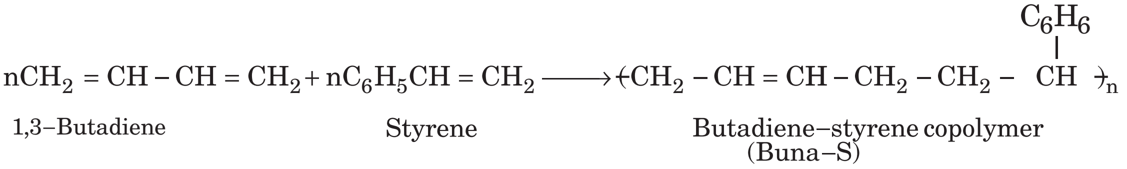
➢ **Cross linked or Network polymers:** They are formed by cross-linking monomers and consist of strong covalent bonds between the chains. For example, Bakelite, melamine etc.

- **Classification Based on Mode of Polymerisation**

➢ **Addition polymers:** They are formed by repeatedly adding monomer molecules that have double or triple bonds. The polymers formed are known as homopolymers. For example, polyethene.

$$\underset{\text{Ethene}}{nCH_2 = CH_2} \longrightarrow \underset{\text{Polythene}}{\left(CH_2 - CH_2 \right)_n} \text{ Homopolymer}$$

The polymers formed by adding two different monomers are called copolymers. For example, Buna-S and Buna-N etc.



$$\underset{\text{1,3–Butadiene}}{nCH_2 = CH - CH = CH_2} + \underset{\text{Styrene}}{nC_6H_5CH = CH_2} \longrightarrow \underset{\substack{\text{Butadiene–styrene copolymer}\\ \text{(Buna–S)}}}{\left(CH_2 - CH = CH - CH_2 - CH_2 - \overset{\overset{C_6H_6}{|}}{CH} \right)_n}$$

➢ **Condensation polymers:** These are formed as a result of condensation reaction between two distinct bi-functional or tri-functional monomeric units. For example, nylon 6, 6. It is made from the condensation of hexamethylene diamine with adipic acid.

$$nH_2N(CH_2)_6\,NH_2 + nHOOC(CH_2)_4\,COOH \longrightarrow \underset{\text{Nylon 6, 6}}{\left[NH(CH_2)_6\,NHCO(CH_2)_4\,CO \right]_n} + nH_2O$$

- **Classification Based on Molecular Forces**

➢ **Elastomers:** The polymer chains are held together by the weakest intermolecular forces due to which these polymers are stretchable. For example, buna-S, buna-N etc.

➢ **Fibers:** These polymers are held together by strong intermolecular forces like hydrogen bonding due to which they have high tensile strength. For example, polyamides (nylon 6, 6), polyesters (terylene), etc.

➢ **Thermoplastic polymers:** These polymer chains are moderately branched and are held together by intermolecular forces of attraction due to which they soften on heating and then harden on cooling. For example, polythene, polystyrene, polyvinyls, etc.

➢ **Thermosetting polymers:** These polymer chains are heavily branched and if heated can create extensive cross-linking and become infusible. For example, bakelite, urea-formaldelyde resins, etc.

- **Classification Based on Growth Polymerisation**

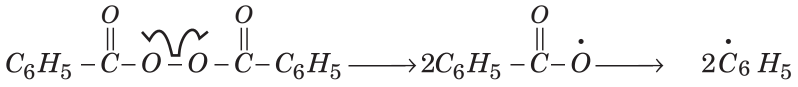
  The addition and condensation polymers are nowadays also known as chain growth polymers and step growth polymers.

Types of Polymerisation Reactions

- **Addition Polymerisation or Chain Growth**

➢ **Free radical mechanism:** Different alkenes or dienes and their derivatives can be polymerized in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. There are 3 steps involved.

(i) Chain initiation step



$$C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5 \longrightarrow 2C_6H_5-\overset{\overset{O}{\|}}{C}-\dot{O} \longrightarrow 2\dot{C}_6H_5$$

Benzoyl peroxide Phenyl radical

$$\dot{C}_6H_5 + CH_2=CH_2 \longrightarrow C_6H_5-CH_2-\dot{C}H_2$$

(ii) Chain propagating step

$$C_6H_5-CH_2-\dot{C}H_2 + CH_2=CH_2 \longrightarrow C_6H_5-CH_2-CH_2-CH_2-\dot{C}H_2$$

$$\downarrow$$

$$C_6H_5\left(CH_2-CH_2\right)_n CH_2-\dot{C}H_2$$

(iii) Chain terminating step

$$\begin{matrix} C_6H_5\left(CH_2-CH_2\right)_n CH_2-\dot{C}H_2 \\ C_6H_5\left(CH_2-\overset{+}{C}H_2\right)_n CH_2-\dot{C}H_2 \end{matrix} \longrightarrow C_6H_5\left(CH_2-CH_2\right)_n CH_2-CH_2-CH_2\left(CH_2-CH_2\right)_n C_6H_5$$

Polythene

➢ Preparation of some important addition polymers

(i) **Polyethene:** There are two types of polyethene.

➢ **Low Density polyethene:** They are obtained through free radical mechanism by the polymerisation of ethene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 K to 570 K in the presence of traces of dioxygen or a peroxide initiator (catalyst) and have highly branched structures. They are poor conductors of electricity and this is why they are used in manufacturing of squeeze bottles, toys and flexible pipes.

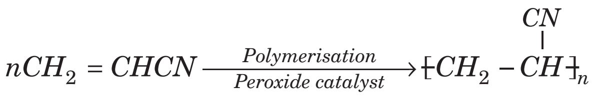
➢ **High Density polyethene:** They are obtained through addition polymerisation of ethene takes place in a hydrocarbon solvent in the presence of a catalyst such as triethylaluminium and titanium tetrachloride (Ziegler Natta catalyst) at a temperature of 333 K to 343 K and under a pressure of 6-7 atmospheres. For example, used in manufacturing of buckets, dustbins, bottles, pipes, etc.

(ii) **Polytetrafluoroethene (Teflon):** It is produced under high pressure by heating tetrafluoroethene with a free radical or persulphate catalyst. It is commonly used in the manufacturing of non – stick surface coated utensils.

$$nCF_2 = CF_2 \xrightarrow[\text{High pressure}]{\text{Catalyst}} \left[CF_2 - CF_2\right]_n$$

Tetrafluoroethene Teflon

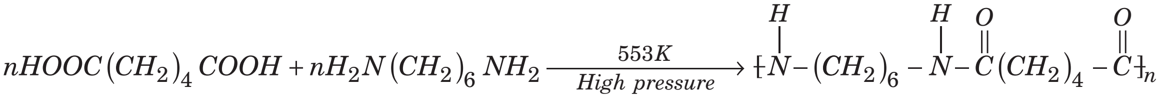
(iii) **Polyacrylonitrile:** It is produced in presence of a peroxide catalyst. It is used in the making of commercial fibres such as orlon or acrilan.



$$nCH_2 = CHCN \xrightarrow[\text{Peroxide catalyst}]{\text{Polymerisation}} \left[CH_2 - \overset{\overset{CN}{|}}{CH} \right]_n$$

Acrylonitrile Polyacrylonitrile

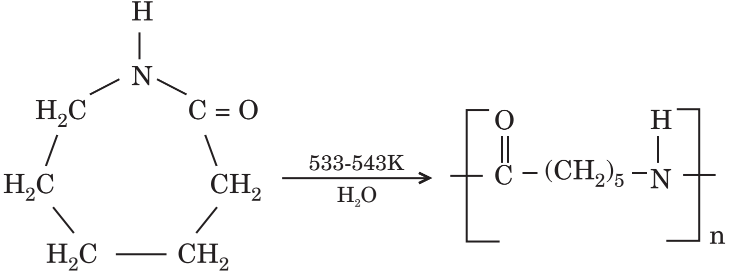
- **Condensation Polymerisation or Step Growth polymerisation**
  - **Polyamides:** They are derived from condensation polymerisation of diamines with dicarboxylic acids and also of amino acids and their lactams.
    (i) **Preparation of Nylon 6,6:** It is produced with adipic acid under high pressure and at high temperatures. For example, in making of sheets, bristles for brushes etc.



$$nHOOC(CH_2)_4COOH + nH_2N(CH_2)_6NH_2 \xrightarrow[\text{High pressure}]{553K} \left[\overset{\overset{H}{|}}{N} - (CH_2)_6 - \overset{\overset{H}{|}}{N} - \overset{\overset{O}{||}}{C}(CH_2)_4 - \overset{\overset{O}{||}}{C} \right]_n$$

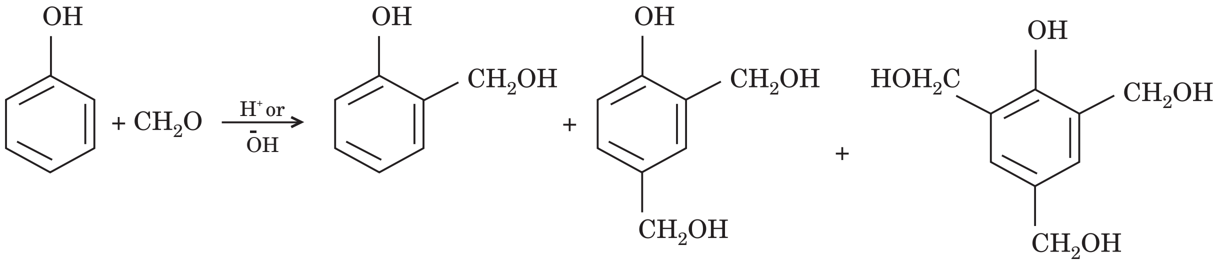
Nylon 6, 6

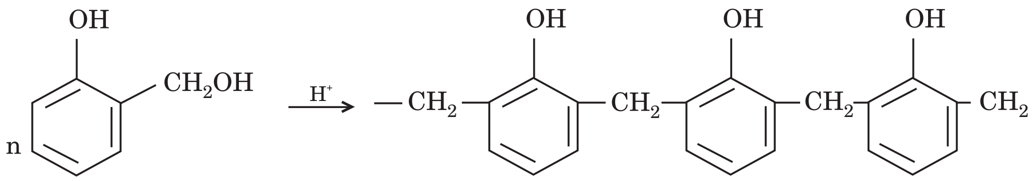
    (ii) **Preparation of Nylon 6:** It is obtained under high temperature by heating caprolactum with water. For example, manufacturing of tyre cords, fabrics and ropes etc.



Caprolactam **Nylon 6**

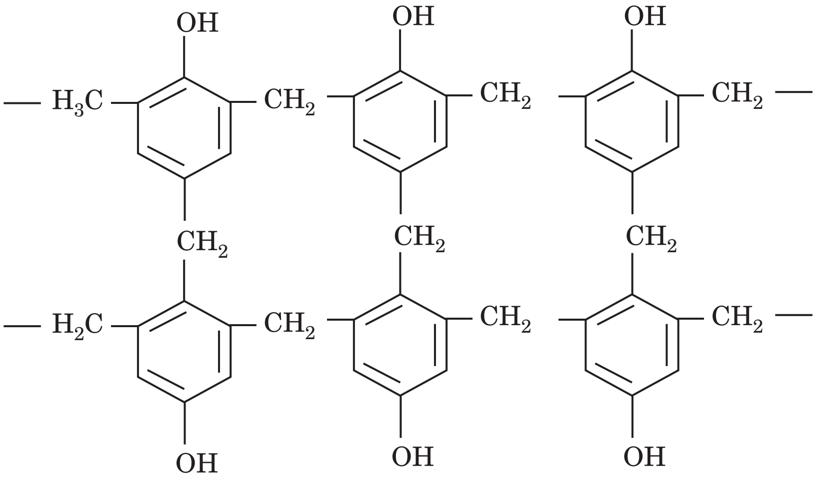
  - **Polyesters:** They are obtained in the presence of zinc acetateantimony trioxide catalyst by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K. For example, Dacron fibre (terylene) is used in safety helmets etc.
  - **Phenol - formaldehyde polymer (Bakelite and related polymers):** It is a condensation reaction of phenol which requires a presence of either acid or base catalyst with formaldehyde. The initial substance produced is known as Novolac which is used in paints.





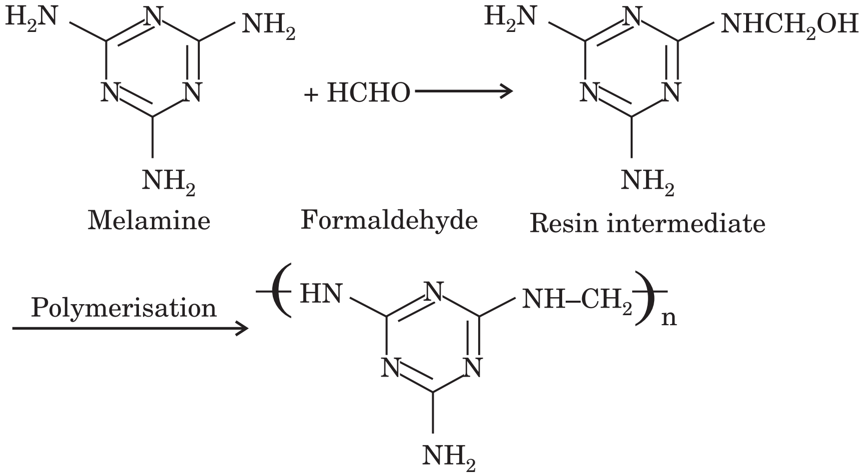
Novolac

On continuous heating of Novolac, infusible solid mass called Bakelite is produced. It is used in manufacturing of combs, electrical switches etc.



Bakelite

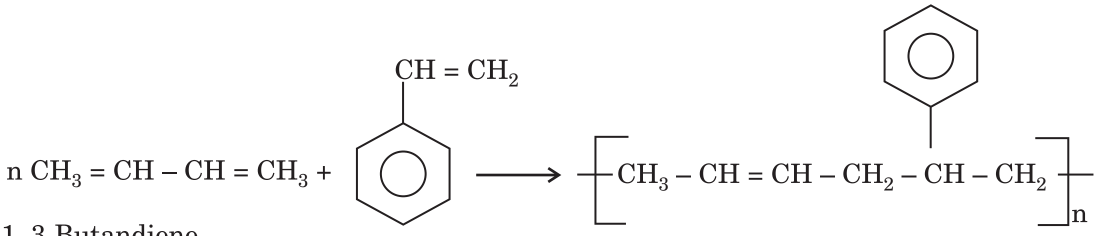
- **Melamine-formaldehyde polymer:** It is another condensation reaction of melamine with formaldehyde.



Melamine Formaldehyde Resin intermediate

Melamine polymer

- **Copolymerisation:** It is a chain growth polymerisation which consists of many units of different monomers used in the same polymeric chain. For example, butadiene - styrene copolymer is used for the making of auto tyres, floor tiles, footwear components etc.

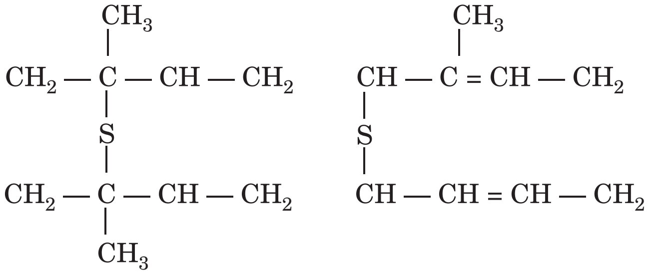


$$n\,CH_3 = CH - CH = CH_3 + C_6H_5CH = CH_2 \longrightarrow \left[CH_3 - CH = CH - CH_2 - \underset{C_6H_5}{CH} - CH_2 \right]_n$$

1, 3-Butandiene Styrene Butadiene - styrene copolymer

- **Rubber**

- **Natural rubber:** It is a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as cis -1,4 polyisoprene and these chains are held together by weak van der Waals interactions and has a coiled structure and that's why it shows elastic properties. The process of formation of natural rubber by heating a mixture of raw rubber with sulphur and an appropriate additive at a temperature range between 373 K to 415 K is called as Vulcanisation of rubber.



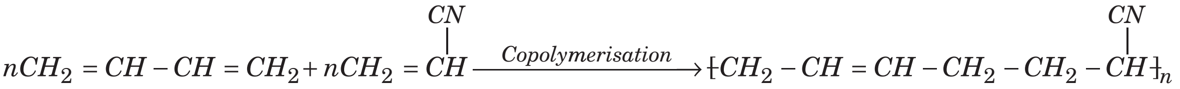
- **Synthetic rubbers:** There are various synthetic rubbers which are obtained from chemical reactions.
  - **(i) Neoprene:** It is obtained by the free radical polymerisation of chloroprene. It is used for manufacturing conveyor belts, gaskets and hoses.

$$nCH_2=\overset{Cl}{\overset{|}{C}}-CH=CH_2 \xrightarrow{Polymerisation} \left[CH_2-\overset{Cl}{\overset{|}{C}}=CH-CH_2\right]_n$$

Chloroprene
2-Chloro-1, 3-butadience

Neoprene

  - **(ii) Buna-N:** It is formed in the presence of a peroxide catalyst. It is used in the manufacturing of oil seals, tank lining, etc.



$$nCH_2=CH-CH=CH_2+nCH_2=\overset{CN}{\overset{|}{CH}} \xrightarrow{Copolymerisation} \left[CH_2-CH=CH-CH_2-CH_2-\overset{CN}{\overset{|}{CH}}\right]_n$$

1,3-Butadience

Acrylonitrile

Buna-N

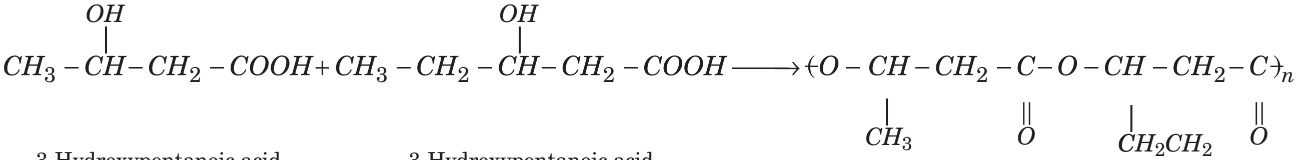
Molecular Mass of Polymers

The molecular mass of any polymer is determined by physical and chemical methods which may vary in their size, mass, synthesis, structure, length and mass.

Biodegradable Polymers of Commercial Importance with their Structures

These are environment friendly polymers.

- **Poly β-hydroxybutyrate – co-β-hydroxy valerate (PHBV):** The following copolymerisation reaction takes place. It is used in speciality packaging.



$$CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-COOH+CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-CH_2-COOH \longrightarrow \left(O-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{||}{C}}-O-\underset{CH_2CH_2}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{||}{C}}\right)_n$$

3-Hydroxypentanoic acid

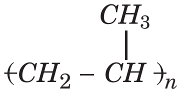
3-Hydroxypentanoic acid

PHBV

- **Nylon 2-nylon 6:** This copolymer is biodegradable and formed from glycine (H2N–CH2–COOH) and amino caproic acid [$H_2N\ (CH_2)_5\ COOH$]

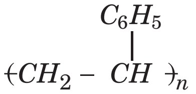
Polymers of Commercial Importance with their Structures

- **Polypropene:** It is used in the Manufacture of ropes, toys, pipes, fibres, etc.



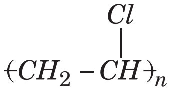
$$\left(CH_2-\overset{CH_3}{\overset{|}{CH}}\right)_n$$

- **Polystyrene:** It is used as insulator, wrapping material, manufacture of toys, radio and television cabinets.



$$\left(CH_2-\overset{C_6H_5}{\overset{|}{CH}}\right)_n$$

- **Polyvinyl chloride (PVC):** It is used in the manufacture of rain (PVC) coats, hand bags, vinyl flooring, water pipes.



$$\left(CH_2-\overset{Cl}{\overset{|}{CH}}\right)_n$$

PREVIOUS YEARS'

EXAMINATION QUESTIONS

▶ 1 Mark Questions

1. Define Biodegradable polymers. **[DELHI 2011]**

2. Define the term 'homopolymerisation' giving an example. **[DELHI 2012]**

3. Give one example of a condensation polymer. **[ALL INDIA 2013]**

4. Which of the following is a fibre?

Nylon, Neoprene, PVC **[ALL INDIA 2014]**

5. What does '6, 6' indicate in the name nylon – 6, 6? **[DELHI 2011]**

▶ 2 Mark Questions

6. Mention two important uses of the following

1. Bakelite
2. Nylon-6 **[DELHI 2011]**

7. Name the sub-groups into which polymers are classified on the basis of magnitude of intermolecular forces. **[DELHI 2011]**

8. Draw the structure of the monomer for each of the following polymers:

(*i*) Nylon – 6

(*ii*) Polypropene **[ALL INDIA 2012]**

9. Define thermoplastic and thermosetting polymers. Give one example of each.

OR

What is a biodegradable polymer? Give an example of a biodegradable aliphatic polyester. **[ALL INDIA 2013]**

10. Write the name of monomers used for getting the following polymers:

(*i*) Teflon

(*ii*) Buna-N **[ALL INDIA 2014]**

11. Differentiate between molecular structures and behaviors of thermoplastic and thermosetting polymers. Give one example of each type. **[DELHI 2017]**

▶ 3 Mark Questions

12. Draw the structures of the monomers of the following polymers:

(*i*) Polythene

(*ii*) PVC

(*iii*) Teflon **[ALL INDIA 2011]**

13. Write the names and structures of the monomers of the following polymers:

(*i*) Buna – S

(*ii*) Neoprene

(*iii*) Nylon-6, 6 **[DELHI 2013]**

14. Write the names and structures of the monomers of the following polymers:

(*i*) Polystyrene

(*ii*) Dacron

(*iii*) Teflon **[DELHI 2013]**

15. Write the names and structures of the monomers of the following polymers:

(*i*) Bakelite

(*ii*) Nylon-6

(*iii*) Polythene **[ALL INDIA 2013]**

16. After the ban on plastic bags, students of a school decided to make the people aware of the harmful effects of plastic bags on the environment and Yamuna River. To make the awareness more impact full, they organized rally by joining hands with other schools and distributed paper bags to vegetable vendors, shopkeepers and departmental stores. All the students pledged not to use polyethene bags in the future to save the Yamuna River.

After reading the above passage, answer the following questions:

(*i*) What values are shown by the students?

(*ii*) What are bio-degradable polymers? Give one example.

(*iii*) Is polyethene a condensation or addition polymer? **[DELHI 2014]**

17. Write the names and structures of the monomers of the following polymers:

(*i*) Nylon-6, 6

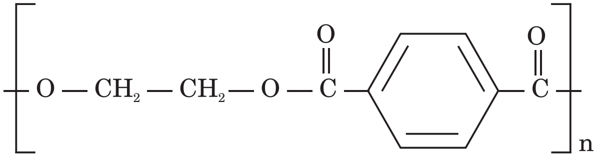
(*ii*) PHBV

(*iii*) Neoprene. **[DELHI 2015]**

18. Write the names and structures of the monomers of the following polymers
(*i*) Nylon-6,6
(*ii*) Bakelite
(*iii*) Polystyrene **[ALL INDIA 2015]**

19. Write the names and structures of the monomers of the following polymers:
(*i*) Buna-S
(*ii*) Neoprene
(*iii*) Nylon-6 **[DELHI 2016]**

20. (*i*) What is the role of Sulphur in the vulcanization of rubber?
(*ii*) Identify the monomers in the following polymer:



(*iii*) Arrange the following polymers in the increasing order of their intermolecular forces: Terylene, Polythene, Neoprene
[ALL INDIA 2016]

21. Write the structures of the monomers used for getting the following polymers:
(*a*) Teflon
(*b*) Melamine-formaldehyde polymer
(*c*) Neoprene **[ALL INDIA 2017]**

22. Give one example each of
(*i*) addition polymers,
(*ii*) condensation polymers,
(*iii*) copolymers.

4 Mark Questions

23. Shyam went to a grocery shop to purchase some food items. The shopkeeper packed all the items in polythene bags and gave them to Shyam. But Shyam refused to accept the polythene bags and asked the shopkeeper to pack the items in paper bags. He informed the shopkeeper about the heavy penalty imposed by the government for using polythene bags. The shopkeeper promised that he would use paper bags in future in place of polythene bags.
Answer the following:
(*a*) Write the values (at least two) shown by Shyam.
(*b*) Write one structural difference between low-density polythene and high-density polythene.
(*c*) Why did Shyam refuse to accept the items in polythene bags?
(*d*) What is a biodegradable polymer? Give an example. **[ALL INDIA 2018]**

Solutions

1. Bio-degradable polymers are natural polymers that disintegrate themselves over a period of time by enzymatic hydrolysis, e.g. starch, cellulose, etc. **[1]**

2. The addition polymers formed by the polymerisation of one type of monomeric species are known as homopolymers and the process is known as homopolymerisation. **[1]**

$$\underset{\text{ethene}}{n\,CH_2=CH_2} \longrightarrow \underset{\substack{\text{Polyethene}\\\text{(Homopolymer)}}}{\left(CH_2=CH_2 \right)_n}$$

3. Nylon-6 **[1]**

4. Nylon **[1]**

5. It indicate the number of carbon atoms present in both the monomers of nylon 6,6 which are hexamethylene diamine and adipic acid. **[1]**

6. **Bakelite:** It is used in the manufacture of electrical switches, protective coatings, barrels, etc. **[1]**

Nylon-6 : It is used in making fabrics, tyre cords, mountaineering ropes etc. **[1]**

7. **Elastomers:** They have weakest intermolecular forces of attraction. **[½]**

Fibres: They have strong intermolecular forces of attraction among its molecules. **[½]**

Thermoplastics Polymers: They are semifluid substances having low molecular weight. **[½]**

Thermosetting polymers – They have intermolecular forces intermediate between those of elastomers and fibres. **[½]**

8. (*i*) $NH-\left(CH_2\right)_5-CO$, which is derived from Caprolactam **[1]**

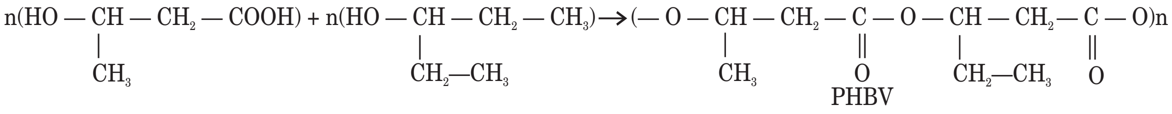
(*ii*) Propene whose structural formula is $\left[CH_3-CH=CH_2\right]$ **[1]**

9. Thermoplastic – polymers in which the intermolecular forces of attraction are in between those of elastomer and fibers are called thermoplastic Ex. PVC **[1]**
Thermosetting polymers – The cross linked polymer which have hard infusible and insoluble mass are called thermosetting polymer. Ex. Bakelite **[1]**

OR

Biodegradable polymer – Polymer, such as starch, cellulose protein, nucleic acid which control the various life processes and are decomposed by microorganisms are called biodegradable polymers **[1]**

Ex. Poly hydroxyl butyrate-CO-β-hydroxy valerate (PHBV)



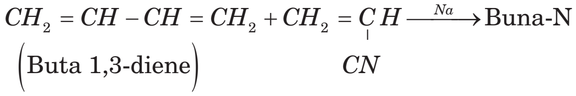
$$n(HO-\underset{CH_3}{\underset{|}{CH}}-CH_2-COOH)+n(HO-\underset{CH_2-CH_3}{\underset{|}{CH}}-CH_2-CH_3)\rightarrow(-O-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-O-\underset{CH_2-CH_3}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-O)n$$

PHBV

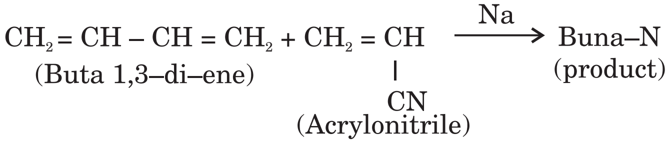
[1]

10. (*i*) $CF_2=CF_2$ (Tetrafluoro ethylene) **[1]**

(*ii*)



$$\underset{\text{(Buta 1,3-diene)}}{CH_2=CH-CH=CH_2}+CH_2=\underset{CN}{\underset{|}{C}}H\xrightarrow{Na}\text{Buna-N}$$



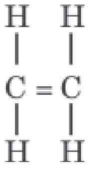
$$\underset{\text{(Buta 1,3–di–ene)}}{CH_2=CH-CH=CH_2}+\underset{\text{(Acrylonitrile)}}{CH_2=\underset{CN}{\underset{|}{CH}}}\xrightarrow{Na}\underset{\text{(product)}}{\text{Buna–N}}$$

[1]

11.

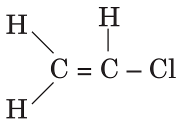
Property	Thermoplastic Polymers	Thermosetting Polymers
Molecular Structure	Linear or slightly branched long chain molecules.	Cross linked or heavily branched molecules.
Behavior	Can undergo softening on heating and hardening on cooling.	Do not soften on heating.
Example	PVC	Bakelite

12. (*i*)



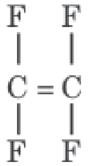
[1]

(*ii*)



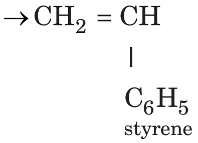
[1]

(*iii*)



$CF_2 = CF_2$ **[1]**

13. (*i*) Buna – S: →



$$CH_2=\underset{C_6H_5}{\underset{|}{CH}}$$

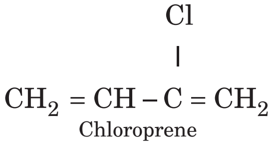
styrene

and

Buta-1,3-diene → $CH_2=CH-CH=CH_2$

[1]

(ii) Neoprene:

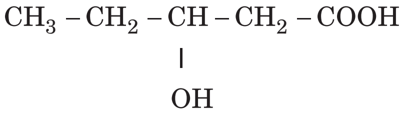


$$CH_2=CH-\overset{Cl}{\overset{|}{C}}=CH_2$$

Chloroprene

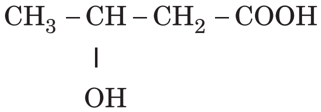
[1]

(iii) Nylon – 6, 6



$CH_3-CH_2-CH(OH)-CH_2-COOH$

3–Hydroxypentanoic acid



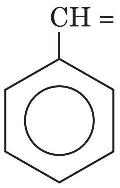
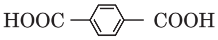
$CH_3-CH(OH)-CH_2-COOH$

3–Hydroxybutanoic acid

and $H_2N-(CH_2)_6-NH_2$ **[1]**

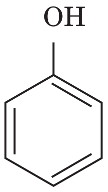
Hexamethylenediamine

14. Polymers with their monomers and their structures:

Polymer	Monomer	Structure
Polystrene	Styrene (Vinyl benzene)	
Dacron	1. Ethylene glycol 2. Terephthalic acid	HOH_2C-CH_2OH 
Teflon	Tetrafluoro-ethene	$CF_2=CF_2$

[1+1+1]

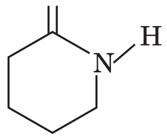
15. (*i*) **[1]**



Phenol

+ HCHO
formaldehyde

(*ii*) **[1]**



Caprolactam

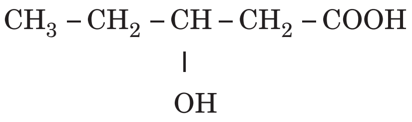
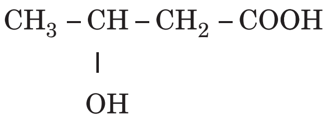
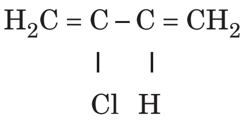
(*iii*) $CH_2=CH_2$ **[1]**
(Ethene)

16. (*i*) The students show awareness about the environment and its protection. They contribute towards a cleaner pollution free environment. They also understand the value of team work as rally organization with other school students imbibe the quality of cooperation. **[1]**

(*ii*) Polymers that are decomposed over a period of time either by themselves or by the action of micro-organisms are called biodegradable polymers. PHBV (Poly β-hydroxy butrate Co-β-hydroxy valerate) **[1]**

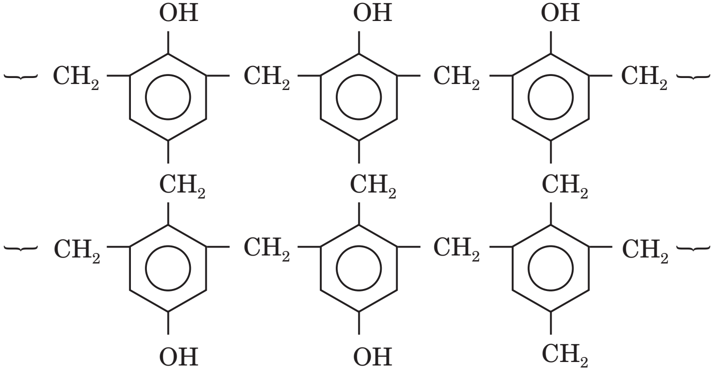
(*iii*) Polythene is an addition polymer. **[1]**

17. **[1+1+1]**

	Polymer	Name of Monomer(s)	Structure of Monomer(s)
(*i*)	Nylon-6, 6	Hexamethylenediamine and adipic acid	$H_2N-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH_2$ Hexamethylenediamine $HOOC-CH_2-CH_2-CH_2-CH_2-COOH$ Adipic acid
(*ii*)	PHBV	3-hydroxypentanoic acid 3-hydroxybutanoic acid	 $CH_3-CH_2-CH(OH)-CH_2-COOH$ 3–Hydroxypentanoic acid  $CH_3-CH(OH)-CH_2-COOH$ 3–Hydroxybutanoic acid
(*iii*)	Neoprene	Chloroprene	 $H_2C=C(Cl)-C(H)=CH_2$ Chloroprene

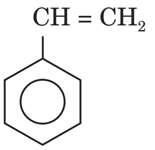
18. (*i*) $\underset{\text{Hexamethylene}}{H_2N-(CH_2)_6-NH_2}\ \&\ \underset{\text{Adipic acid}}{HOOC-(CH_2)_4-COOH}$ **[1]**

(*ii*) Phenol + formaldehyde

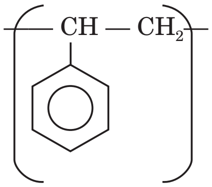


[1]

(*iii*) **[1]**

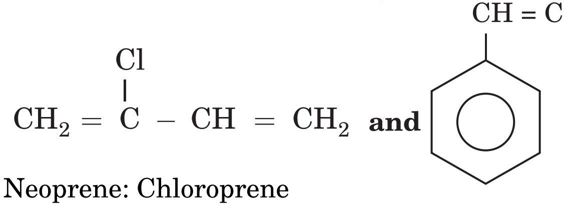


(Styrene)



(Polystyrene)

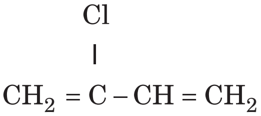
19. (*i*) Buna-S: 1,3- Butadiene and Styrene



$CH_2=\overset{\overset{\textstyle Cl}{|}}{C}-CH=CH_2$ **and**

[1]

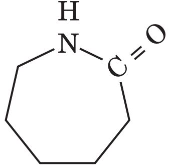
(*ii*) Neoprene: Chloroprene



$CH_2=\overset{\overset{\textstyle Cl}{|}}{C}-CH=CH_2$

[1]

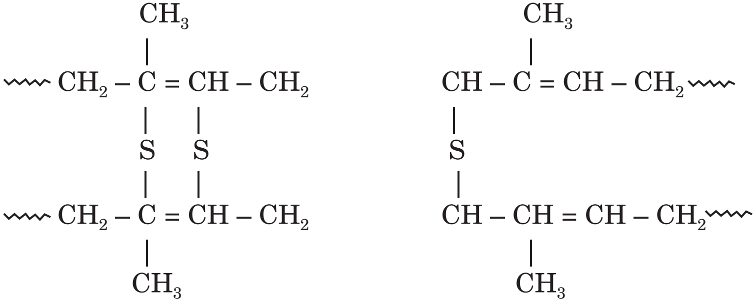
(*iii*) Nylon -6: Caprolactum



[1]

20. (*i*) Role of sulphur in the vulcanisation of rubber:-

Natural rubber becomes soft at high temperatures (> 335K) and brittle at low temperatures (< 283K). Moreover, it is soluble in non-polar solvents and is non-resistant to the attacks by oxidising agents. Sulphur is therefore added during its manufacturing to overcome these limitations. Sulphur forms cross linkages at reactive sites of double bonds and thus, the rubber gets stiffened. The following are the probable structures of a vulcanised rubber: **[1]**



(*ii*) Name of the polymer: Glyptal Monomers:(*a*) Ethylene glycol, (*b*) Pthalic acid **[1]**

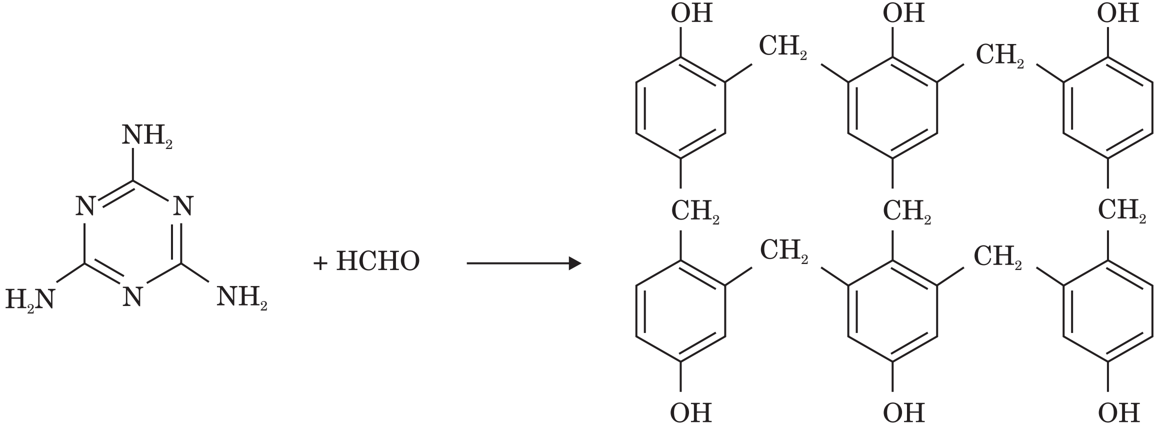
(*iii*)Fibres have the strongest intermolecular forces, while elastomers have the least. Thermoplastics have the intermolecular forces intermediate between elastomers and fibres. Thus, the increasing order of the intermolecular forces of the given polymers is as follows:

Neoprene < Polythene < Terylene **[1]**

21. (*a*)Teflon (PTFE) - The monomeric unit present is tertrafluoroethene $n\ (F_2C = CF_2)$.

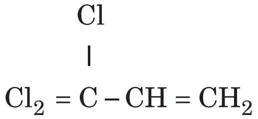
Teflon is used as a material resistant to heat and chemical attack. It is also used for making gaskets, pumps packing, valves, oil seals, non lubricated bearings. **[1]**

(*b*) Melamine-formaldehyde polymer



[1]

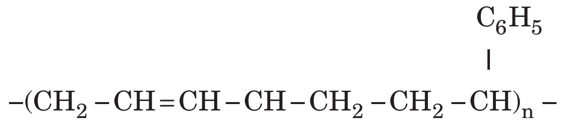
(*c*) Neoprene - It is prepared by the free radical polymerization of chloroprene. It is used as insulator for making belts , gaskets , hoses etc.



$$Cl_2 = \overset{\displaystyle Cl \atop |}{C} - CH = CH_2$$

[1]

22.

Type of polymer	Example	Structure
(*i*) Addition polymers	Polyethene or Polythene	$-(CH_2 - CH_2)_n -$
(*ii*) Condensation polymers	Nylon 6,6	$-[NH(CH_2)_6\,NHCO(CH_2)_4\,CO]_n -$
(*iii*) Copolymer	Buna-S	 $-(CH_2 - CH{=}CH - CH - CH_2 - CH_2 - \overset{\displaystyle C_6H_5 \atop \mid}{CH})_n -$

[1+1+1]

23. (*a*) Shyam is a responsible citizen and has moral values. **[1]**

(*b*) LDPE is branched.

HDPE is linear. **[1]**

(*c*) Polythene is a non-biodegradable polymer and it will accumulate in land-fills. If burnt polythene will cause air pollution. **[1]**

(*d*) Biodegradable polymers are the polymers which are degraded by microorganisms within a suitable time period so that biodegradable polymers and their degraded products do not cause any serious effects on the environment. eg:- (*a*) PHBV (*b*) Dextron (*c*) Nylon-2-nylon-6 **[1]**

Smart Notes ....

Smart Notes ....

CHAPTER 16

Chemistry in Everyday Life

Chapter Analysis with respect to Last 3 Years' Board Exams

List of Topics	**2016**		**2017**		**2018**	
	Delhi	**All India**	**Delhi**	**All India**	**Delhi**	**All India**
Chemicals in medicines - analgesics, tranquilizers antiseptics, disinfectants, antimicrobials, antifertility drugs, antibiotics, antacids, antihistamines	(1 mark)		(2, 3 marks)	(3 marks)		
Chemicals in food - preservations, artificial sweetening agents, elementary idea of antioxidants.						
Cleansing agents - soaps and detergents, cleansing action.	(2 marks)				(3 marks)	(3 marks)
Value Based Questions		(4 marks)				

Summary

Chemistry influences our daily life and is used in following ways to benefit the human life:

- Production of cleanliness products such as soaps, detergents, toothpaste etc.
- Use of chemicals in food as preservatives, artificial sweetening agents etc.
- Use of chemicals in medicines as antiseptics, antacids, antibiotics etc.

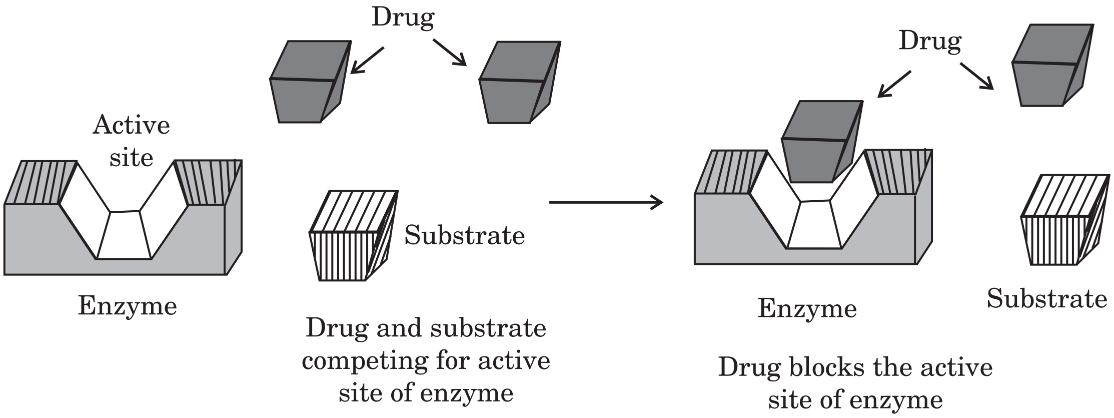
Drugs and their classification

- Chemical substances of low molecular masses which produce biological responses are called drugs. When the effects of these drugs are therapeutic and useful, they are called medicines.
- **Classification of Drugs**
  - On the basis of pharmacological effects: These are the types of drugs that are prescribed for the treatment of particular problem or sickness. For example, antacids bring relief from acidity.
  - On the basis of drug action: These are the types of drugs that have a particular biochemical process for targeted effects. For example, antihistamines that inhibits the actions of histamines that cause inflammation in the body.
  - On the basis of chemical structure: These are the types of drugs that have a particular chemical structure. For example, sulphonamides have common chemical structural feature.
  - On the basis of molecular targets: These are the types of drugs that interact with different biomolecules such as proteins and carbohydrates and directly affect the targets.
- **Drug-target interaction**
  - Enzymes are the proteins that act as biological catalysts
  - Catalytic action of enzymes: For this action of enzymes interactions such as hydrogen bonding or dipole-dipole interactions are required. The substrate molecule is held by the active site of enzyme by using the strong interactions which is attacked by the reagent and then the chemical reaction is carried out.

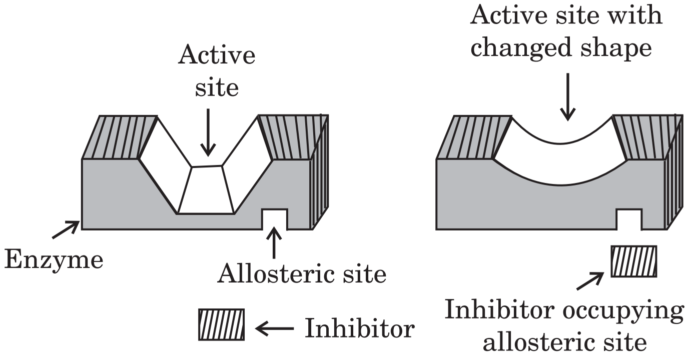
(a) Enzyme (b) Substrate (c) Enzyme holding substrate

  - Drug-enzyme interaction: Enzyme inhibitors are the drugs that block the binding site of the enzyme and the substrate. There are two ways in which this action takes place:

    (i) Some drugs called as competitive inhibitors compete for the active site of the enzyme attachment as shown in the diagram.



(ii) There are some drugs that do not bind with the active site of the enzyme but different site called allosteric site. In this interaction, a strong covalent bond is required which cannot be broken easily.

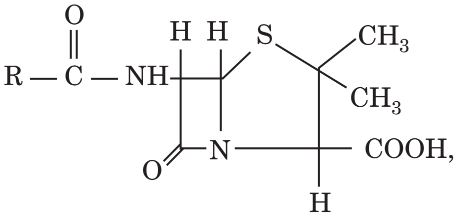


- ➢ Receptors are proteins that are important for communication in the body. For communication between neurons to muscles, chemical messengers are required which forwards the message to the cell without entering the cell. Different receptors have different binding shapes, structures and composition.
- ➢ Antagonists are those drugs that bind to the receptor site and inhibit its natural function whereas agonists are the drugs that act as natural messengers by swapping on the receptors.

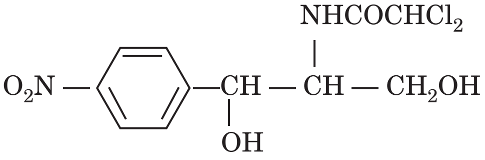
Different classes of drugs on basis of therapeutic action

- **Antacids:** These are the drugs that stop the excess production of acids in the stomach that causes pain and irritation. The most common antacids are sodium hydrogencarbonate or mixture of magnesium hydroxide and aluminium.
- **Antihistamines:** These are the drugs that have a particular biochemical process and have targeted effects. For example, histamine is a chemical that activates the secretion of pepsin and hydrochloric acid in the stomach. Antihistamines react with the receptors and helps lessen the amount of such acids released in the stomach. For example, common antihistamines are brompheniramine (Dimetapp) and terfenadine (Seldane).
- **Tranquilizers:** These are the types of drugs that act on neurological issues such as stress, anxiety, severe or mild mental diseases and affect the transfer mechanism from nerve to receptors. For example, sleeping pills and nonadrenaline that act on mood changes. Iproniazid and phenelzine are the two drugs that act as antidepressants, which activate receptors for a person suffering from depression.
    - ➢ There are some mild tranquilizers that are suitable for relieving tension such as chlordiazepoxide and meprobamate. The drug that helps in controlling hypertension and depression is Equanil.
    - ➢ There are some strong tranquilizers called Barbiturates which are hypnotic such as veronal, amytal, nembutal, luminal, valium and serotonin.
- Analgesics: These are the types of drugs that minimize or stop pain without actually causing any imbalance to nervous system. There are two types:
    - ➢ **Non-narcotic(non-addictive) analgesics:** These are the drugs that have a relieving effect on skeletal pain(joints pain), helps in reducing fever and platelet coagulation and also prevention of heart attacks as these drugs have anti blood clotting action.
    - ➢ **Narcotic analgesics:** These are the types of drugs that also have relieving properties but then taken in excess amount can have severe side effects such as coma, stupor and untimely death. This is the reason they are mainly used in child birth, cardiac pain and terminal cancer pain. For example, Morphine, also referred to as opiates.
- **Antibiotics:** These are the types of drugs that stop the growth of microorganisms and kill them eventually these are drugs that are synthesized from chemicals that are low in concentration and they act on metabolic processes.
    - ➢ A German bacteriologist, Paul Ehrlich produced arsphenamine, known as salvarsan, for the treatment of syphilis. He was awarded the Nobel Prize in medicine in 1980. In 1932, he succeeded in preparing the first effective antibacterial agent, prontosil, which later was converted to sulphanilamide.

- ➢ H.W. Florey and Alexander Fleming shared the Nobel prize for Medicine in 1945 for their independent contributions to the development of penicillin.



General Structure of Penicillin



Chloramphenicol

- ➢ There are two types of antibiotics, Bactericidal and Bacteriostatic. Bactericidal have killing effects and examples are Penicillin, Aminoglycosides and Ofloxacin. Bacteriostatic have inhibitory effects on microbes and examples are Erythromycin, Tetracycline and Chloramphenicol.
- ➢ Chloramphenicol can be given orally in case of typhoid, meningitis, acute fever, some form of urinary infections, dysentery and pneumonia.

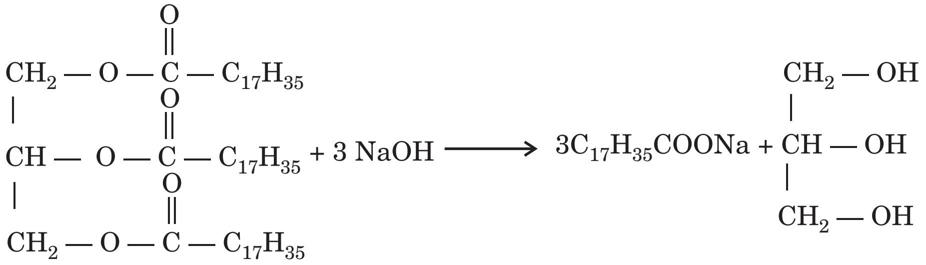
- **Antiseptics and Disinfectants:** These are used to kill or stop the growth of microorganisms.
  - ➢ Antiseptics are used on outer wounds on skin surface. For example, soframicine, furacine, Iodoform and Iodine tincture etc. Dettol is a mixture of chloroxylenol and terpineol.
  - ➢ Disinfectants are the chemicals or drugs that are used in cleaning objects. For example, Phenol is an antiseptic while its one percent solution is disinfectant.
- **Anti-fertility drugs:** These are the drugs that help in the prevention of unwanted pregnancy. For example, Birth control pills contain a mixture of synthetic estrogen and progesterone derivatives. both of which are hormones and known to suppresses ovulation.The commonly used anti-fertility drug is Norethindrone is an example of synthetic progesterone derivative.

Chemicals in Food

- **Artificial sweetening agents:** These are the chemicals added in food to enhance their appeal such as food colouring, flavours and sweeteners. Sucrose is a natural sweetener, whereas Saccharin is the first popular artificial sweetening agent. This is useful for diabetic people. Some artificial sweeteners are Aspartame, Sucrolose and Alitame.
- Food preservatives:They are added to increase the nutritive value of the food since they prevent spoilage of food that happens due to microbial growth. For example, table salt, sugar, vegetable oils and sodium benzoate, C_6H_5COONa are commonly used preservatives.

Cleansing agents

- **Soaps:** These are used for cleaning purposes and are mainly made of sodium or potassium salts of long chain fatty acids.



$$\begin{array}{l} CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35} \\ | \\ CH-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35} \\ | \\ CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35} \end{array} + 3\,NaOH \longrightarrow 3C_{17}H_{35}COONa + \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Gylceryl ester of stearic acid (Fat)	Sodium hydroxide	Sodium stearate	Glycerol (or Glycerine

- ➢ The process of obtaining sodium salts soaps by heating fat with aqueous sodium hydroxide solution is called Saponification.

- ➢ There are different types of soaps such as toilet soaps, transparent soaps, medicated soaps, shaving soaps, laundry soaps, soap powders or granules.
- ➢ Soaps don't work in hard water because hard water contains calcium and magnesium ions which are insoluble in water and separate out as scum in water and become useless. This is the reason why hairs and clothes are not washed in hard water.

$$2C_{17}H_{36}COONa + CaCl_2 \longrightarrow 2NaCl + (C_{17}H_{35}COO)_2Ca$$

Soap

Insoluble calcium stearate (Soap)

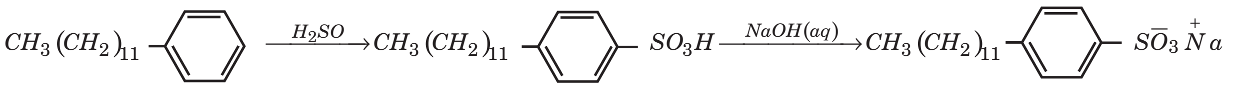
- Synthetic detergents:These have the same property as those of soaps but they work in hard water as well. They have 3 main categories.
  - ➢ **Anionic detergents:** These are the sodium salts of sulphonated long chain alcohols or hydrocarbons. The anionic part of the molecule is involved in the cleansing action in anionic detergents. They are used in toothpastes.

$$CH_3(CH_2)_{10}CH_2OH \xrightarrow{H_2SO_4} CH_3(CH_2)_{10}CH_2OSO_3H \xrightarrow{NaOH(aq)} CH_3(CH_2)_{10}CH_2OS\overline{O}_3\overset{+}{N}a$$

Lauryl alcohol

Lauryl hydrogensulphate

Sodium laurylsulphate (Anionic detergent)



Dodecylbenzene

Dodecylbenzenesulphonic acid

Sodium dodecylbenzenesulphonate

  - ➢ **Cationic detergents:** They are quarternary ammonium salts of amines with acetates, chlorides or bromides as anions. These detergents have germicidal properties. For example, Cetyltrimethylammoniumbromide is used in hair conditioners.
  - ➢ **Non-ionic detergents:** They do not contain any ion in their constitution. The grease and oil are removed by micelle formation. For example, liquid dishwashing detergents.

PREVIOUS YEARS'

EXAMINATION QUESTIONS

1 Mark Question

1. Name a substance that can be used as an antiseptic as well as a disinfectant.

[DELHI 2016]

2 Marks Questions

2. What are biodegradable and non-biodegradable detergents? Give one example of each class. **[DELHI 2016]**

3. Name two fat soluble vitamins, their sources and the diseases caused due to their deficiency in diet. **[DELHI 2017]**

3 Marks Questions

4. Explain the following terms with one suitable example for each:

1. A sweetening agent for diabetic patients
2. Enzymes
3. Analgesics **[DELHI 2011]**

5. Answer the following questions:

1. Why do soaps not work in hard water?
2. What are the main constituents of dettol?
3. How do antiseptics differ from disinfectants?

[DELHI 2011]

6. What are the following substances? Give one example of each.

(i) Food preservatives
(ii) Synthetic detergents
(iii) Antacids

[ALL INDIA 2011]

7. What are the following substances? Give one example of each one of them.

(i) Tranquilizers

(ii) Food preservatives

(iii) Synthetic detergents **[ALL INDIA 2012]**

8. (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? **[DELHI 2013]**

9. (i) What class of drug is 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

[ALL INDIA 2013]

10. (i) Give two examples of macromolecules that are chosen as drug targets.

(ii) What are antiseptics? Give an example.

(iii) Why is use of aspartame limited to cold foods and soft drinks? **[DELHI 2014]**

11. (i) Name the sweetening agents used in the preparation of sweets for a diabetic patient.

(ii) What are antibiotics? Give an example.

(iii) Give two examples of macro molecules that are chosen as drug targets. **[DELHI 2014]**

12. (i) What are disinfectants? Give an example.

(ii) Give two examples of macro molecules that are chosen as drug targets.

(iii) What are anionic detergents? Give an example. **[DELHI 2014]**

13. (i) Deficiency of which vitamin causes rickets?

(ii) Give an example for each of fibrous protein and globular protein.

(iii) Write the product formed on reaction of D-Glucose With Br_2 water. **[DELHI 2014]**

14. (i) Deficiency of which vitamin causes night-blindness?

(ii) Name the base that is found in nucleotide of RNA only.

(iii) Glucose on reaction with HI gives n-hexane. What does it suggest about the structure of glucose? **[DELHI 2014]**

15. Define the following:

(a) Cationic detergent

(b) Broad spectrum antibiotics

(c) Tranquillizer **[ALL INDIA 2017]**

16. Describe the following substances with one suitable example of each type:

i. Non - ionic detergents

ii. Food preservatives

iii. Disinfectants **[DELHI 2017]**

17. What are analgesic medicines? How are they classified and when are they commonly recommended for use?

18. (a) Why is bithional added to soap?

(b) What is tincture of iodine? Write its one use.

(c) Among the following, which one acts as a food preservative?

Aspartame, Aspirin, Sodium Benzoate, Paracetamol. **[ALL INDIA 2018]**

Solutions

1. Phenol, 0.2 percent solution of phenol is used as an antiseptic, while 1 per cent of its solution is used as a disinfectant. [1]

2. Biodegradable detergents are those detergents which are easily degraded by micro-organisms and hence are pollution free. Ex: Soap/ Sodium lauryl sulphate / any other unbranched chain detergent. Non- Biodegradable Detergents are those detergents which cannot be degraded by the bacteria easily and hence create pollution. Ex: Sodium -4- (1, 3, 5, 7- tetra methyl octyl) benzene sulphonate. [1]

3.

Vitamins	Sources	Disease
A	Carrots, butter	Xerophthalmia
B	Exposure to sunlight, fish	Rickets

[1+1]

4. 1. Artificial sweeting agent are chemicals that sweeten food. However, unlike natural sweeteners, they do not add calories to our body, and are not harmful to diabetic patients, e.g. Saccharin, aspartame. [1]

2. Enzymes are biocatalysts which are structurally globular proteins. They are sensitive to substrate, pH and temperature changes, e.g. Trypsin [1]

3. Analgesics are chemical substances which reduce pain without causing impairment of consciousness, mental confusion, paralysis or any other disturbance of nervous system, e.g. Aspirin, (non-narcotic analgesic) and morphine (narcotic analgesic) [1]

5. 1. Hard water contains insoluble chloride

of calcium and magnesium which form insoluble ppt. (scum) with soap and thus cannot be rinsed off easily. [1]

2. The main constituents of dettol are chloroxylenol and a-terpine. [1]

3. Antiseptics: These are chemical substances which either kill or prevent the growth of micro-organism but do not cause harm to the living tissues.

Disinfectants: These are chemical substances which kill the microbes. They are toxic in nature and thus cause harm to the tissues of the skin. [1]

6. (i) Food preservatives: are the compounds which prevent spoilage of food due to microbial growth. [1]

E.g: sodiumbenzoate, vinegar, etc.

(ii) Synthetic detergents are sodium salts of long chain alkyl sulphonates or benzene sulphonates. [1]

e.g: Sodium Lauryl sulphate.

(iii)Antacids: are the drugs used to prevent the overproduction of acid in the stomach. e,g, Sodium hydrogencarbonate. [1]

7. (i) **Tranquilizers:** The chemical substances

used for the treatment of stress, mild and severe mental diseases are called tranquilizers. Example: Noradrenaline [1]

(ii) **Food Preservatives:** These are the chemical substances which are added to the food materials to prevent their spoilage and to retain their nutritive value for long periods. Example: Vinegar [1]

(iii)**Synthetic detergents:** Synthetic detergents are cleansing agents which have all the properties of soaps but actually do not contain any soap. These can be used both in soft and hard water. Example: Sodium p-dodecylbenzenesulphonate. [1]

8. (a) Sodium benzoate is used as a food preservative whereas equanil is a tranquilizer and morphine is a narcotic analgesic. [1]

(b) Bithional is an antiseptic so it is added to soaps to reduce the odours produced by bacterial decomposition of organic matter on the skin. [1]

(c) Tranquilizers relieve stress, fatigue by inducing sense of well being, so they are used in sleeping pills. [1]

9. (i) It is an antacid [1]

(ii) In this case we use synthetic detergents because it gives foams even with hard water and washes properly. [1]

(iii)0.2% phenol is an antiseptic. [1]

10. (i) Proteins, enzymes, nucleic acids and lipids are called drug targets as drug interacts with these macro-molecules. [1]

(ii) Antiseptics are the chemical substances which prevent the growth of micro-organism and are capable of killing them without harming the human tissues. These are applied on wounds, ulcer, cuts and diseased skin surfaces, e.g. savlon, 0.2% solution of phenol, dettol, iodine tincture etc. [1]

(iii)Aspartame decomposes on heating hence it is used as an artificial sweetener for foods and soft drinks at low temperatures. [1]

11. (i) Saccharine, aspartame. [1]

(ii) Antibiotics are the chemicals substances produced wholly or partly by chemical synthesis which in low concentrations inhibit the growth or destroy microorganisms by intervening in their metabolic processes, e.g. Penicillin, Tetracyline. [1]

(iii)Carbohydrate, lipid, proteins, enzymes, nucleic acid. [1]

12. (i) Chemicals which are used to kill micro-organisms and applied on non-living objects like floors and drains are called disinfectants e.g. 1% phenol solution. [1]

(ii) Proteins, amino acids and enzymes. [1]

(iii)Detergents in which the anionic part of the molecule is responsible for cleansing action are called anionic detergents eg. Sodium laurylsulphate. [1]

13. (i) Vitamin D. [1]

(ii) Fibrous protein: Keratin or myosin Globular protein: Insulin or albumin. [1]

(iii) D-Gluconic acid [1]

i.e. $HOOC\left(CH_2OH\right)_4CH_2OH$.

14. (i) Vitamin A. [1]

(ii) Uracil [1]

(iii) Glucose exists in acyclic straight six membered carbon chain => open structure of Glucose. [1]

$CHO-\left(CHOH\right)_4-CH_2OH$

15. (a) Cationic detergent: A type of detergent in which the active part of the molecule is a positive ion (cation). Cationic detergents are usually quaternary ammonium salts and often also have bactericidal properties. [1]

(b) Broad spectrum antibiotics: The term broad-spectrum antibiotic refers to an antibiotic that acts against a wide range of disease-causing bacteria. A broad-spectrum antibiotic acts against both Gram-positive and Gram-negative bacteria eg. Amoxicillin, Streptomycin [1]

(c) Tranquilizers: a drug used to reduce stress or tension without reducing mental clarity. [1]

16. (i) Non ionic detergents do not contain any ion in their constitution. **Example:** Non- ionic detergent is formed when stearic acid reacts with polyethyleneglycol. [1]

$$\underset{\text{(Stearic acid)}}{CH_3\left(CH_2\right)_{16}COOH}+\underset{\text{(polyethylene glycol)}}{HO\left(CH_2CH_2O\right)_nCH_2CH_2OH}\xrightarrow{-H_2O}CH_3\left(CH_2\right)_{16}COO\left(CH_2CH_2O\right)_nCH_2CH_2OH$$

(ii) Food preservatives are substances which prevent spoilage of food due to microbial growth. Example: sodium benzoate [1]

(iii) Disinfectants are chemicals which either kill or prevent the growth of microorganisms. They cannot be applied on a living tissue. Example: 1% solution of phenol. [1]

17. Analgesic medicines are those medicines which reduce or abolish pain causing impairment of consciousness, mental confusion, in-coordination or paralysis or some other disturbances of nervous system. These are classified as follows: [1]

(i) Non-narcotic (non-addictive)

analgesics: These drugs are effective in relieving skeletal pain such as that due to arthritis and preventing platelet coagulation. [1]

(ii) Narcotic drugs: These analgesics are chiefly used for the relief of severe pain like postoperative pain, cardiac pain and pains of terminal cancer, and in childbirth.

[1]

18. (a) Bithional is added to medicated soap, to reduce the odour produced by bacterial decomposition of organic matter on the skin. [1]

(b) Tincture of iodine is a 2 - 3 percent solution of iodine in alcohol - water mixture. It is applied to wounds as an antiseptic. [1]

(c) Sodium Benzoate-Food preservative. [1]

Value Based

PREVIOUS YEARS'

EXAMINATION QUESTIONS

3 Mark Questions

1. Shanti, a domestic helper of Mrs.Anuradha, fainted while mopping the floor. Mrs.Anuradha immediately took her to the nearby hospital where she was diagnosed to be severely 'anaemic.' The doctor prescribed an iron rich diet and multivitamins supplement to her. Mrs. Anuradha supported her financially to get the medicines. After a month, Shanti was diagnosed to be normal. After reading the above passage, answer the following questions:

(i) What values are displayed by Mrs. Anuradha?

(ii) Name the vitamin whose deficiency causes 'pernicious anaemia'.

(iii) Give an example of water soluble vitamin.

[ALL INDIA 2013]

2. After watching a programme on TV about the adverse effects of junk food and soft drinks on the health of school children, Sonali, a student of Class XII, discussed the issue with the 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. **[DELHI 2013]**

3. On the occasion of World Heath Day, Dr. Satpal organized a 'health camp' for the poor farmers living in a nearby village. After check-up, he was shocked to see that most of the farmers suffered from cancer due to regular exposure to pesticides and many were diabetic. They distributed free medicines to them. Dr. Satpal immediately reported the matter to the National Human Rights Commission (NHRC). On the suggestions of NHRC, the government decided to provide medical care, financial assistance, setting up of super-speciality hospitals for treatment and prevention of the deadly disease in the affected villages all over India.

(i) Write the values shown by (a) Dr.Satpal (b) NHRC

(ii) What type of analgesics are chiefly used for the relief of pains of terminal cancer ?

(iii) Give an example of artificial sweetener that could have been recommended to diabetic patients.

[ALL INDIA 2014]

4 Mark Questions

4. Seeing the growing cases of diabetes and depression among young children, Mr.Lugani, the principal of one reputed school organized a seminar in which he invited parents and principals. They all resolved this issue by strictly banning junk food in schools and introducing healthy snacks and drinks like soup, lassi, milk, etc. in school canteens. They also decided to make compulsory half an hour of daily physical activities for the students in the morning assembly. After six months, Mr.Lugani conducted the health survey in most of the schools and discovered a tremendous improvement in the health of the students. After reading the above passage, answer the following questions :

(i) What are the values (at least two) displayed by Mr.Lugani?

(ii) As a student, how can you spread awareness about this issue?

(iii) What are antidepressant drugs? Give an example.

(iv) Name the sweetening agent used in the preparation of sweets for a diabetic patient.

[ALL INDIA 2015]

5. Mr. Roy, the principal of one reputed school organized a seminar in which he invited parents and principals to discuss the serious issue of diabetes and depression in students. They all resolved this issue by strictly banning the junk food in school and to introduce healthy snacks and drinks like soup, lassi, milk etc. in school canteens. They also decided to make compulsory half an hour physical activities for the students in the morning assembly daily. After six months, Mr. Roy conducted the health survey in most of the schools and discovered a tremendous improvement in the health of students.

After reading the above passage, answer the following:

(i) What are the values at least two, displayed by Mr. Roy?

(ii) As a student, how can you spread awareness about this issue?

(iii) What are tranquilizers? Give an example.

(iv) Why is use of aspartame limited to cold foods and drinks?

[DELHI 2015]

6. Due to hectic and busy schedule, Mr. Singh started taking junk food in the lunch break and slowly became habitual of eating food irregularly to excel in his field. Once during a meeting, he felt severe chest pain and fell down. Mr.Khanna, a close friend of Mr. Singh, took him to the doctor immediately. The doctor diagnosed that Mr. Singh was suffering from acidity and prescribed some medicines. Mr.Khanna advised him to eat homemade food and change his lifestyle by doing yoga, meditation and some physical exercise. Mr. Singh followed his friend's advice and after a few days he started feeling better.

After reading the above passage, answer the following:

(i) What are the values (at least two) displayed by Mr.Khanna?

(ii) What are antacids? Give one example.

(iii) Would it be advisable to take antacids for a long period of time? Give reason.

[ALL INDIA 2016]

Solutions

1. (i) Mrs. Anuradha does not panic, is helpful and considerate. [1]

(ii) Vitamin B_{12}. [1]

(iii) Vitamin – C [1]

2. (a) The values showed by Sonali are awareness regarding adverse effect of junk food and concern for the health of her school mates. The values showed by the Principal are responsible behaviour in listening to Sonali's views and taking prompt action in replacing junk food with healthy food. [2]

(b) The two water soluble vitamins are vitamin B2 (Riboflavin) and Vitamin C (Ascorbic acid). [1]

3. (i) (a) Dr. Satpal distributed free medicines to people. So showed a caring and aware nature. [1]

(b) National Human Rights Commission showed responsibility and action orientedness. [1]

(ii) Aspirin

(iii) Aspartame [1]

4. (i) Mr.Lugani is well aware of harmful effects of junk food & diseases related to it, he is caring and concerned for others. [1]

(ii) As a student we can make posters and plays to make people aware about adverse effects of junk foods [1]

(iii) Antidepressant drugs help in treatment of stress, relieve anxiety & induce a sense of well being by inhibiting the enzyme which catalyses degradation of noradrenaline [1]

(iv) Aspartame [1]

5. (i) Mr. Roy showed concern for the health of the students, and is caring in nature and aware towards the harmful effects of junk food. [1]

(ii) As a student, I can spread awareness regarding diabetes and depression among students by conducting seminars, health camps, distribution of pamphlets, and workshops by doctors, to highlight the need to follow healthy eating habits. [1]

(iii) Tranquilizers are neurologically active drugs that induce a sense of well-being and are used to treat stress, anxiety and mild or severe mental disease. They perform their function by inhibiting the message transfer mechanism from nerve to receptor e.g., equanil, meprobamate and iproniazid etc. [1]

(iv) Because aspartame is unstable at cooking temperature and decomposes. [1]

6. (i) The following values are displayed by Mr.Khanna: (a) Care and concern: He cared for the well-being of his friend, Mr. Singh. (b) Knowledge: He suggested effective measures to Mr. Singh to counter acidity and improve his health. (c) Presence of mind: He acted immediately by taking his friend to the doctor. [1]

(ii) Antacids are a class of drugs used to treat acidity. They contain either sodium hydrogen bicarbonate or aluminum/ magnesium hydroxide. For example, milk of magnesia. [1]

(iii) Long-time exposure to sodium bicarbonate can increase the pH of the stomach, making it alkaline. This will lead to more production of acid. So metal hydroxides are a better alternative to bicarbonate as they do not tend to increase the pH level above neutrality. Antacids only stop the symptoms of acidity. They are not the cure for acidity. If the acidity advances, it leads to formation of ulcers whose only treatment is removal of the affected area of the stomach. Hence, it is not advisable to take antacids for a long period of time. [1+1]

Smart Notes ....

CBSE
Sample Question Paper 1

Chemistry
Class XII

Time : 3 hrs **Maximum Marks : 70**

General Instructions

(i) All questions are compulsory.
(ii) Question number 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Question number 6 to 10 are short answer questions and carry 2 marks each.
(iv) Question number 11 to 22 are also short answer questions and carry 3 marks each.
(v) Question number 23 is a value based question and carries 4 marks.
(vi) Questions number 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables, if necessary. Use of calculators is not allowed.

SECTION A

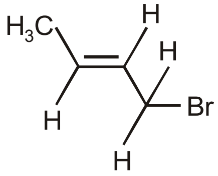
(1 × 5 = 5)

1. Which type of stoichiometric defect is shown by ZnS ?

2. Name the two groups in which catalysis is divided into.

3. Draw the geometrical isomers of $Pt(NH)_3Cl_2$.

4. Write the IUPAC name of:



5. What is the order of reactivity of alcohols in the given reaction?

$$R-OH + HCl \xrightarrow{ZnCl_2} R-Cl + H_2O$$

SECTION B

(2 × 5 = 10)

6. Calculate the freezing point of a solution containing 90 g of glucose (Molar mass = 180 g mol^{-1}) in 300 g of water. (K_f of water = 1.86K kg mol^{-1})

7 Assign reasons for the following:

1. Copper (I) ion is not known in aqueous solution.

2. Actinoids exhibit greater range of oxidation states than lanthanoids.

8 How will you convert the following?

(a) Toluene to Benzadehyde

(b) Butanal to Butanoic acid

OR

Account for the following:

(a) Electrophilic substitution in benzoic acid takes place at meta position.

(b) Carboxylic acids do not give characteristic reactions of carbonyl group.

9 Complete the following equations:

(a) $5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow$

(b) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow$

10 The decomposition of NH_3 on platinum surface is zero order. What is the rate of production of H_2 if $k = 2.5 \times 10^{-4}$ mol $L^{-1}s^{1}$.

SECTION C

(3 × 12 = 36)

11 Explain the following:

(a) Why on adding 1 mol of glucose to 1 litre water increases the boiling point of water.

(b) Liquid ammonia bottle is first cooled in ice before opening it.

(c) Aquatic species are more comfortable in cold water but not in warm water.

12 An element with molar mass 27g mol^{-1} forms a cubic unit cell with edge length of 4.05×10^{-8} cm. If its density is 2.7 g cm^{-3}, what is the nature of the cubic unit cell?

13 (a) Classify the solids on the basis of the nature of intermolecular forces: Silicon carbide, Argon

(b) ZnO turns yellow on heating. Why?

(c) What is meant by groups 12-16 compounds? Give an example.

OR

How would you account for the following?

(i) Transition metals exhibit variable oxidation states.

(ii) Zr(Z = 40) and Hf (Z = 72) have almost identical radii.

(iii) Transition metals and their compounds act as catalyst.

14 (a) What is the principle of electrolytic refining?

(b) Why does copper obtained in the extraction from copper pyrites have a blistered appearance?

(c) What is the role of depressants in the froth floatation process

15 Write the name and magnetic behaviour of the following:

At. Nos. Mn = 25, Co = 27, Ni = 28

(i) $K_4[Mn(CN)_6]$

(ii) $[Co(NH_3)_5Cl]Cl_2$

(iii) $K_2(Ni(CN)_4)$

16 (a) In reference to Freundlich adsorption isotherm, write the expression for adsorption of gases on solids in the form of an equation.

(b) Write an important characteristic of lyophilic sols.

(c) Based on type of particles of dispersed phase, give one example each of associated colloid and multi molecular colloid.

17 A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed?

(Given: log2 = 0.3010, log3 = 0.4771, log4 = 0.6021)

18 Rearrange the compounds of each of the following sets in order of reactivity towards S_N2 displacement:

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane

(iii) 1-Bromobutane, 1-Bromo-2, 2-dimethylpropane, 1-Bromo-2-methylbutane

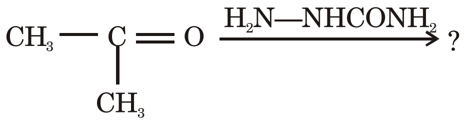
19. What are the following substances? Give one example of each.

(i) Food preservatives

(ii) Synthetic detergents

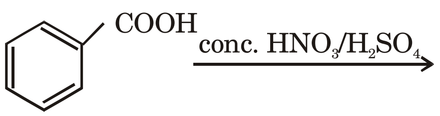
(iii) Antacids

20 Predict the products of the following reactions:

(i) 

$$CH_3-\underset{\underset{CH_3}{|}}{C}=O \xrightarrow{H_2N-NHCONH_2} ?$$

(ii) $C_6H_5-CH_2-CH_3 \xrightarrow[(b)H^+]{(a)KMnO_4/KOH} ?$

(iii) 

21 Write the names and structures of the monomers of the following polymers

(i) Nylon-6,6

(ii) Bakelite

(iii) Polystyrene

22 (A), (B) and (C) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers (A) and (C) give positive Tollen's test whereas isomer (B) does not give Tollen's test but gives positive iodoform test. Isomers (A) and (B) on reduction with Zn (Hg)/conc. HCl give the same product (D).

(a) Write the structures of (A), (B), (C) and (D).

(b) Out of (A), (B) and (C) isomers, which one is least reactive towards addition of HCN?

SECTION D

(1 × 4 = 4)

23 Seeing the growing cases of diabetes and depression among young children, Mr. Lugani, the principal of one reputed school organized a seminar in which he invited parents and principals. They all resolved this issue by strictly banning junk food in schools and introducing healthy snacks and drinks like soup, lassi, milk, etc. in school canteens. They also decided to make compulsory half an hour of daily physical activities for the students in the morning assembly. After six months, Mr. Lugani conducted the health survey in most of the schools and discovered a tremendous improvement in the health of the students.

After reading the above passage, answer the following questions :

(i) What are the values (at least two) displayed by Mr. Lugani?

(ii) As a student, how can you spread awareness about this issue?

(iii) What are antidepressant drugs? Give an example.

(iv) Name the sweetening agent used in the preparation of sweets for a diabetic patient.

SECTION E

(3 × 5 = 15)

24 (a) Calculate E^0_{cell} for the following reaction at 298 K:

$$2A1(s) + 3Cu^{2+}(0.01M) \longrightarrow 2Al^{3+}(0.01M) + 3Cu(s)$$

Given: E_{cell} = 1.98 V

(b) Using the E^0 values of A and B, predict which is better for coating the surface of iron $\left[E^0_{(Fe^{2+}/Fe)} = -0.44V\right]$ to prevent corrosion and why?

Given: $E^0_{(A^{2+}/A)} = -2.37V : E^0_{(B^{2+}/B)} = -0.14V$

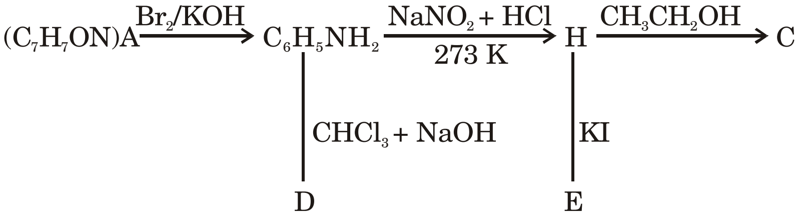
OR

(a) The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is 3.905×10^{-5}S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).

Given $E^0_{(H+)} = 349.6 S\ cm^2 mol^{-1}$ and $\lambda^0_{(CH_3COO^-)} = 40.9\ S cm^2 mol^{-1}$

(b) Define electrochemical cell. What happens if external potential applied becomes greater than E^0_{cell} of electrochemical cell?

25. An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions.



OR

(a) Write the structures of main products when aniline reacts with the following reagents:

(i) Br_2 water

(ii) HCl

(iii) $(CH_3CO)_2O$/pyridine.

(b) Arrange the following in the increasing order of their boiling point:

$C_2H_5NH_2$, C_2H_2OH, $(CH_3)_3N$.

(c) Give a simple chemical test to distinguish between the following pair of compounds:

$(CH_3)_2NH$ and $(CH_3)_3N$.

26 (a) Explain why:

(i) F_2 has less bond enthalpy than Cl_2.

(ii) PH_3 has lower boiling point than NH_3.

(b) Draw the structures of the following molecules:

(i) $(HPO_3)_3$ (ii) BrF_3 (iii) XeF_4

OR

(a) Account for the following:

(i) Helium is used in diving apparatus.

(ii) Flourine does not exhibit positive oxidation state.

(iii) Oxygen shows catenation behaviour less than sulphur.

(b) Draw the structures of the following molecules.

(i) XeF_2 (ii) $H_2S_2O_8$

CBSE
Sample Question Paper 2

Chemistry
Class XII

Time : 3 hrs **Maximum Marks : 70**

General Instructions

(i) All questions are compulsory.
(ii) Question number 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Question number 6 to 10 are short answer questions and carry 2 marks each.
(iv) Question number 11 to 22 are also short answer questions and carry 3 marks each.
(v) Question number 23 is a value based question and carries 4 marks.
(vi) Questions number 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables, if necessary. Use of calculators is not allowed.

SECTION A

(1 × 5 = 5)

1 A coordination compound with molecular formula $CrCl_3.4H_2O$ when precipitates, it gives one mole of AgCl present in $AgNO_3$ solution. The molar conductivity of the solution is equivalent to two ions. What is the name and structural formula of the compound?

2 Give reason how stability of sols is explained using Brownian movement.

3 Which crystal defect reduces the density of an ionic solid?

4 A noble gas species A is isostructural with IBr_2. Give the formula of A.

5 Out of the two isomers, o-nitrophenol and p-nitrophenol, which one is more volatile?

SECTION B

(2 × 5 = 10)

6 Calculate the emf of the cell at 298 K:

$Cr(s)/Cr^{3+}$ (0.1M)//Fe^{2+} (0.1M)/Fe(s) [Given: $E^0_{cell} = +0.30V$]

OR

The conductivity of 10^{-3} mol/L acetic acid at 25°C is 4.1×10^{-5} Scm^{-1}. Calculate the degree of dissociation, if Λ^0_m for acetic acid at 25°C is 390.5 Scm^2mol^{-1}.

7 (i) Name the compound which is stable in acidic medium and is an oxoanion of chromium.

(ii) Identify the lanthanoid element which exhibits +4 oxidation state.

8 Out of the two solutions, which one has higher freezing point and why?

$0.1MK_3[Fe(CN)_6]$, $0.05M\ Al_2(SO_4)_3$

9 Find the values of equilibrium constant (K_c) and ΔG^0 and for the following reaction:

$$Ni(s) + 2Ag^+(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$$

$E^0 = 1.05V$ ($1F = 96500C\ mol^{-1}$)

10 Write the reagents used in the following reactions:

(i) $CH_3 - COOH \xrightarrow{?} CH_3 - COCl$

(ii) $C_6H_5 - CO - CH_3 \xrightarrow{?} C_6H_5 - CH_2 - CH_3$

SECTION C

(3 × 12 = 36)

11 Explain the principle involved in the following operations in metallurgy along with an example of each:

(i) Zone refining

(ii) Hydraulic washing

12 The rate constant for a first order reaction is 40 s^{-1}. How much time will it take to reduce 1g of the reactant to 0.0482g?

OR

The rate of a reaction becomes four times when the temperature changes from 293 K to 313 K. Calculate the energy of activation (E_a) of the reaction assuming that it does not change with temperature.

[$R = 8.314\ J\ K^{-1}mol^{-1}$, log4 = 0.6021]

13 Which type of reaction is involved in the formation of following polymers from their monomers?

(i) Nylon-6

(ii) PVC

(iii) PHBV

14 The freezing point of benzene decreases by 2.12 K when 2.5 g of benzoic acid (C_6H_5COOH) is dissolved in 25g of benzene. Calculate the percentage association of benzoic acid and the van't Hoff factor when benzoic acid forms a dimer. (K_f for benzene = 5.12 K kg mol^{-1})

15 What will be the product formed when:

(i) Chloroethane is treated with silver nitrite.

(ii) 2-Methyl-1-bromopropane is treated with sodium in the presence of dry ether.

(iii) 1-methyl cyclohexene is treated with HI.

16 A metal ion M^{n+} combines with three bidentate ligands to form a complex compound. It has d^4 valence electronic configuration. Assuming $\Delta_n > P$:

(i) What will be the electronic configuration of d^4 ion.

(ii) What is the type of hybridization of M^{n+} ion?

(iii) Name the type of isomerism exhibited by the compound.

17 (i) When glucose reacts with acetic acid, glucose penta acetate is formed. What does it explain about the structure of glucose?

(ii) Which vitamin deficiency causes rickets?

(iii) Which base is only found in nucleotide of RNA?

18 Iron has a body centered cubic unit cell with a cell dimension of 286.65 pm. The density of iron is 7.874 g cm^{-3}. Use this information to calculate Avogadro's number. (At. Mass of Fe = 55.845 u)

19 Calculate the boiling point of solution when 4g of $MgSO_4$ (M = 120 g mol^{-1})was dissolved in 100 g of water. Assuming $MgSO_4$ undergoes complete ionization.

(K_b for water = 0.52 K kg mol^{-1})

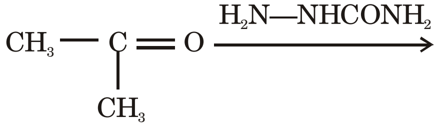
20 How would you account for the following?

(i) Many of the transition elements are known to form interstitial compounds.

(ii) The metallic radii of the third (5d) series of transition metals are virtually the same as those of the corresponding group member of the second (4d) series.

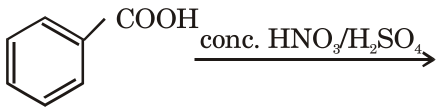
(iii) Lanthanoids from primarily +3 ions, while the actinoids usually have higher oxidation states in their compounds, +4 or even + 6 being typical.

21 Predict the products of the following reactions:

(i) 

$CH_3-\underset{\underset{CH_3}{|}}{C}=O \xrightarrow{H_2N-NHCONH_2}$

(ii) $C_6H_5-CH_2-CH_3 \xrightarrow[(b)H^+]{(a)KMnO_4/KOH} ?$

(iii) 

22 Give reasons for the following:

(i) p-nitrophenol is more acidic than p-methylphenol.

(ii) Bond length of C — O bond in phenol is shorter than that in methanol.

(iii) $(CH_3)_3C - Br$ on reaction with sodium methoxide ($Na^{+}\,{}^{-}OCH_3$) gives alkene as the main product and not an ether.

SECTION D

(1 × 4 = 4)

23 Mr. Roy, the principal of one reputed school organized a seminar in which he invited parents and principals to discuss the serious issue of diabetes and depression in students. They all resolved this issue by strictly banning the junk food in school and to introduce healthy snacks and drinks like soup, lassi, milk etc. in school canteens. They also decided to make compulsory half an hour physical activities for the students in the morning assembly daily. After six months, Mr. Roy conducted the health survey in most of the schools and discovered a tremendous improvement in the health of students.

After reading the above passage, answer the following:

(i) What are the values (at least two) displayed by Mr. Roy?

(ii) As a student, how can you spread awareness about this issue?

(iii) What are tranquilizers? Give an example.

(iv) Why is use of aspartame limited to cold foods and drinks?

SECTION E

(3 × 5 = 15)

24 (a) Account for the following:

(i) Adding character increases from HF to HI.

(ii) There is large difference between melting and boiling points of oxygen and sulphur.

(iii) Nitrogen does not form pentahalide.

(b) Draw the structures of the following:

(i) ClF_3

(ii) XeF_4

OR

(i) Which allotrope of phosphorus is more reactive and why?

(ii) How the supersonic jet aeroplanes are responsible for the depletion of ozone layers?

(iii) F_2 has lower bond dissociation enthalpy than Cl_2. Why?

(iv Which noble gas is used in filling balloons for meteorological observations?

(v) Complete the equation: $XeF_2 + PF_5$

25 Conductivity of 0.00241 M acetic acid solution is 7.896×10^{-5} Scm^{-1}. Calculate its molar conductivity in this solution. If $\Delta^0{}_m$ for acetic acid be 390.5 S cm^2 mol^{-1}, what would be its dissociation constant?

OR

Three electrolytic cells A, B and C containing solutions of zinc sulphate, silver nitrate and copper sulphate, respectively are connected in series. A steady current of 1.5 ampere was passed through them until 1.45 g of silver were deposited at the cathode of cell B. How long did the current flow? What mass of copper and what mass of zinc were deposited in the concerned cells? (Atomic masses of Ag = 108, Zn = 65.4, Cu = 63.5)

26. (a) Write the reactions involved in the following:

(i) Hofmann bromamide degradation reaction

(ii) Diazotisation

(iii) Gabriel phthalamide synthesis

(b) Give reasons:

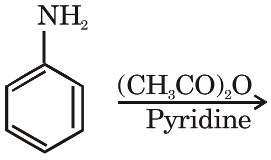
(i) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.

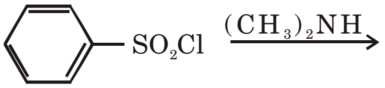
(ii) Aromatic diazonium salts are more stable than aliphatic diazonium salts.

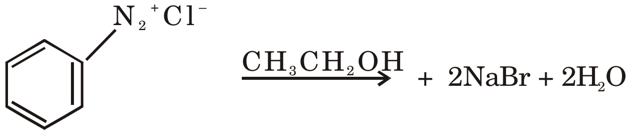
OR

(a) Write the structures of the main products of the following reactions:

(i)



(ii) 

(iii) 

(b) Give a simple chemical test to distinguish between Aniline and N,N-dimethylaniline.

(c) Arrange the following in the increasing order of their pK$_b$ values:

$C_6H_5NH_2$, $C_2H_5NH_2$, $C_6H_5NHCH_3$