ON TIPS NOTES

Note Making is a skill that we use in many walks of life : at school, university and in the world of work. However, accurate note making requires a thorough understanding of concepts. We, at Oswaal, have tried to encapsulate all the chapters from the given syllabus into the following "On Tips Notes". These notes will not only facilitate better understanding of concepts, but will also ensure that each and every concept is taken up and every chapter is covered in totality. So go ahead and use these to your advantage… Go get the **Oswaal Advantage!!**

UNIT-I	SOLID STATE

- ➢ **Solids :** Solids are chemical substances which are characterized by definite mass, shape, volume, rigidity, high density and low compressibility.
- ➢ Solids have high melting and boiling points.
- ➢ **Two types of solids :**
  - **(i) Crystalline solids :** Solids in which constituent particles have an ordered arrangement (long range order) are crystalline solids. *e.g.,* NaCl, diamond, etc.

    Classification of crystalline solids :
    - (a) **Molecular solids :** Solids in which constituent particles are molecules, joined with London forces (*e.g.,* Ar, CCl_4 etc.), Dipole-dipole interactions (*e.g.,* HCl, SO_2, etc.) or Hydrogen bonding (H_2O – ice).
    - (b) **Ionic solids :** Solids in which constituent particles are ions (positive and negative), joined with Coulombic or electrostatic forces. *e.g.,* NaCl, MgO, etc.,
    - (c) **Metallic solids :** Solids in which constituent particles are positive ions (kernels) in a sea of delocalized electrons joined by metallic bond. *e.g.,* Fe, Ag, etc.
    - (d) **Covalent or Network solids :** Solids in which constituent particles are atoms joined by covalent bond. *e.g.,* SiO_2 (Quartz), C (Diamond), C (Graphite), etc.
  - **(ii) Amorphous solids :** Solids in which constituent particles do not have an ordered arrangement (short range order) are amorphous solids. *e.g.,* plastic, glass, etc.
- ➢ **Isotropy :** In the amorphous solids, there is no regular arrangement of particles, thus properties like electrical conductivity, thermal expansion are identical in all direction. This property is called as isotropy.
- ➢ **Anisotropy :** Due to regular arrangement of constituent particles, the different particles fall in different ways of a crystalline solid. The values of properties like electrical conductivity and thermal expansion varies in all the direction, this property is called as anisotropy.
- ➢ **Crystal lattice :** The regular three dimensional arrangement of the constituent particles in a crystal in which each particle is represented by point is called as a crystal lattice and points are called lattice points.
- ➢ **Unit cell :** Smallest, fundamental repeating three dimensional unit of a crystal lattices.
- ➢ **Types of unit cell :**
  - **(i) Primitive cell :** Constituent particles are present only at the corner positions of a unit cell.
  - **(ii) Centred unit cell or non-primitive unit cell :** Particles (or points) are present at corners and at other positions also.
- ➢ **Bravais lattice :** These are the arrangement of lattice points in three dimensional space of crystal shown by relative distance and facial angles along the three axes.
- ➢ **There are 14 Bravais lattices, as shown in table below :**

S. No.	Unit cell	Crystal system basic	Relative axial distances	Axial angles	Symmetry	Bravais lattice	Examples
1. 2. 3.	Primitive Body-centred Face-centred	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	9 planes, 13 axis	3	NaCl, KCl, ZnS, Diamond
4. 5.	Primitive Body-centred	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	5 planes, 5 axis	2	TiO_2, SnO_2, $PbSO_4$, NH_4Br
6. 7. 8. 9.	Primitive Body-centred Face-centred End-centred	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	3 planes, 3 axis	4	KNO_3, $BaSO_4$, K_2SO_4
10.	Primitive	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	7 planes, 7 axis	1	ZnO, CdS
11.	Primitive	Trigonal or Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	7 planes, 7 axis	1	$NaNO_3$, HgS
12. 13.	Primitive End-centred	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$ $\beta \neq 90°$	7 planes, 10 axis	2	Monoclinic sulphur, $PbCrO_4$
14.	Primitive	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	No planes, No axis	1	$CuSO_4.5H_2O$, $K_2Cr_2O_7$

➢ Number of atoms in a unit cell (Z) : For scc, Z = 1, for bcc Z = 2, for fcc Z = 4.

Type of cell	Number of atoms at corner	Number of atoms at faces	Number of atoms at centre of cube	Total	Radius of atom a = edge
Simple cubic crystal (*scc*)	$8 \times \dfrac{1}{8} = 1$	0	0	1	$\dfrac{a}{2}$
Body-centred cubic (*bcc*)	$8 \times \dfrac{1}{8} = 1$	0	1	2	$\dfrac{\sqrt{3}}{4}a$
Face-centred cubic (*fcc*)	$8 \times \dfrac{1}{8} = 1$	$6 \times \dfrac{1}{2} = 3$	0	4	$\dfrac{a}{2\sqrt{2}}$

➢ **Closed-packed structures :** In solids, the constituent particles are closely packed with minimum space between particles.

Types of close packing :

(i) **Close packing in one dimension :** When the spheres representing particles touch each other in a row, it is called close packing in one dimension.

(ii) **Close packing in two dimensions :** It is obtained by placing the rows of close-packed spheres. This can be done in two ways :

    (a) **Square close packing :** The particle in the adjacent rows may show a horizontal as well as vertical alignment forming squares. A central sphere is surrounded by four spheres.

    (b) **Hexagonal close packing :** The second row is placed above the first row. It is repeated in next row with each sphere is in contact with six other spheres.

(iii) **Close packing in three dimensions :** It is obtained by placing two dimensional layers one above other. They are of two types :

    (a) **Square close packed layers :** Spheres of both the layers are perfectly aligned horizontally as well as vertically. ('AAA' type pattern, C.N. = 6)

    (b) **Hexagonal close packed layers :** It is more efficient with less space unoccupied by spheres. The central sphere is in contact with six other spheres in two dimensions.

➢ **Co-ordination number :** Number of closest neighbors of any constituent particle. Simple cubic = 6, fcc = 12, bcc = 8.

➢ **Voids/Interstitial sites :** Holes left in the close packing of spheres.
    (a) Trigonal voids are the voids enclosed by three spheres in contact. Radius ratio is 0.155.
    (b) Tetrahedral voids are the voids surrounded by four point lying at the vertices of a regular tetrahedron. It is calculated by, formula = 2 × Number of particles in close packing.
    (c) Octahedral voids are the voids surrounded by six spheres lying at the vertices of a regular octahedron. It is equal to number of particles in close packing. R = 0.414.

➢ $$\text{Radius ratio} = \frac{\text{Radius of cation } (r^+)}{\text{Radius of anion } (r^-)}$$

➢ **Structural arrangement of different radius ratio of ionic solids :**

Radius ratio $\left(\dfrac{r^+}{r^-}\right)$	Possible C.N.	Structural arrangement	Examples
0.155 – 0.225	3	Trigonal planar	B_2O_3
0.225 – 0.414	4	Tetrahedral	ZnS, SiO_4^{4-}
0.414 – 0.732	6	Octahedral	$NaCl$
0.732 – 1	8	Body-centred cubic	$CsCl$

➢ **Packing efficiency :** It is the percentage of entire space covered by the particles.
hcp or ccp : 74%; bcc = 68%; simple cubic = 52.4%

➢ $$\text{Density of the unit cell } (d) = \frac{Z \times M}{N_A \times a^3}$$

Where
    Z = Number of atoms per unit cell
    M = Molar mass or atomic mass
    a = Edge Length
    N_A = Avogadro's constant

➢ **Defects or imperfection** in solids is any departure from perfectly ordered arrangement of atom in crystal.

    Point defect : When deviations exist from the regular arrangement around a point or an atom in a crystalline substance, the defect is called as point defect. It is of 3 types.

    (a) **Stoichiometric defects** are the defects which do not change the stoichiometry of solids.
      (1) **Vacancy defect** occurs when some lattice sites in a crystalline solid are vacant.
      (2) **Interstitial defect** occurs when some extra constituent particles occupy the interstitial site in crystal.
      (3) **Frenkel defect** arises when an ion leaves its fixed position and occupies an interstitial space. *e.g.*, ZnS, AgCl, etc.
      (4) **Schottky defect** arises due to vacancy of equal numbers of cations and anions *e.g.*, NaCl, FeO, etc.

    (b) **Impurity defects** arise when foreign atoms are present in the lattice site or in the interstitial site. *e.g.*, $CdCl_2$-AgCl.

    (c) **Non-stoichiometric defects** are the defects which lead to change in composition of solids. These are of two types :
      (1) **Metal excess defect :**
        ■ **Metal excess defect due to anionic vacancies :** Negative ion from the crystal lattice may be missing from its lattice leaving a vacancy, which is occupied by the electron originally associated with anion. F-centres are anionic sites occupied by unpaired electrons.
        ■ **Metal excess defect due to interstitial cation :** In this defect, an extra cation occupies interstitial position in the lattice and the free electron is trapped in the vacancy of this interstitial cation but crystal remains neutral.

(2) **Metal deficient defect :** It this, a cation is missing from its lattice site.

➤ Types of solids on the basis of electrical conductivity :
  (i) **Conductors** are the solids which permit maximum flow of electricity with conductivity order of 10^4 to 10^7 ohm^{-1} m^{-1}. *E.g.*, all metals, aqueous solution of NaCl, etc.
  (ii) **Semi-conductors** are the solids which permit less flow of electricity as compared to conductors with less conductivity order of 10^{-6} to 10^4 ohm^{-1} m^{-1}. *E.g.*, Si, Ge.
  (iii) **Insulators** are the solids which are unable to conduct electricity with conductivity order of 10^{-20} to 10^{-10} ohm^{-1} m^{-1}. *E.g.*, S, P, etc.

➤ **Band Theory** explains conductivities of solids.
  ■ **Conductors :** Negligible energy gap such that electrons can jump from valance band to conduction band easily.
  ■ **Semi-conductors :** Small energy gap such that electrons can jump from valance band to conduction band on providing little energy.
  ■ **Insulators :** Large energy gap such that electrons cannot jump from valance band to conduction band.

➤ **Doping** is mixing of impurity in semi-conductors.
  ■ *n*-type semiconductors : Silicon and germanium (Group 14) doped with donor impurity (like P or As of Group 15).
  ■ *p*-type semiconductors : Silicon and germanium (Group 14) doped with acceptor impurity (like B, Al or Ga of Group 13).

➤ **Classification of substances on the basis of magnetic properties :**
  (i) **Paramagnetic substances** are attracted in external magnetic field. *E.g.*, Cu^{2+}, O_2, etc.
  (ii) **Diamagnetic substances** are repelled in external magnetic field. E.g., Zn, TiO_2, etc.
  (iii) **Ferromagnetic substances** are most easily attracted in external magnetic field. *E.g.*, Fe, Co, Ni, etc.
  (iv) **Anti-Ferromagnetic substances** have zero magnetic moment. *E.g.*, MnO.
  (v) **Ferrimagnetic substances** are paramagnetic with magnetic moment less than that of ferromagnetic substances. *E.g.*, Fe_3O_4, $MgFe_2O_4$, etc.

UNIT-II   SOLUTIONS

➤ **Solution** is a homogeneous mixture of two or more pure substances.
➤ **Constituents of a solution :**
  (i) Solute = Dissolved in smaller quantity. *e.g.*, sugar, salt, etc.
  (ii) Solvent = Dissolved in larger quantity. *e.g.*, water, milk, etc.
➤ **Types of solutions :**

S. No.	Types of Solution	Solute	Solvent	Examples
1.	Solid – Solid	Solid	Solid	Alloys like brass, bronze, etc.
2.	Solid – Liquid	Solid	Liquid	Solution of sugar, salt, urea, etc. in water.
3.	Solid – Gas	Solid	Gas	Sublimation of substance like iodine, camphor, etc., into air, dust or smoke particles in air.
4.	Liquid – Solid	Liquid	Solid	Hydrated salts, mercury in amalgamated zinc, etc.
5.	Liquid – Liquid	Liquid	Liquid	Alcohol in water, benzene in toluene.
6.	Liquid – Gas	Liquid	Gas	Aerosol, water vapour in air.
7.	Gas – Solid	Gas	Solid	Hydrogen adsorbed in palladium.
8.	Gas – Liquid	Gas	Liquid	Aerated drinks.
9.	Gas – Gas	Gas	Gas	Mixture of gases, etc.

- **Solubility** is the maximum amount of solute that can be dissolved in 100 g solvent to form a saturated solution at a given temperature.

  Causes : Interionic attraction in the solute molecules, intermolecular attraction between solvent molecules, solvation and temperature.

  Factors affecting solubility: Nature of solute and solvent, temperature, hydration energy and pressure.

- **Mass percentage** $\left(\dfrac{w}{W}\right) = \dfrac{\text{Mass of solute present in the solution}}{\text{Total mass of the solution}} \times 100$

- **Volume percentage** $\left(\dfrac{v}{V}\right) = \dfrac{\text{Volume of solute}}{\text{Total volume of the solution}} \times 100$

- **Mass by volume percentage of solute** $\left(\dfrac{w}{V}\right) = \dfrac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$

- **Parts per million (ppm)**$= \dfrac{\text{Number of parts of component (A)}}{\text{Total number of parts of all components of the solution}} \times 10^6$

- **Mole fraction :**

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

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

$$\chi_A + \chi_B = 1$$

- **Molarity (M) :** Number of moles of solute per litre of solution.

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

  where W_B is weight of solute, V is volume of solution, M_B is molar mass of solute and n_B is number of moles of solute.

  Unit : mol L^{-1} or M (molar)

- **Molality (*m*)**$= \dfrac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}} = \dfrac{W_B \times 1000}{W \times W_A} = \dfrac{n_B}{W}$

  where W_A is weight of solvent, W_B is quantity of solute, W is molar mass of solute.

  Unit : mol kg^{-1} or *m* (molal)

- **Normality (N)**$= \dfrac{\text{Number of gram equivalent of solute}}{\text{Volume of solution in Litre}} = \dfrac{W_B \times 1000}{E_B \times V}$

  where W_B is mass of solute, E_B is equivalent weight of solute and V is volume of solution.

  Unit: eq/L or N.

- **Relationship between Molarity (M) and Molality (*m*) :**

$$m = \frac{1000\,M}{1000d - M \times M_B}$$

- **Relationship between mole fraction of solute (χ_B) and molality (*m*) :**

$$m = \frac{\chi_B \times 1000}{\chi_A \times M_A}$$

- **Relationship between molarity and density :**

$$\text{Molarity (M)} = \frac{\%\,\text{Strength} \times \text{Density} \times 10}{M_B}$$

➢ **Relationship between normality and density :**

$$\text{Normality (N)} = \frac{\% \text{Strength} \times \text{Density} \times 10}{\text{Equivalent mass of solute}}$$

➢ **Henry's law :** "The mass of a gas dissolved in given volume of the liquid at a constant temperature depends upon the pressure applied."

$$p = K_H x$$

where K_H = Henry's constant.

➢ **Vapour pressure** is the pressure exerted by vapours of a liquid at equilibrium state at constant temperature.

➢ **Raoult's law for a solution of volatile liquids** states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction in solution.

$$p_A = p°_A x_A$$
$$p_B = p°_B x_B$$

➢ **Raoult's law for non-volatile solute** states that relative lowering of vapour pressure for a solution is equal to the mole fraction of solute.

$$\chi_B = \frac{p°_A - p_A}{p°_A \times M_A}$$

➢ **Ideal solutions** obey Raoult's law.
  (i) $p_A = p_A^0 x_A; p_B = p_B^0 x_B$
  (ii) $\Delta_{mix}H = 0$
  (iii) $\Delta_{mix}V = 0$
  (iv) The force of attraction between A–A and B–B is nearly equal to A–B.

➢ **Non-ideal solutions** do not obey Raoult's law.
  (i) $p_A \neq p_A^0 x_A; p_B \neq p_B^0 x_B$
  (ii) $\Delta_{mix}H \neq 0$
  (iii) $\Delta_{mix}V \neq 0$
  (iv) The force of attraction between A–A and B–B is not equal to A–B.

➢ **Positive deviation from Raoult's law :** A–B interactions are weaker than the interactions between A–A or B–B leading to an increase in vapour pressure.

➢ **Negative deviation from Raoult's law :** A–B interactions are stronger than the interactions between A–A or B–B leading to decrease in vapour pressure.

➢ **Azeotropes** are liquid mixtures which distil over without change in composition.
  ■ **Maximum boiling azeotropes :** Large negative deviation from Raoult's law.
  ■ **Minimum boiling azeotropes :** Large positive deviation from Raoult's law.

➢ Colligative properties ∝ Number of particles in the the solute (molecule or ions) in definite volume of the solvent.

➢ **Relative lowering of vapour pressure :**

$$\frac{p_A° - p_A}{p_A°} = x_B = \frac{n_B}{n_A + n_B}$$

➢ **Elevation of boiling point :**

$$\Delta T_b = K_b \times m$$

or,
$$\Delta T_b = K_b \times \frac{W_B}{M_B} \times \frac{1000}{W_A}$$

or,
$$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A}$$

➢ **Depression of freezing point :**

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

or,
$$\Delta T_f = K_f \times \frac{W_{solute}}{M_{solute}} \times \frac{1000}{W_{solvent}}$$

or,
$$M_B = \frac{1000 \times W_B \times K_f}{\Delta T_f \times W_A}$$

➢ **Osmotic pressure :**

$$\pi = CRT$$

or,
$$\pi = \frac{\text{Number of moles of solute}}{\text{Volume of solution}} \times R \times T$$

or,
$$\pi = \frac{W_B}{M_B} \times \frac{RT}{V}$$

or,
$$M_B = \frac{W_B \times RT}{\pi \times V}$$

➢ **Osmosis** is the process in which, there is net flow of solvent from the solution of lower concentration to the higher concentration by a semipermeable membrane.

➢ **Osmotic pressure** is the extra pressure that is applied to just stop the flow of solvent to solution across a semipermeable membrane.

➢ **Abnormal molecular mass :** Molecular mass calculated with the help of colligative property which is different from theoretical molecular mass.

➢ **van't Hoff factor (i) =** $\dfrac{\text{Observed (experimental) value of a colligative property}}{\text{Normal (calculated) value of the same colligative property}}$

$$= \frac{\Delta_{obs}}{\Delta_{cal}}$$

➢ **Degree of association,** $\quad \alpha = \dfrac{i-1}{1-\dfrac{1}{n}}$

where i is van't Hoff factor and n is number of ions produced per formula of the compound.

➢ **Degree of dissociation,** $\quad \alpha = \dfrac{i-1}{n-1}$

where i is van't Hoff factor and n is number of ions produced per formula of the compound.

UNIT-III — ELECTROCHEMISTRY

➢ **Electrochemistry** is the branch of chemistry which deals with the study of the production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to result in non-spontaneous chemical transformations.

➢ **Electrolyte** is a substance that dissociates in solution to produce ions and hence conducts electricity in dissolved state or molten state.
   Weak electrolyte: H_2CO_3, CH_3COOH, *etc.*
   Strong electrolyte: NaCl, HCl, *etc.*

➢ **Resistance** is the property of given substance to obstruct the flow of charge.

$$R = \frac{V}{I}$$

Where, V = Potential difference
       I = Electric current
Unit: Ohm

Specific resistivity: If a solution is placed between two parallel electrodes having cross-sectional area 'A' and distance 'l' apart then, $R = \rho \dfrac{l}{A}$ (where ρ = Specific resistivity)

Unit: Ohm metre

➢ **Conductance** is the ease with which current flows through a conductor.

$$C = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l}$$

Unit: Siemens (S) or ohm^{-1}.

It depends upon the nature of the material, temperature and pressure.

It always decreases on dilution for both, strong and weak electrolytes.

➢ **Metallic conductance** is the electrical conductance in metals that occurs due to the movement of electrons. It depends upon the nature and structure of the metal, number of valence electrons per atom and temperature.

➢ **Electrolytic or ionic conductance** is the conductance of electricity that occurs due to ions present in the solution. It depends upon the nature of electrolyte or interionic attractions, solvation of ions, nature of solvent and its viscosity and temperature.

➢ **Specific conductivity** (κ) is reciprocal of the specific resistivity of an electrolytic solution.

$$\kappa = C \frac{l}{A}$$

Unit: S m^{-1}

➢ The resistance of electrolytic solution is determined by Wheatstone bridge method,

$$\text{Unknown, } R_4 = \frac{R_3 R_2}{R_1}$$

➢ **Cell constant (G)** is the ratio of distance between electrodes to the cross-sectional area between electrodes.

$$\text{Cell constant (G)} = \frac{l}{A}$$

Unit: cm^{-1} or m^{-1}

➢ **Molar conductivity (Λ_m)** is the conducting power of all the ions produced by one gram mole of an electrolyte in a solution.

$$\Lambda_m = \frac{\kappa}{C} \times 1000$$

Unit: S cm^2 mol^{-1}

On dilution, molar conductivity increases.

➢ **Debye Huckel Onsager equation:** $\Lambda_m = \Lambda°_m - AC^{\frac{1}{2}}$

where Λ_m = molar conductivity, $\Lambda°_m$ = limiting molar conductivity, A = constant and C = concentration of solution.

➢ **Kohlrausch's law of independent migration of ions** states that the limiting molar conductivity of an electrolyte at infinite dilution can be expressed as the sum of contributions from its individual ions.

$\Lambda_m{}^\infty = v_+\Lambda_+{}^\infty + v_-\Lambda_-{}^\infty$ and $\Lambda° = v_+\Lambda_+{}° + v_-\Lambda_-{}°$

where, v_+ and v_- are the number of cations and anions respectively.

➢ **Applications of Kohlrausch's Law:**

   (i) Calculation of molar conductivities of weak electrolyte at infinite dilution.

   (ii) Calculation of degree of dissociation(α) = $\dfrac{\Lambda_m^c}{\Lambda_m°}$

   (iii) Determination of dissociation constant (K) of weak electrolytes

$$K = \frac{C\alpha^2}{1-\alpha} = \frac{C\,(\Lambda_m^c)}{\Lambda_m°\,(\Lambda_m° - \Lambda_m^c)}$$

(iv) Determination of solubility of sparingly soluble salts:

$$\text{Solubility} = \frac{\kappa \times 1000}{\Lambda_m^\circ}$$

- **Electrochemical/Galvanic/Voltaic cell** is a device in which the redox reaction is carried out indirectly and chemical energy is converted to electrical energy.

- **Daniell cell:** $\text{Zn}(s) \mid \text{Zn}^{2+}(aq)(\text{C}_1) \mid\mid \text{Cu}^{2+}(aq)(\text{C}_2) \mid \text{Cu}(s)$

- **Electrode potential** is the potential difference set up between the metal and solution of its own ions.

- Electrode potential at 25°C, 1 bar pressure and 1 M solution is known as standard electrode potential ($E°$).

- EMF of the cell (E_{cell}) = $E_{cathode} - E_{anode}$

  In terms of standard reduction electrode potential

  $$E°_{cell} = E°_{cathode} - E°_{anode}$$

  OR

  $$E°_{(cell)} = E°_{(right)} - E°_{(left)}$$

- **Electrochemical series:** The arrangement of elements in order of increasing reduction potential values is called electrochemical series. It is also called activity series of some typical electrodes.

- **Nernst equation:**

  For general electrode: $\text{M}^{n+}(aq) + n\text{e}^- \longrightarrow \text{M}(s)$

  Nernst equation $\qquad E_{(\text{M}^{n+}/\text{M})} = E°_{(\text{M}^{n+}/\text{M})} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$

  At equilibrium $\qquad E°_{cell} = \frac{0.059}{n} \log K_c$

  For cell reaction: $a\text{A} + b\text{B} \xrightarrow{ne^-} m\text{M} + n\text{N}$

  Nernst equation at 298 K $\qquad E_{cell} = E°_{cell} - \frac{0.059}{n} \log \frac{[M]^m[N]^n}{[A]^a[B]^b}$

- **Gibbs energy for spontaneous reaction:**

  $$\Delta_r G° = -nFE°_{cell}$$
  $$\Delta G° = -2.303\, RT \log K$$

- **Electrolysis** is the process of decomposition of an electrolyte when electric current is passed through either its aqueous solution or molten (fused) state.

- **Faraday's first law of electrolysis:** The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte.

  $$m = Z \times I \times t \qquad \text{(Here, Z is electrochemical equivalent)}$$

- **Faraday's second law of electrolysis:** Amount of various substances liberated by the same quantity of electricity passed through the electrolytic solution is proportional to their chemical equivalent weights.

  $$\frac{w_1}{E_1} = \frac{w_2}{E_2}$$

- **Primary battery (non-chargeable) :** *E.g.,* Lechlanche cell and Dry cell.
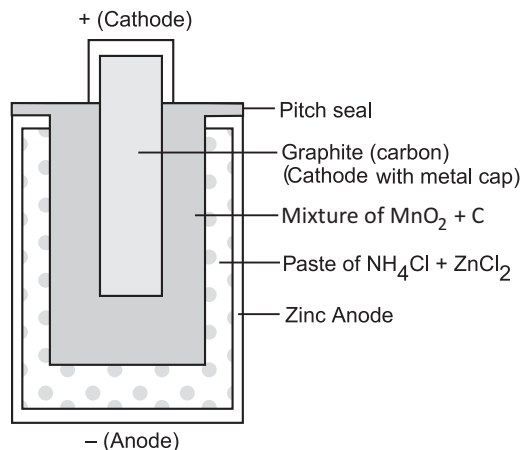 **Secondary battery (chargeable) :** *E.g.,* Pb storage battery, Ni–Cd cell.

➢ **Dry cell :**

Fig. 1 : A 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 : $Zn + NH_4^+(aq) + MnO_2 \rightarrow Zn^{2+} + MnO(OH) + NH_3$

➢ **Lead storage battery :**
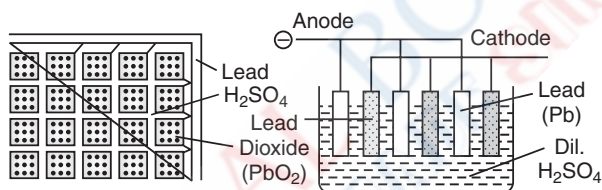
Fig. 2 : Lead storage battery

At anode : $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

At cathode : $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$

Net reaction : $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

➢ **Fuel cell :**
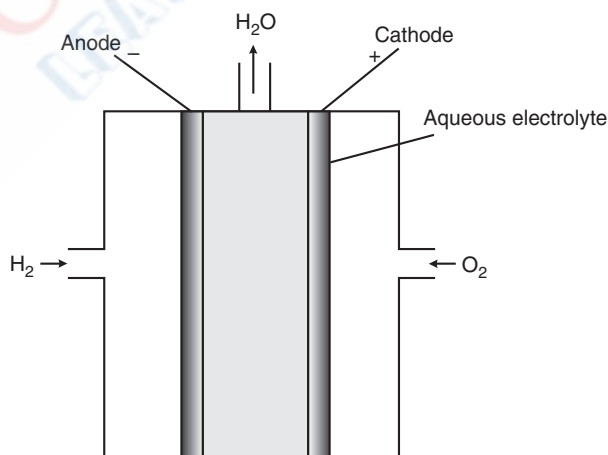
Fig. 3 : Fuel cell using H_2 and O_2 produces electricity

At anode : $[H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-] \times 2$

At cathode : $\underline{O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)}$

Net reaction : $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

➢ **Rusting of iron :** Rusting is a electrochemical phenomenon.

$$Fe(s) + 2H^+(aq) + \frac{1}{2} O_2(g) \rightarrow Fe^{2+}(aq) + H_2O(l)$$

$$2Fe^{2+}(s) + \frac{1}{2} O_2(g) + 2H_2O(l) \rightarrow Fe_2O_3(s) + 4H^+$$

$$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3 \cdot xH_2O$$
$$\text{Rust}$$
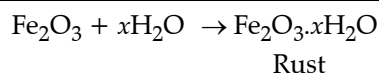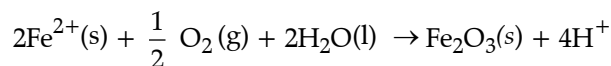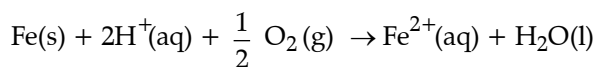
➤ **Prevention of corrosion:**
  (i) Barrier protection
  (ii) Sacrificial protection
  (iii) Alloying

| UNIT-IV | CHEMICAL KINETICS |

➤ Rate of reaction is the change of concentration of any reactant or product with time for a reaction.
  $A + B \longrightarrow C$

  Rate of reaction: For $A = \dfrac{-\Delta A}{\Delta t}$, For $B = \dfrac{-\Delta B}{\Delta t}$, For $C = \dfrac{\Delta C}{\Delta t}$

  Unit: mol $L^{-1}s^{-1}$ and atm s^{-1} or atm m^{-1} (in gaseous form).

➤ **Instantaneous rate of reaction** (The rate of change in concentration of the any one of the reactant or product at a particular time.) $= \dfrac{dx}{dt} = \dfrac{-d[A]}{dt} = \dfrac{-d[B]}{dt} = \dfrac{+d[C]}{dt}$

➤ **Average rate of reaction** (The rate of reaction measured over a long time interval.) $= \dfrac{\Delta x}{\Delta t}$, where $\Delta x =$
  Change in concentration in given time and $\Delta t =$ Time taken

➤ **Factors affecting the rate of a chemical reaction:** Concentration of the reactants, temperature, pressure, presence of catalyst, nature of the reactants, surface area of the reactants, effect of radiations and effect of physical state.

➤ **Rate law:** "The rate of reaction is directly proportional to the product of concentration of reactant and each concentration is raised to some power which may or may not be equal to stereochemistry experimentally."
  $$\text{Rate } = k[A]^m[B]^n$$

➤ **Rate constant (k)** is equal to rate of reaction when the concentration of all the reactants is unity.

➤ **Molecularity** is the total number of atoms, ions or molecules of the reactants taking part in elementary chemical reaction.

➤ The sum of the powers to which the concentration terms are raised in the rate law expression is called the **order of the reaction.**
  Order of a reaction can be zero, whole number and fractional.

➤ **Zero order reaction** → rate $= k[R]_o = k$
  Unit: mol $L^{-1} s^{-1}$.

➤ **First order reaction** → $k = \dfrac{2.303}{t} \log \dfrac{[R]_o}{[R]} \begin{array}{l} \text{(initial conc.)} \\ \text{(conc. of reactant at time } t) \end{array}$

  for 1st order reaction, half-life is independent of $[R]_o$
  Unit: s^{-1} or min^{-1}

➤ **Second order reaction** → $\dfrac{dx}{dt} = k[A]^1[B]^1$

  Unit: mol^{-1} L s^{-1} or $M^{-1}s^{-1}$ where M is molarity.

➤ **Pseudo first order reactions** are not truly first order but become first order under certain conditions. *e.g.,* inversion of sugar and acidic hydrolysis of an ester.
  Unit: s^{-1}

➢ **Half-life of a reaction** is the time taken for a reaction when half of the initial value has reacted.

For zero order reaction, $$t_{1/2} = \frac{[R]_o}{2k}$$

For first order reaction, $$t_{1/2} = \frac{0.693}{k}$$

➢ $t_{1/2} \propto [R]$ for zero order

$t_{1/2}$ is independent of $[R]$ for first order.

➢ $$\textbf{Temperature coefficient} = \frac{k(T+10)}{k(T)}$$

➢ Activation energy is the minimum amount of energy that is required to activate atoms or molecules to a condition in which they can undergo chemical transformation.

Activation energy = Threshold energy – Kinetic energy

➢ **Arrhenius equation :**

$$k = Ae^{-E_a/RT}$$

$$\log k = \log A - \frac{E_a}{2.303\, RT}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\, R}\left[\frac{T_2 - T_1}{T_2 \cdot T_1}\right]$$

➢ Rate of reaction $= f \times Z$

where, Z = collision frequency

f = fraction of collisions

➢ According to collision theory, $R = Z_{AB}e^{-E_a/RT}$

➢ $R = PZ_{AB}e^{-E_a/RT}$

$P \rightarrow$ Steric factor

➢ Intermediate complex theory :

A + B + X $\longrightarrow$ A⋯B $\longrightarrow$ A—B + X
Reactants Catalyst   Products Catalyst
                   X
              Intermediate
                complex
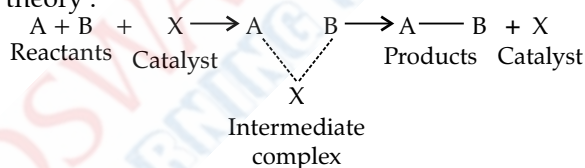
➢ **Integrated rate laws for the reactions of zero and first order:**

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half life	Units of k
0	R→P	$d[R]/dt = -k$	$kt = [R]_o - [R]$	$[R]$ *vs t.*	$[R]_o/2k$	conc time^{-1} **OR** mol L$^{-1}s^{-1}$
1	R→P	$d[R]/dt = -k[R]$	$[R] = [R]_o\, e^{-kt}$ **OR** $kt = ln([R]_o/[R])$	*ln* $[R]$ *vs t.*	*ln* 2/k	time^{-1} **OR** s^{-1}

➢ **Difference between:**

■ **Order of Reaction and Molecularity:**

S. No.	Order of Reaction	Molecularity
1.	It is the sum of the power of the concentration terms in the rate law expression.	It is the number of reacting species undergoing simultaneous collision in the reaction.

| 2.	It is determined experimentally.	It is a theoretical concept.
3.	It can have fractional values also and can be zero.	It can have integral value only and cannot be zero.
4.	It changes with temperature and pressure.	It does not change with change in temperature and pressure.

■ **Rate of reaction and Rate constant:**

S. No.	Rate of reaction	Rate constant
1.	It is the change in the concentration of reactants/products per unit time.	It is equal to the rate of the reaction when the molar concentration of each reactant is unity.
2.	The unit of rate of reaction is always mol $L^{-1}s^{-1}$.	The unit of rate constant varies with the order of reaction.
3.	It depends upon the molar concentration of reactants at that time.	It is constant for a particular reaction at constant temperature and does not depend on concentration of reactants.

UNIT-V   SURFACE CHEMISTRY

➢ **Surface chemistry** is the branch of chemistry which deals with the phenomenon that occurs at the surfaces.

➢ **Adsorption** is a surface phenomenon in which the substance gets accumulated on the surface of a solid rather than in the bulk of a solid or liquid.

➢ **Adsorbent** is the surface that adsorbs and the one that gets adsorbed is called an **adsorbate**.

➢ **Types of adsorption:**
   (i) **Physical adsorption** (van der Waals forces are involved.)
   (ii) **Chemical adsorption** (chemical bonds are involved.)

➢ **Desorption** is the process of removing an adsorbed substance from a surface on which it is adsorbed.

➢ **Sorption** is when adsorption and absorption takes place simultaneously.

➢ **Adsorption isobar** is a plot of extent of adsorption (x/m) vs. temperature at constant pressure.

■ **Adsorption isotherm** is the plot of extent of adsorption (x/m) vs. pressure (p) at constant temperature, where, 'x' is the quantity of gas adsorbed by unit mass 'm' of the solid adsorbed.

■ **Freundlich adsorption isotherm:** It is a graph which shows relationship between magnitude of adsorption (x/m) and pressure at a constant temperature.

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$
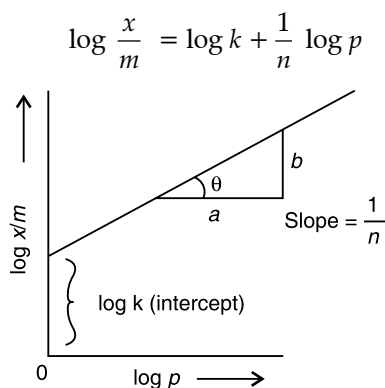
➤ **Catalysts** are the substances which alter the rate of a chemical reaction and the phenomenon is known as catalysis.

➤ **Promoters** are substances that enhance the activity of catalyst.

$$N_2(g) + 3H_2(g) \xrightleftharpoons[\text{Mo}]{\text{Fe}} 2NH_3(g)$$

catalyst

Promoter
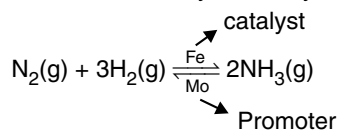
➤ Poisons or Inhibitors are the substances which decrease the activity of catalyst.

➤

Catalyst

Homogeneous
(Reactant and catalyst are in same phase)

Heterogeneous
(Reactant and catalyst are in different phase)
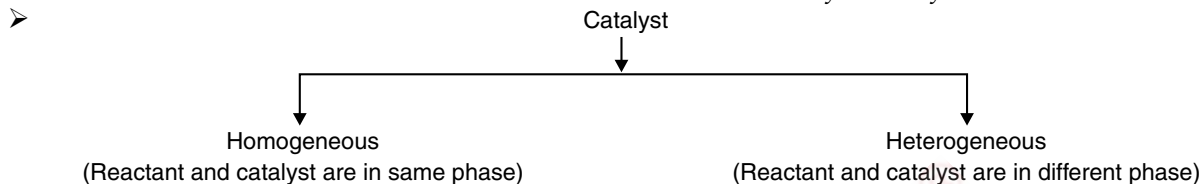
According to **Adsorption Theory of Catalysis,** the reactants in gaseous state or in solutions are adsorbed on the surface of the solid catalyst.

Important feature of solid catalyst : (i) Activity : Ability of catalyst to accelerate a chemical reaction.
(ii) Selectivity : Ability of catalyst to direct a reaction to yield particular product.

Shape selective catalysis is a reaction that depends upon the pore structure of the catalyst and the molecular size of the reactant and products.

Example : Zeolites (honey comb like structure)

➤ **Mechanism of enzyme catalysis :**

Step 1 : Binding of enzyme to substrate to form an activated complex.

$$E + S \rightarrow ES^*$$
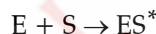
Step 2 : Decomposition of the activated complex to form product.

$$ES^* \rightarrow E + P$$
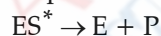
➤ A **colloid** is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium.

➤ **Dispersed phase** is the component present in small proportion like solute in the solution.

➤ **Dispersion medium** is the medium in which the colloidal particles are dispersed.

➤ **Types of Colloidal solutions:**

S. No.	Dispersed phase	Dispersion medium	Name	Examples
1.	Solid	Gas	Aerosol	Smoke, dust particles.
2.	Solid	Liquid	Sol	As_2S_3, Gold sol, starch, gum, muddy water
3.	Solid	Solid	Solid sol	Coloured gem stones, some alloys, pearls, ruby glass
4.	Liquid	Solid	Gel	Jellies, cheese, butter
5.	Liquid	Liquid	Emulsion	Milk, hair cream, cod-liver oil
6.	Liquid	Gas	Aerosol	Fog, mist, cloud
7.	Gas	Solid	Solid sol	Pumice stone, foam rubber, cork
8.	Gas	Liquid	Foam	Whipped cream, soap lather, froth

➤ **Classification based on:**

(i)   Nature of interaction between dispersed phase and dispersion medium:

- ■ **Lyophilic colloids:** ("Solvent loving")
- ■ **Lyophobic colloids:** ("Solvent hating")

(ii) Type of particles of the dispersed phase:
- ■ **Multimolecular colloids** contain large number of dispersed particles having diameter less than 1 nm to form aggregates of many molecules (lyophobic). *e.g.*, sulphur sol, gold sol, *etc.*
- ■ **Macromolecular colloids** are molecularly dissolved solutions of a polymer with particle size of colloidal range (lyophilic). *e.g.*, starch (naturally occurring), polythene (man-made).
- ■ **Associated colloids (Micelles)** behave as normal strong electrolytes at low concentrations, show colloidal properties at higher concentrations due to formation of aggregate particles of colloidal dimensions.

➢ **Preparation of colloids:**
- **(i) Mechanical dispersion:** A suspension of coarse ground particles prepared in dispersion medium is fed into a colloidal mill and speed of rotation is adjusted.
- **(ii) Electrodispersion: (Bredig's arc method)** Two rods of the metal (Au, Cu, Pt, Ag) to be dispersed are kept immersed in cold and a direct electric arc is struck between them. In this way, vapours of metal are formed which then immediately condense to form particles of colloidal size.
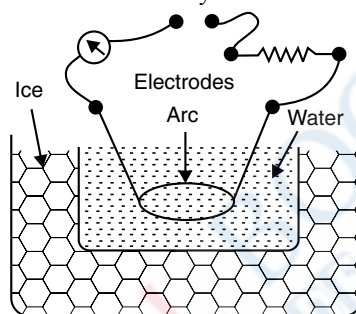
Fig. 1: Bredig's arc method

➢ **Chemical methods:**
- ■ **Oxidation:** Solutions of non-metals are prepared by this method. *e.g.*, colloidal solution of sulphur.
$$2H_2S + 2(O) \xrightarrow{HNO_3(conc.)} 2S + 2H_2O$$
- ■ **Reduction:** Metal sols can be prepared by this method. *e.g.*, gold sol.
$$2AuCl_3 + 3SnCl_2 \longrightarrow 2Au + 3SnCl_4$$
$$2AuCl_3 + 3HCHO + 3H_2O \longrightarrow 2Au \text{ (sol)} + 3HCOOH + 6HCl$$
- ■ **Hydrolysis:** Hydroxide sols are prepared by this method. *e.g.*, $Fe(OH)_3$, $Al(OH)_3$.
$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$$
- ■ **Double decomposition:** This method is used to prepare colloids from inorganic salts. *e.g.*,
$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$
- ■ **Exchange of solvent**
- ■ **Excessive cooling**
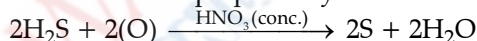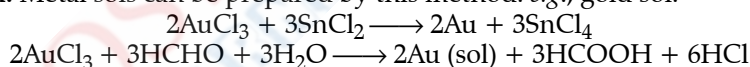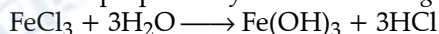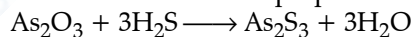
➢ **Peptization** is the conversion of precipitate into colloidal solution in presence of peptizing agent.

➢ **Purification methods of colloidal solutions:**
- **(i) Dialysis:** Particles of true solutions can pass through parchment paper or cellophane membrane.
- **(ii) Electrodialysis:** Movement of ions across the membrane can be quickened by applying electric potential through two electrodes.
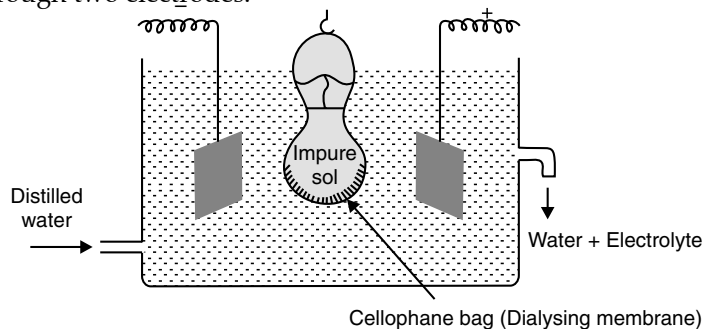

Fig. 2: Electrodialysis

(iii) Ultrafiltration is the process of separating colloidal particles by specially prepared filter papers whose pore size is reduced by dipping it in colloidal solution.

➢ **Properties of colloids:**

(i) **Brownian movement:** Zig-zag movement when seen under powerful microscope.

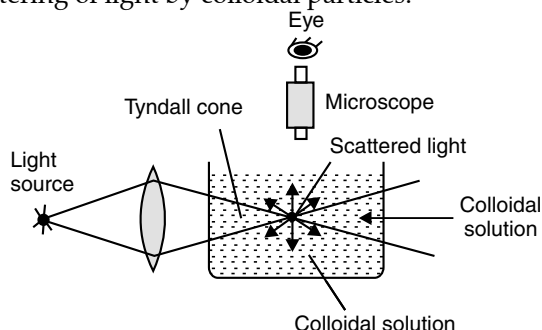**(ii)** **Tyndall effect:** Scattering of light by colloidal particles.

Fig. 3: Tyndall effect

(iii) Electrophoresis is the movement of colloidal particles towards one of the electrodes on passage of electricity through colloidal solution.

➢ **Hardy - Schulze rules:**

(i) Opposite charged ions are effective for coagulation.

(ii) The coagulating power of electrolyte increases with increase in charge on the ions used for coagulation.

➢ Coagulation value $\propto \dfrac{1}{\text{Coagulating power}}$

➢ **Gold number** is the number of milligram of protective colloids which must be added to 10 ml of given gold sol to prevent it from coagulation by addition of 1 ml of 10% of NaCl solution.

➢ **Difference between:**

■ **True solution, Colloids and Suspension:**

S. No.	True Solution	Colloids	Suspension
(i)	It is homogeneous.	It appears to be homogeneous but actually it is heterogeneous.	It is heterogeneous.
(ii)	It's particle size is less than 1 nm.	It's particle size is 1 nm to 1000 nm.	It's particles are larger than 1000 nm.
(iii)	It passes through filter paper and membrane.	It passes through ordinary filter paper but not through ultrafilter and membrane.	It does not pass through filter paper and animal membrane.
(iv)	It does not show Tyndall effect.	It shows Tyndall effect.	It does not show Tyndall effect appreciably.
(v)	It has higher value of colligative property.	It has low value of colligative property.	It has very low value of colligative property.
(vi)	It's particles cannot be seen even with powerful microscope.	It's particles can be seen by powerful microscope due to scattering of light.	It's particles can be seen even with naked eye.

■ **Adsorption and Absorption:**

S. No.	Adsorption	Absorption
(i)	It is surface phenomenon. Adsorbate molecules are held at the surface of adsorbent.	Absorption occurs in the bulk of absorbing substance.

(ii)	The concentration of the adsorbate at the adsorbent is much more than that in the bulk.	Absorbed material is uniformly distributed throughout the bulk. Thus, concentration is same throughout.
(iii)	Initially rate of adsorption is rapid. It decreases slowly till equilibrium is attained.	Absorption occurs with uniform rate.
(iv)	Example: Water vapours on silica gel.	Example: Water vapours are absorbed by anhydrous $CaCl_2$.

■ **Physisorption and Chemisorption:**

S. No.	Physisorption	Chemisorption
(i)	It usually takes place at a low temperature and decreases with increasing temperature.	It takes place at a high temperature.
(ii)	It is reversible.	It is irreversible.
(iii)	It is related to the ease of liquefaction of the gas.	The extent of adsorption is not related to liquefaction of the gas.
(iv)	It is not very specific.	It is highly specific.
(v)	It forms multi-molecular layers.	It forms mono-molecular layers.
(vi)	It does not require any activation energy.	It requires activation energy.
(vii)	Heat of adsorption is low.	Heat of adsorption is high.

■ **Multi-molecular, Macro-molecular and Associated colloids:**

S. No.	Multi-molecular Colloids	Macro-molecular Colloids	Associated Colloids
(i)	These are mostly lyophobic.	There are mostly lyophilic.	They are both lyophobic and lyophilic.
(ii)	In this type of colloids, colloidal particles are aggregates of atoms or small molecules with molecular size less than 1 nm. e.g., Gold sol.	In this type of colloids, colloidal particles are themselves large molecules having colloidal dimensions. e.g., starch,cellulose, proteins, etc.	These are substances which behave as normal, strong electrolyte at low concentration but at higher concentration behave as colloidal solution due to aggregation, e.g., Soap and detergents.

■ **Lyophilic and Lyophobic colloids:**

S. No.	Lyophilic colloids	Lyophobic colloids
(i)	They are easily formed by direct mixing.	They are formed by special method.
(ii)	Particles of colloids are not easily visible even under ultra microscope.	They are easily visible under ultra microscope.
(iii)	They are very stable.	They are unstable.
(iv)	Highly solvated and are reversible sols.	Not solvated and are irreversible sols.
(v)	For e.g., Gums, starch, albumin.	For e.g., As_2S_3, sulphur.

UNIT-VI	GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

➢ The chemical substances in the earth's crust obtained by mining are called **minerals**.
➢ Those minerals which act as a source of metal are called **ore**.
➢ The unwanted impurities present in ore are called **gangue**.
➢ Process of extraction of metal from its ore is called **metallurgy**.
➢ Removal of gangue from ore is called **concentration, dressing or benefaction of ore**.
➢ **Concentration** is a process for removing gangue from the ore.

   (i) Concentration by **hydraulic washing** is based on the differences in gravities (densities) of ore and gangue particles.

   (ii) Concentration by **magnetic separation** is based on differences in magnetic and non-magnetic properties of ore components.
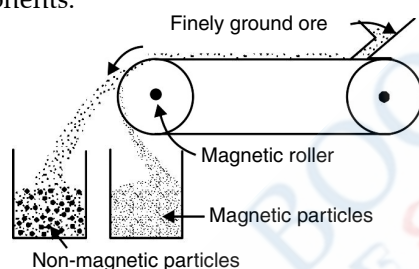
Fig. 1 : Magnetic separation method

   (iii) Concentration by **froth floatation process** is based on the facts that sulphide ore is wetted by pine oil and gangue particles are wetted by water.
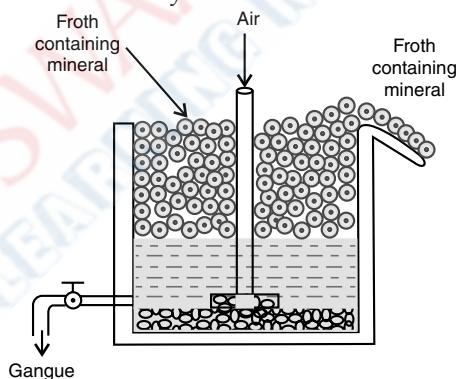
Fig. 2 : Froth floatation process

   (iv) Concentration by **leaching** is based on the fact that the ore is soluble in some suitable reagent and gangue is insoluble in the same reagent.

➢ **Conversion of ore into oxide :**

■ **Calcination** involves heating of ore in absence of air below melting point of metal. In this process, moisture and volatile impurities escape leaving behind the metal oxide.

$$Fe_2O_3 \cdot xH_2O \xrightarrow{\Delta} Fe_2O_3 \, (s) + xH_2O \, (g)$$

$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$$
Calamine

$$CaCO_3 \cdot MgCO_3 \, (s) \xrightarrow{\Delta} CaO \, (s) + MgO \, (s) + 2CO_2 \, (g)$$
Dolomite
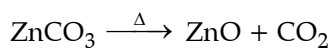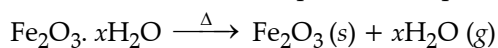
- ■ **Roasting** involves heating of ore in presence of air below melting point of metal in reverberatory furnace. Here volatile impurities escape leaving behind metal oxide and metal sulphide converts to metal oxide.
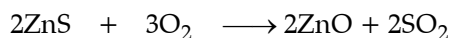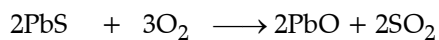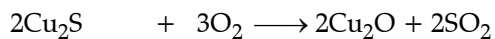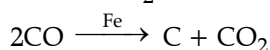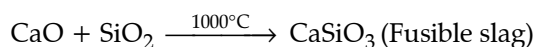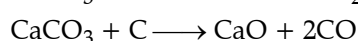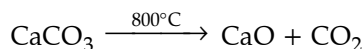
$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$
Zinc blende
$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$
Galena
$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$
Copper glance

- ➤ **Reduction of oxide to metal :** Auto-reduction, smelting, aluminothermic reduction, reaction with hydrogen.

- ➤ **Reactions taking place at different zones of blast furnace in extraction of iron :**

$3Fe_2O_3 + CO \xrightarrow{300°C} 2Fe_3O_4 + CO_2$

$Fe_3O_4 + 4CO \xrightarrow{500°C} 3Fe + 4CO_2$

$FeO + CO \xrightarrow{700°C} Fe + CO_2$

$CaCO_3 \xrightarrow{800°C} CaO + CO_2$

$CaCO_3 + C \longrightarrow CaO + 2CO$

$CaO + SiO_2 \xrightarrow{1000°C} CaSiO_3$ (Fusible slag)

$2CO \xrightarrow{Fe} C + CO_2$
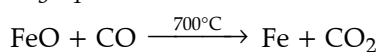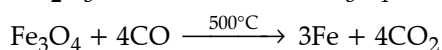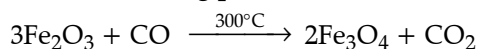
$Fe + C \longrightarrow$ Carbon saturated iron

Spongy iron $\xrightarrow{1300°-1600°C}$ Impure molten iron $\xrightarrow{cooled}$ Cast iron

- ➤ **Electrode potential** is useful in isolation of metals (like Al, Ag, Au, etc), where the sum of two redox couples is positive, so that the Gibb's energy change is negative.

- ➤ **Techniques used to obtain metal of high purity :**
  - (i) **Distillation**– For metals with low boiling points such as Zn and Hg.
  - (ii) **Electrolytic refining** – For Cu, Al, etc.
  - (iii) **Zone refining** – It is based on principle that impurities are more soluble in molten state than in solid state of metal. *e.g.,* for purifying semiconductors like Ge, Si.
  - (iv) **Vapour phase refining** – Here metal is converted into volatile compound which on decomposition gives pure metal. *e.g.,* Ni.
  - (v) **Chromatographic method** – Here different components of a mixture are differentially adsorbed on the adsorbent.

- ➤ **Chief Ores and Methods of Extraction of Some Common Metals :**

Metal	Occurrence	Extraction Method	Remark
Copper	Copper pyrites, $CuFeS_2$ Cuprite, Cu_2O Malachite, $CuCO_3.Cu(OH)_2$ Copper glance, Cu_2S Azurite, $2CuCO_3.Cu(OH)_3$	Roasting of sulphide partially and reduction $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$	It is self reduction in a specially designed converter. Sulphuric acid leaching is also employed.
Aluminium	Bauxite, $Al_2O_3.xH_2O$ Cryolite, Na_3AlF_6 Kaolinite, $[Al_2(OH)_4Si_2O_5]$ Aluminosilicates	Electrolysis of Al_2O_3 dissolved in molten cryolite or in Na_3AlF_6	A good source of electricity is needed in the extraction of Al.
Zinc	Zinc blende or Sphalerite, ZnS Zincite, ZnO Calamine, $ZnCO_3$	Roasting and then reduction with C.	The metal may be purified by fractional distillation.

Iron	Haematite, Fe_2O_3	Reduction with the help of CO and coke in blast furnace.	Limestone is added as flux which removes SiO_2 as calcium silicate (slag) floats over molten iron and prevents its oxidation. Temperature approaching 2170 K is required.
	Magnetite, Fe_3O_4	Chemical reduction with CO.	
	Siderite, $FeCO_3$	Calcination followed by reduction with CO.	
	Iron pyrites, FeS_2	Roasting followed by reduction.	
	Limonite, $Fe_2O_3.3H_2O$	Chemical reduction with CO.	

UNIT-VII p-BLOCK ELEMENTS

- General electronic configuration of p-block elements : $ns^2 np^{1-6}$
- **Group 15 elements** – [N (7), P(15), As(33), Sb(51), Bi (83)]
- **Properties of Group 15 elements Electronic Configuration :** $ns^2 np^3$
  - Atomic radii- smaller than group 14, increases down the group.
  - Ionization enthalpy- Higher than group 14, decreases down the group.
  - Electronegativity- Decreases down the group.
  - Except dinitrogen, all are solid.
  - Metallic character increases down the group.
  - Boiling point increases from top to bottom.
  - Melting point increases up to arsenic and decreases up to bismuth.
  - Oxidation states : – 3 to + 5
  - **Stability** – $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
  - **Bond dissociation enthalpy** – $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
  - **Reducing character** – $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
  - **Basic character** – $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
  - **Acidic character** – $N_2O_3 > P_2O_3 > As_2O_3 > Sb_2O_3 > Bi_2O_3$
- Anomalous behaviour of nitrogen is due to small size, high electronegativity, high ionization enthalpy and absence of d-orbitals.
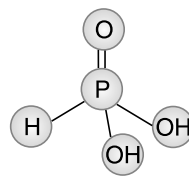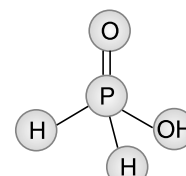- **Structure of Oxides of Nitrogen :**

Structure of some important oxoacids of phosphorus
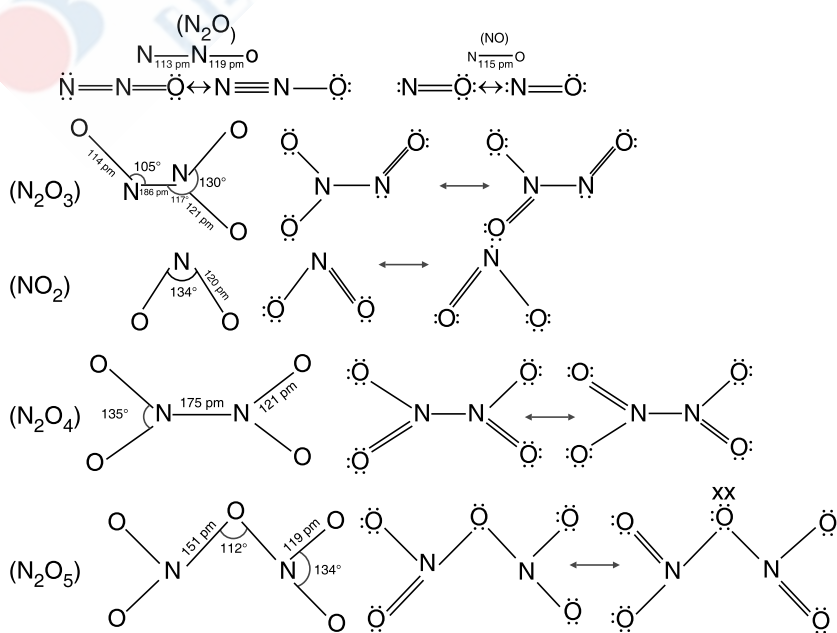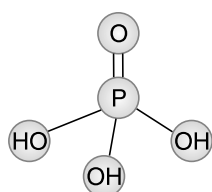
Under the structures:
- H_3PO_4 — Orthophosphoric acid
- $H_4P_2O_7$ — Pyrophosphoric acid
- H_3PO_3 — Orthophosphorous acid
- H_3PO_2 — Hypophosphorous acid
- Cyclotrimetaphosphoric acid. $(HPO_3)_3$
- Polymetaphosphoric acid. $(HPO_3)_3$
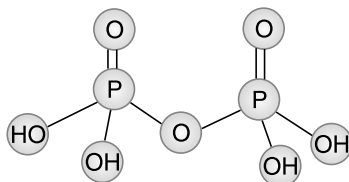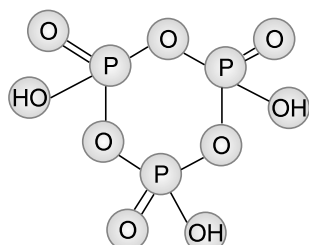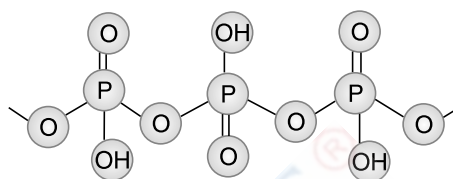
➤ **Dinitrogen (N_2) :**
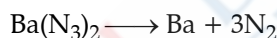
Preparation :

(i) In laboratory : $NH_4Cl_{(aq)} + NaNO_{2(aq)} \xrightarrow{heat} N_{2(g)} + 2H_2O_{(l)} + NaCl_{(aq)}$
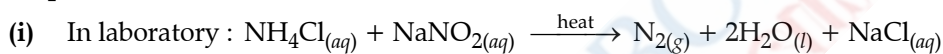
(ii) By thermal decomposition :

$$Ba(N_3)_2 \longrightarrow Ba + 3N_2$$

Properties :

(i) N_2 has very little reactivity at ordinary temperature.

(ii) Forms nitrides with highly electropositive metals like

$$3Mg + N_2 \xrightarrow{heat} Mg_3N_2$$

$$6Li + N_2 \xrightarrow{heat} 2Li_3N$$
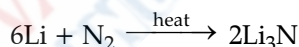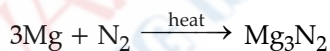
➤ **Ammonia (NH_3) :**

Preparation :

(i) In laboratory : $2NH_4Cl + Ca(OH)_2 \xrightarrow{heat} CaCl_2 + 2NH_3 + 2H_2O$

(ii) By Haber's process :

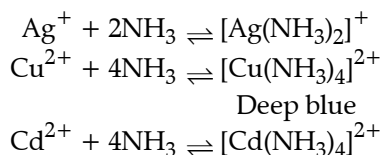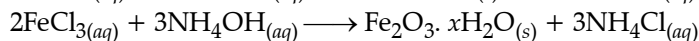$$N_{2(g)} + 3H_{2(g)} \underset{773\ K}{\overset{Fe/Mo}{\rightleftharpoons}} 2NH_{3(g)}, \Delta H = -46.1\ kJ\ mol^{-1}$$

Properties :

(i) Extremely soluble in water, colourless gas with pungent odour.

(ii) Acts as Lewis base

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$
$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$
$$\text{Deep blue}$$
$$Cd^{2+} + 4NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}$$

(iii) Forms salts with acids

$$ZnSO_{4(aq)} + 2NH_4OH_{(aq)} \longrightarrow Zn(OH)_{2(s)} + (NH_4)_2SO_{4(aq)}$$
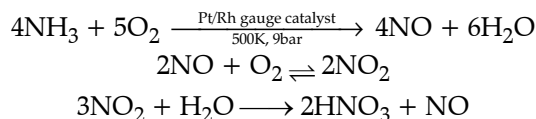$$2FeCl_{3(aq)} + 3NH_4OH_{(aq)} \longrightarrow Fe_2O_3 . xH_2O_{(s)} + 3NH_4Cl_{(aq)}$$
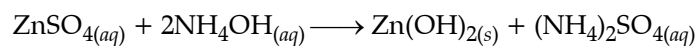
➤ **Nitric Acid (HNO_3) :**

Preparation :

In laboratory : $\quad NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

$\qquad\qquad\qquad\qquad$ (conc.) $\qquad$ (Brown ppt.)

(i) **By Ostwald's process :**

$$4NH_3 + 5O_2 \xrightarrow[\text{500K, 9bar}]{\text{Pt/Rh gauge catalyst}} 4NO + 6H_2O$$

$$2NO + O_2 \rightleftharpoons 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$
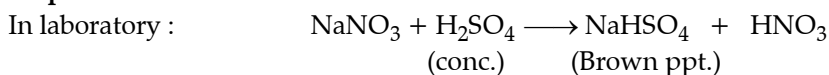
Properties :

(i) Colourless liquid.

(ii) Concentrated nitric acid is a strong oxidising agent.

(iii) **Reactions :**

$$HNO_{3(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + NO^-_{3(aq)}$$

$$\underset{\text{(dil)}}{3Cu + 8HNO_3} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$\underset{\text{(conc.)}}{Cu + 4HNO_3} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$\underset{\text{(dilute)}}{4Zn + 10HNO_3} \longrightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$

$$\underset{\text{(conc.)}}{Zn + 4HNO_3} \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$$

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

$$S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$
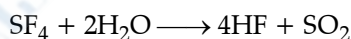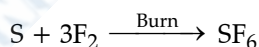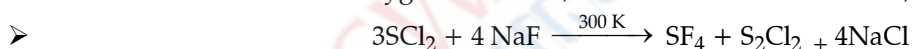
1 phosphine (PH_3)
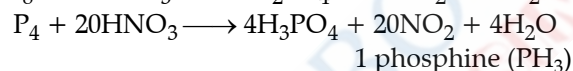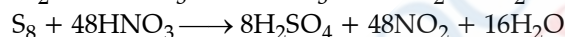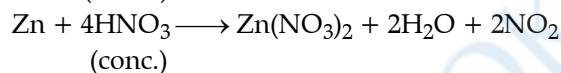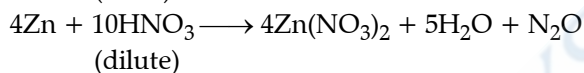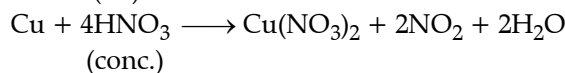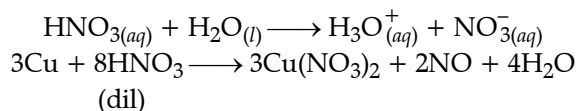
*preparation & properties

2 Phosphorus Tri chloride (PCL)

3 Phosphorus pertachlorde (PCLS)

- **Group 16 elements (Oxygen family) :** $_8$O, $_{16}$S, $_{34}$Se, $_{52}$Te, $_{84}$Po
- Electronic configuration : $ns^2\, np^4$
  - **O and S :** non-metals ; Se and Te : metalloids, Po : metal
  - Oxidation number : Oxygen shows – 2, all other elements show + 2, + 4 and + 6.
-
$$3SCl_2 + 4\,NaF \xrightarrow{300\,K} SF_4 + S_2Cl_2 + 4NaCl$$

$$S + 3F_2 \xrightarrow{\text{Burn}} SF_6$$

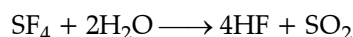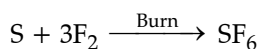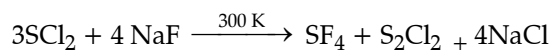$$SF_4 + 2H_2O \longrightarrow 4HF + SO_2$$

- **Physical Properties:**
  - **Atomic and ionic radii :** Smaller than group 15 elements, increases down the group.
  - **Ionization enthalpy :** IE_1 lower than group 15 elements while IE_2 is higher, decreases down the group.
  - **Electron gain enthalpy :** O < S. From sulphur onwards the value again become less negative upto polonium.
  - **Electronegativity:** More electronegative than group 15 elements and decreases down the group.
  - **Melting and boiling points :** Increases regularly from O to Te while Po has lesser than Te.
  - **Density** increases down the group.
  - O and S : non-metals ; Se and Te : metalloids, Po : metal
  - **Oxidation number :** Oxygen shows –2, all other elements show +2, +4 and +6.
- **Chemical Properties:**
  - With hydrogen forms hydrides of type H_2E.

  Properties of hydrides :

  (i) **Thermal stability :** Decreases down the group.

  (ii) **Acidic character :** Increases down the group.

  (iii) **Reducing nature :** All are reducing agents except H_2O.

  (iv) **Boiling point :** From H_2O to H_2S there is a sudden drop which increases from H_2S to H_2Te.
  - With halogens form halides of type EX_2, EX_4 and EX_6.

$$3SCl_2 + 4\,NaF \xrightarrow{\text{300 K}} SF_4 + S_2Cl_2 + 4NaCl$$

$$S + 3F_2 \xrightarrow{\text{Burn}} SF_6$$

$$SF_4 + 2H_2O \longrightarrow 4HF + SO_2$$

➢ **Dioxygen (O_2)**

Preparation : $\qquad 2\,KClO_3 \xrightarrow{\text{MnO}_2} 2KCl + 3O_2$
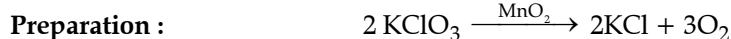
Properties : Slightly soluble in water, appreciably soluble in alkaline pyrogallol solution and paramagnetic.

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$
$$C(s) + O_2(g) \longrightarrow CO_2(g)$$
$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$
$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$
$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$
$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$
$$4HCl + O_2 \longrightarrow 2Cl_2 + 2H_2O$$

➢ **Ozone (O_3)**

Preparation : $\qquad 3O_2(g) \xrightarrow{\text{Discharge}} 2O_3(g), \Delta H = +\,284\ kJ$
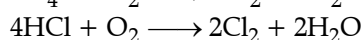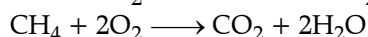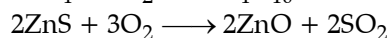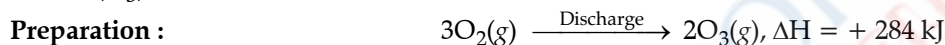
Properties : Poisonous, powerful oxidising agent.

$$PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$$
$$2I^- + H_2O + O_3 \longrightarrow 2OH^- + I_2 + O_2$$
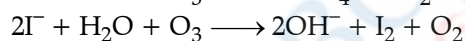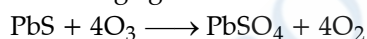
Structure :

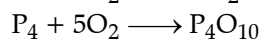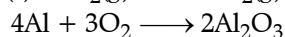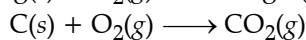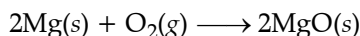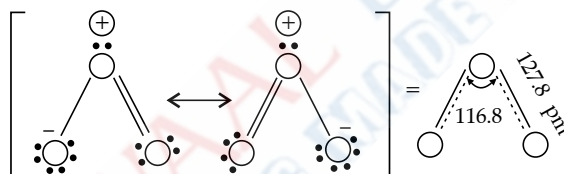

Uses: As bleaching agent, disinfectant and germicide, for purification of air in hospitals, railway tunnels, cinema house and for bleaching oils, ivory flour, starch, etc.

➢ **Shape of S_8 and S_6 molecules :**

➢ **Sulphur dioxide (SO_2) :**

Preparation : $\qquad S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$
$\qquad\qquad\qquad$ (conc.)
$\qquad\qquad\qquad Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$
$\qquad\qquad\qquad$ (conc.)
$\qquad\qquad\qquad Na_2SO_3 + 2HCl \longrightarrow 2NaCl + SO_2 + H_2O$
$\qquad\qquad\qquad$ (dil.)

Properties : $\qquad SO_2 + H_2O \longrightarrow H_2SO_3$
$\qquad\qquad\qquad 2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$
$\qquad\qquad Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$
$\qquad\qquad\qquad\qquad Cl_2 + SO_2 \longrightarrow SO_2Cl_2$

$$O_2 + SO_2 \longrightarrow 2SO_3$$

$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

$$5SO_2 + 2MnO_4^- + 2H_2O \longrightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$
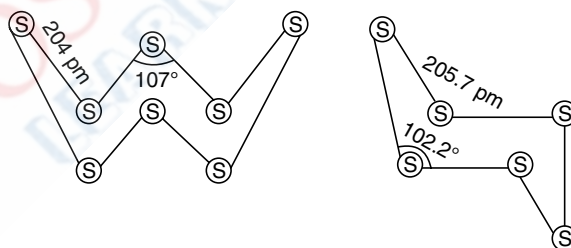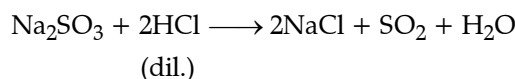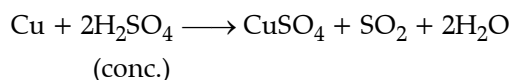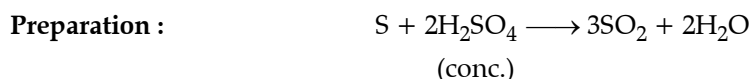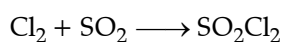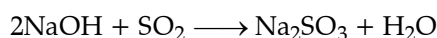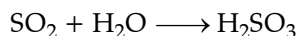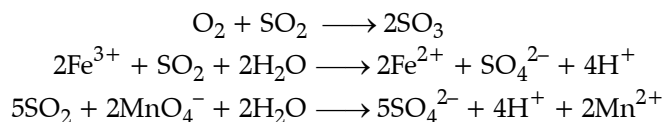
Uses : In refining petroleum and sugar, as bleaching agent for wool and silk and as anti-chlor, disinfectant and preservative.

➢ **Sulphuric acid (H_2SO_4) :**

Properties :

$$Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$
(conc.)

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$
(conc.)

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$
(conc.)

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$
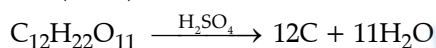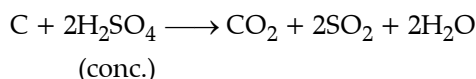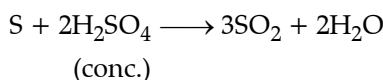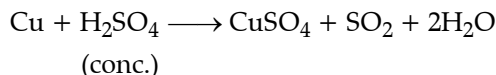
Uses: In petroleum refining, manufacture of pigments, paints and dye stuff, detergent industry and storage batteries.

➢ **Oxoacids of Sulphur :**
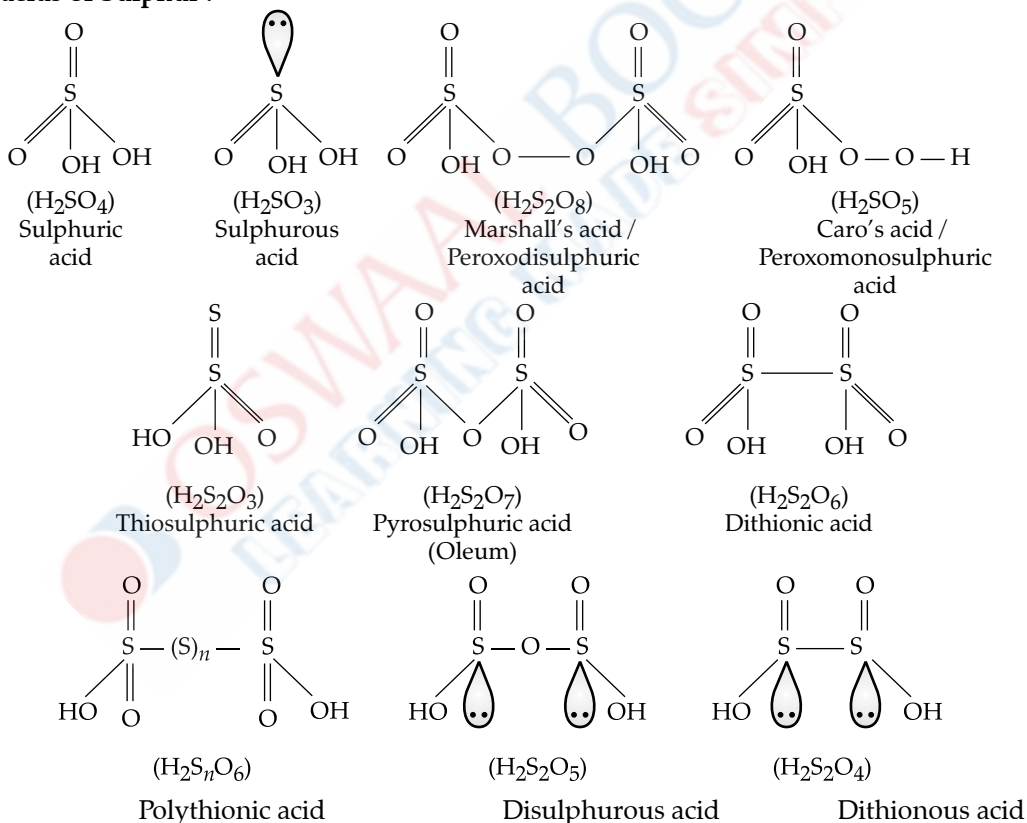
➢ **Group 17 Elements (Halogen family) :** $_9$F, $_{17}$Cl, $_{35}$Br, $_{53}$I, $_{85}$At

Electronic Configuration : $ns^2\, np^5$

Properties :

■ **Atomic and ionic radii :** Smallest in corresponding periods, increases down the group.

■ **Oxidation state :** F shows only –1 while others show +1, +3, +5 and +7.

■ **Ionization enthalpy :** Higher than group 16 elements, decreases down the group.

■ **Electron gain enthalpy :** Maximum negative.

■ They are non metals and coloured.

■ **M.p. and b.p.** increases down the group.

■ $\qquad F_2 + 2X^- \longrightarrow 2F^- + X_2$ (X = Cl, Br or I)

$$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2 \ (X = Br \ or \ I)$$
$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$
$$2F_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$
$$X_2(g) + H_2O(l) \longrightarrow HX(aq) + HOX(aq) \ (X = Cl \ or \ Br)$$
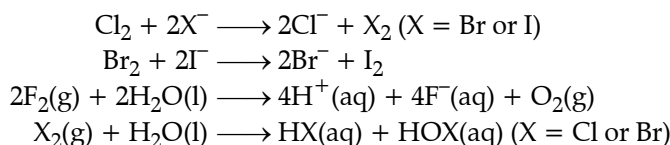
■ **Oxidizing property :** $F_2 > Cl_2 > Br_2 > I_2$
■ **Acidic strength :** $HF < HCl < HBr < HI$
■ **Stability and bond dissociation enthalpy :** $HF > HCl > HBr > HI$
■ **Stability of oxides of halogens :** $I > Cl > Br$
■ **Acidic strength of oxoacids :** $HClO > HBrO > HIO$
■ **Acidic strength of oxoacids containing the same halogen :**
  $HOCl > HClO_2 < HClO_3 < HClO_4$

➢ **Structure of oxoacids of Chlorine :**

Hypochlorous acid   Chlorous acid   Chloric acid   Perchloric acid
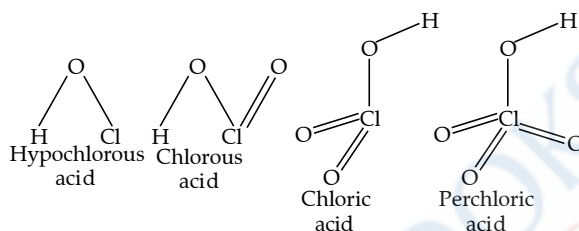
➢ **Chlorine (Cl_2)**

Preparation :
$$MnO_2 + 4HCl \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$$
$$2KMnO_4 + 16HCl \xrightarrow{\Delta} 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$
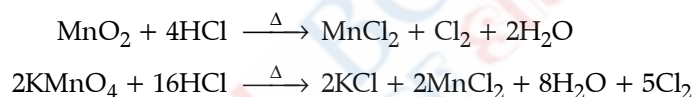
In laboratory,

(i) $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$ (Deacon's process)

(ii) $4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$

(iii) Electrolytic process : By electrolysis of brine.

At cathode : $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$; $Na^+ + OH^- \longrightarrow NaOH$

At anode : $Cl^- \longrightarrow Cl + e^-$; $Cl + Cl \longrightarrow Cl_2$
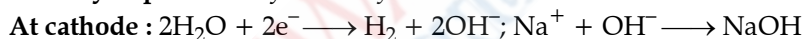
Properties : Greenish yellow, pungent suffocating smell, soluble in water and heavier than air.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3; \quad 2Na + Cl_2 \longrightarrow 2NaCl$$
$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3; \quad S_8 + 4Cl_2 \longrightarrow 4S_2Cl_2$$
$$P_4 + 6Cl_2 \longrightarrow 4PCl_3; \quad H_2 + Cl_2 \longrightarrow 2HCl$$
$$H_2S + Cl_2 \longrightarrow 2HCl + S; C_{10}H_{16} + 8Cl_2 \longrightarrow 16HCl + 10C$$
$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl; \quad 8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$$
$$\text{(excess) \quad (explosive) \qquad\qquad (excess)}$$
$$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$
$$\text{(cold and dilute)}$$
$$6NaOH + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$
$$\text{(hot and conc.)}$$
$$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$
$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$
$$HOCl \longrightarrow HCl + O$$
$$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$
$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl$$
$$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$$
$$I_2 + 6H_2O + 5Cl_2 \longrightarrow 2HIO_3 + 10HCl$$

Uses : For bleaching cotton and textiles, sterilizing drinking water, in the extraction of gold and platinum and manufacture of dyes, drugs, refrigerant and other organic compounds like $CHCl_3$, DDT, CCl_4, etc.

➢ **Hydrogen Chloride (HCl)**

Preparation :

$$NaCl + H_2SO_4 \xrightarrow{420 \text{ K}} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{823 \text{ K}} Na_2SO_4 + HCl$$
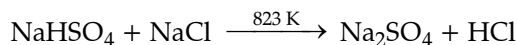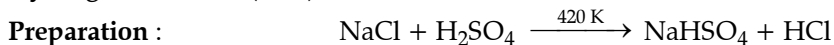
HCl gas can be dried by passing conc. H_2SO_4 through it.

Properties : Colourless, pungent smelling and soluble in water.

$$Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$$
$$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$
$$NH_3 + HCl \longrightarrow NH_4Cl$$
$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$
$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$
$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$$
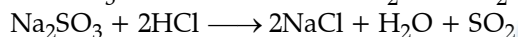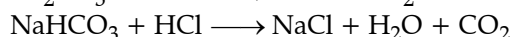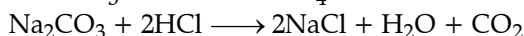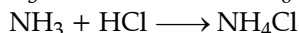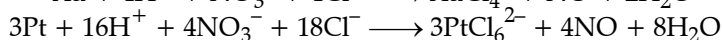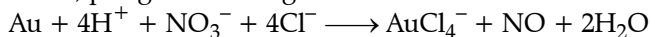
➢ **Interhalogen compounds :** General formula- XX', XX'$_3$, XX'$_5$ and XX'$_7$.

Preparation :

$$\underset{\text{(Equal volume)}}{Cl_2 + F_2} \xrightarrow{437 \text{ K}} 2ClF; \qquad \underset{\text{(excess)}}{I_2 + 3Cl_2} \longrightarrow 2ICl_3$$

$$\underset{\text{(excess)}}{Cl_2 + 3F_2} \xrightarrow{573 \text{ K}} 2ClF_3; \qquad \underset{\text{(Diluted with water)}}{Br_2 + 3F_2} \longrightarrow 2BrF_3$$

$$\underset{\text{(Equimolar)}}{I_2 + Cl_2} \longrightarrow 2ICl, \qquad \underset{\text{(excess)}}{Br_2 + 5F_2} \longrightarrow 2BrF_5$$
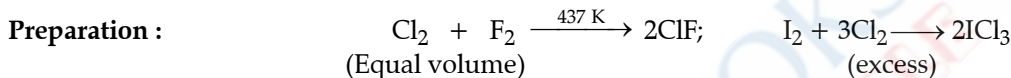
Properties : Covalent compounds, diamagnetic in nature and more reactive than halogens.

$$XX' + H_2O \longrightarrow HX' + HOX$$

➢ **Group 18 elements (Noble gases) :** $_2$He, $_{10}$Ne, $_{18}$Ar, $_{36}$Kr, $_{54}$Xe, $_{86}$Ra.

Electronic Configuration : $ns^2 np^6$ except He.

Properties :

■ Gases.
■ **Atomic radii** increase down the group and highest in respective periods.
■ **Ionization enthalpy:** Highest in respective periods, decreases down the group.
■ Large positive values of electron gain enthalpy.
■ **M.p. and b.p.** increases down the group.
■ Difficult to liquefy. Down the group, the ease of liquefaction increases.

$$O_2 + PtF_6 \longrightarrow O_2^+[PtF_6]^-$$
$$\text{Dioxygenyl hexafluoro}$$
$$\text{platinate}$$

$$Xe + PtF_6 \xrightarrow{289 \text{ K}} Xe^+[PtF_6]^-$$
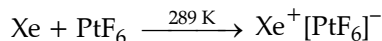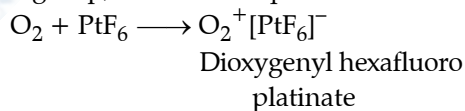
➢ **Preparation of Xenon fluorides :** Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6.

$$\underset{\text{(excess)}}{Xe(g) + F_2(g)} \xrightarrow{673 \text{ K, 1 bar}} XeF_2(s)$$

$$Xe(g) + 2F_2(g) \xrightarrow{873 \text{ K, 7 bar}} XeF_4(s)$$

$$\underset{\text{(1 : 20 ratio)}}{Xe(g) + 3F_2} \xrightarrow{573 \text{ K, 60–70 bar}} XeF_6(s)$$

$$XeF_4 + O_2F_2 \xrightarrow{143 \text{ K}} XeF_6 + O_2$$
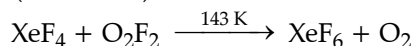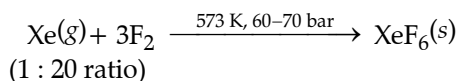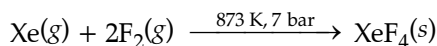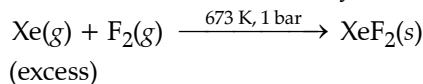
➢ **Preparation of Xenon trioxide (XeO_3) :**

$$6XeF_4 + 12H_2O \longrightarrow 2XeO_3 + 4Xe + 3O_2 + 24HF$$
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$
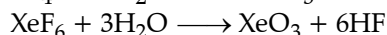
➢ **Preparation of Xenon oxyfluorides :**

$$XeF_4 + H_2O \longrightarrow XeOF_2 + 2HF$$

$$XeF_6 + H_2O \xrightarrow[\text{Hydrolysis}]{\text{Partial}} XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \xrightarrow[\text{Hydrolysis}]{\text{Complete}} XeO_2F_2 + 4HF$$
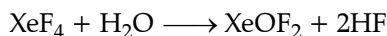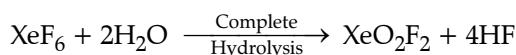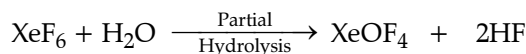
➤ **Structures of Xenon-fluorine compounds :**

| $XeF_2(sp^3d)$ [Linear] | XeF_4 (sp^3d^2) [Square Planar] | XeF_6 (sp^3d^3) [Distorted Octahedral] | $XeOF_2$ (sp^3d) [T-shaped] | $XeOF_4$ (sp^3d^2) [Square Pyramidal] | $XeO_3(sp^3)$ [Trigonal Pyramidal] |
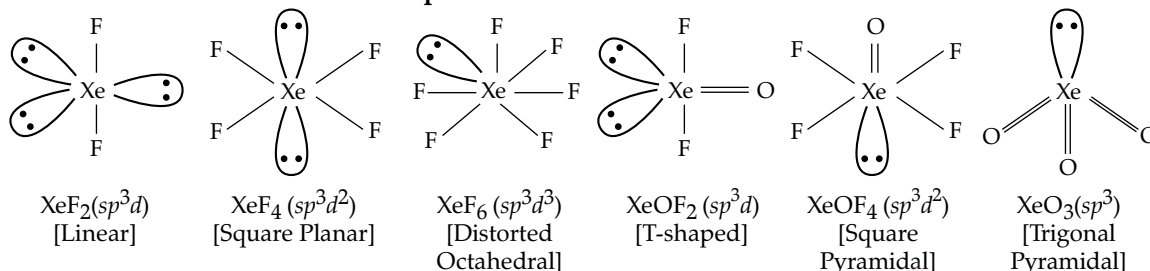
Uses:

(i) Helium (He) is used in filling balloons for meteorological observations, in gas-cooled nuclear reactors.

(ii) Liquid He is used as cryogenic agent, to produce and sustain powerful super conducting magnets, as a diluent for oxygen in modern diving apparatus.

(iii) Ne is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Ne bulbs are used in botanical gardens and in green houses.

(iv) Ar is used to provide an inert atmosphere in high temperature metallurgical processes, for filling electric bulbs, in the laboratory for handling substances that are air-sensitive.

UNIT-VIII   *d*- and *f*-BLOCK ELEMENTS

➤ **d-Block elements:** Group 3 – 12 (Transition elements)

➤ **General electronic configuration of transition elements:** $(n–1)d^{1-10}ns^{1-2}$

➤ **Physical properties:**

■ All are metals.

■ Malleable, ductile, lustrous and sonorous except mercury which is a liquid.

■ **Atomic radii:** In period, first decreases till the middle, becomes constant and then increases.

■ **Ionic radii:** Decreases with increase in oxidation state.

■ **Ionization enthalpy:** From left to right, it increases.

■ Variable oxidation state.

■ Complex and interstitial compounds are formed.

■ The magnetic moment increases with the increasing number of unpaired electrons.

■ Formation of colored compounds and alloys.

➤ **Potassium dichromate** $(K_2Cr_2O_7)$

Preparation :

(i) Chromate ore is fused with sodium carbonate in the presence of air to give sodium chromate.

$$2\,FeCr_2O_4 + 4Na_2CO_3 + 7/2O_2 \longrightarrow Fe_2O_3 + 4Na_2CrO_4 + 4CO_2$$
$$\text{Sodium chromate}$$
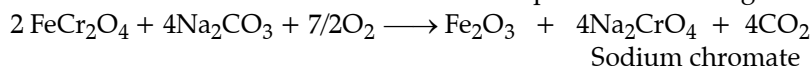
(ii) Na_2CrO_4 is filtered and acidified with conc. H_2SO_4 to give $Na_2Cr_2O_7$.

$$Na_2CrO_4 + 2H_2SO_4 \longrightarrow Na_2Cr_2O_7 + 2Na_2SO_4 + H_2O.$$
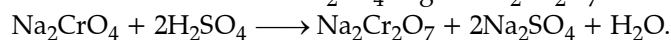
(iii) Sodium dichromate solution is treated with KCl to give $K_2Cr_2O_7$.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Properties :

■

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$
$$\text{Chromate ion}$$
$$\text{(Yellow)}$$

- $$Cr_2O_7^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$
  <div align="center">Dichromate ion
(orange red)</div>

- $$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
  $$[Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 6$$
  $$\overline{Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O}$$

- $$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
  $$[Sn^{2+} \longrightarrow Sn^{4+} + 2e^-] \times 3$$
  $$\overline{Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O}$$

- $$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
  $$[SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-] \times 3$$
  $$\overline{Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O}$$

- $$Cr_2O_7^{2-} + 14H + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
  $$[H_2S \longrightarrow 2H^+ + S + 2e^-] \times 3$$
  $$\overline{Cr_2O_7^{2-} + 3H_2S + H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O}$$

- $$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
  $$[2I^- \longrightarrow I_2 + 2e^-] \times 3$$
  $$\overline{Cr_2O_7^{2-} + I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O}$$

Structure :

<div align="center">**Chromate ion**   **Dichromate ion**</div>

➢ **Potassium permanganate (KMnO$_4$) :**

Preparation :

(i)
$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$
$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

(ii)
$$MnO_2 \xrightarrow[\text{Oxidised with air/KNO}_3]{\text{Fused with KOH}} MnO_4^{2-}$$

<div align="right">Manganate ion</div>

$$MnO_4^{2-} \xrightarrow[\text{in alkaline solution}]{\text{Electrolytic oxidation}} MnO_4 + 1e^-$$

<div align="right">Permanganate ion</div>

Properties : $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$
<div align="center">Peroxodisulphate</div>

- $$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$
- $$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
  $$[2I^- \longrightarrow I_2 + 2e^-] \times 5$$
  $$\overline{2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O}$$

- $$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
  $$[Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 5$$
  $$\overline{MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O}$$

- $[MnO_4^- + 8H^+ \; 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$
  $[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$

  $\overline{2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O}$

- $[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$
  $[S^{2-} \longrightarrow S + 2e^-] \times 5$

  $\overline{2MnO_4^- + 5S^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 5S + 8H_2O}$

- $[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$
  $[SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5$

  $\overline{5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O}$

- $[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$
  $[NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ \; 2e^-] \times 5$

  $\overline{2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O}$

- $[MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-] \times 2$
  $I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-$

  $\overline{2\,MnO_4^- + I^- + H_2O \longrightarrow IO_3^- + 2MnO_2 + 2OH^-}$

- $3Mn^{2+} + 12OH^- \longrightarrow 3MnO_2 + 6H_2O + 6e^-$

Structure :

Tetrahedral manganate
ion (Green)

Tetrahedral permanganate
ion (Purple)

➤ **General electronic configuration of *f* - block elements** is $(n-2)f^{1-14}\,(n-1)d^{0-1}\,ns^2$

➤ **Lanthanoids:** Ce (Z = 58) to Lu (Z = 71)

Electronic Configuration: $[Xe]\,4f^{1-14}\,5d^{0-1}\,6s^2$

Properties:

- Highly dense metals, soft, malleable and ductile.

- High melting point.

- Atomic and ionic size decreases with increasing atomic number. This steady decrease is known as lanthanide contraction.

- **Oxidation state:** Mainly +3 but some show +2 and +4 also.

-
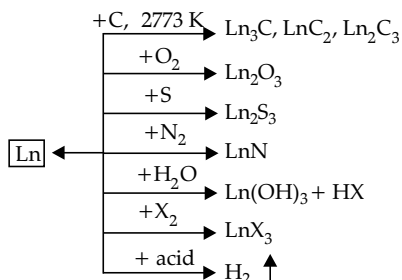
➤ **Actinoids :** Ac (Z = 89) to Lr (Z = 103)

Electronic configuration : $[Rn]\,5f^{1-14}\,6d^{0-1}\,7s^2$

Properties :

- Highly dense metals and forms alloys.

- High electropositivity and melting point.
- Atomic and ionic radii decreases with an increase in atomic size due to poor shielding effect of $5f$ electrons (actinoid contraction).
- Paramagnetic, ions are coloured and radioactive.
- **Oxidation state :** Commonly +3 but exhibit +4, +5, +6 and +7 also.
- Less reactive towards acids.

➤ **Difference between Lanthanoids and Actinoids :**

S. No.	Lanthanoids	Actinoids
(i)	4f orbital is progressively filled.	5f orbital is progressively filled.
(ii)	+ 3 oxidation state is most common along with + 2 and + 4.	+ 3 oxidation state is most common, but exhibit higher oxidation state of + 4, + 5, + 6, + 7.
(iii)	Except promethium, all are non-radioactive.	All are radioactive.
(iv)	Less tendency of complex formation.	Strong tendency of complex formation.
(v)	Chemically less reactive than actinoids.	More reactive than lanthanoids.

Uses:

(i) Misch metal is used in lighter flints.

(ii) Lanthanoid oxides are used for polishing glass.

(iii) Cerium salts are used in dyeing cotton and as catalysts.

UNIT-IX   COORDINATION COMPOUNDS

➤ The compounds which contain a central metal atom or ion surrounded by number of oppositely charged ions or neutral molecules are called coordination compounds. *e.g.*, $[Cu(NH_3)_4]^{2+}$.

➤ According to **Werner's theory of coordination compounds:**

  (i) Metal possesses 2 types of valencies – ionizable (Primary) and non-ionizable (Secondary) valencies.

  (ii) Every metal ion has a fixed number of secondary valency and this is known as **coordination number.**

  (iii) **Primary valencies** are satisfied by anions while secondary valencies are satisfied by negative group or neutral molecules with lone pair of electrons.

  (iv) **Secondary valencies** are directed in space towards internal positions.

➤ **Double Salt:** When two or more salts are added to form a stable solid together and break into constituent ions when dissolved in water or any solvent. *e.g.*, for $FeSO_4(NH_4)_2SO_4.6H_2O$ (Mohr's salt).

➤

Co-ordinate sphere
|
$[Co(NH_3)_6]$
Central —↑   ↑— Ligand
metal ion
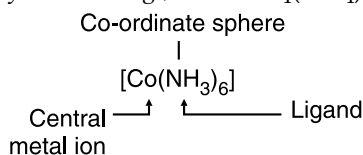
➤ The metal ion surrounded by fixed number of ions or molecules is called central metal atom or ion, *e.g.*, in $K_4[Fe(CN_6)]$, Fe^{2+} is central metal ion.

➤ A **ligand** is the ion or molecule bound to the central atom/ion in the coordination entity. For example, Cl^-, OH^-, CN^-, CO, NH_3, H_2O, *etc.* A ligand may be neutral or charged species.

➤ **Monodentate ligands** ligate through one donor atom, **bidentate ligands** ligate through two donor atoms and **polydentate ligands** ligate through more than two donor atoms.

➤ When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a **chelate ligand.**

➤ **Ambidentate ligand** is a ligand which contains two donor atoms but only one of them forms a coordinate bond at a time with central metal/ion.

➢ **Coordination number:** Number of ligands through which the metal is directly bonded. The number of such ligating groups is called the denticity of the ligand.

➢ **Charge on the complex ion:** The charge on the complex ion is equal to the algebraic sum of the charges on all the ligands coordinated to the central metal ion.

➢ **Oxidation number of central atom** is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. It is represented by Roman numerical.

➢ **Counter ions:** The ions which are not included in the primary coordination sphere are known as **counter ions**, *e.g.*, in $K_4[Fe(CN)_6]$, K^+ ions are counter ions.

➢ **Homoleptic complexes** are complexes in which metal atom or ion is bound to only one type of ligands *e.g.*, $[Co(NH_3)_6]^{3+}$, whereas complexes bound to more than one kind of ligands are known as **hetero-leptic complexes**. *e.g.*, $[Co(NH_3)_4Cl_2]^+$.

➢ Complexes in which only one metal atom is present are known as **homonuclear complexes.** *e.g.*, $[Co(NH_3)_6]Cl_3$ and $[Cu(NH_3)_4]SO_4$. Complexes in which more than one metal atom is present are known as **polynuclear complexes.**

➢ **Nomenclature of coordination compounds:**

    (i) The cation whether simple or complex is named first followed by anion.

    (ii) Ligands are named in alphabetical order.

    (iii) For indicating the number of individual ligand within the coordination entity, numerical pre-fixes di, tri, tetra, *etc.* are used. For ligands containing any of these prefixes in their names, their numbers are indicated by prefixes bis, tris, tetrakis *etc.* Anionic ligands end in –o. Neutral ligands retain their names while cationic end in -ium.

    (iv) The coordination sphere is written in square bracket.

    (v) In naming, ligands are named first in alphabetical order followed by metal atom and then the oxidation state of metal by a Roman numeral in parenthesis.

    (vi) Name of coordination compounds starts with a small letter and the complex part is written as one word.

➢ Two or more coordination compounds which have the same molecular formula but have their ligands attached to the isomers metal atom or ion in different ways are known as **isomers**. The phenomenon of different isomers is known as **isomerism**.

➢ Isomerism in co-ordination compounds :

    (a) Structural isomerism

        (i) Linkage isomerism : $[CO(NH_3)_5(NO_2)]Cl_2$

        (ii) Co-ordination isomerism : $[CO(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][CO(CN)_6]$,

        (iii) Ionization isomerism : $[CO(NH_3)_5SO_4]$ Br and $[CO(NH_3)_5Br]SO_4$,

        (iv) Solvate isomerism : $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_3O)_5Cl]2H_2O$

➢ **Geometrical Isomerism :**

cis   *trans*

fac–   *mer–*
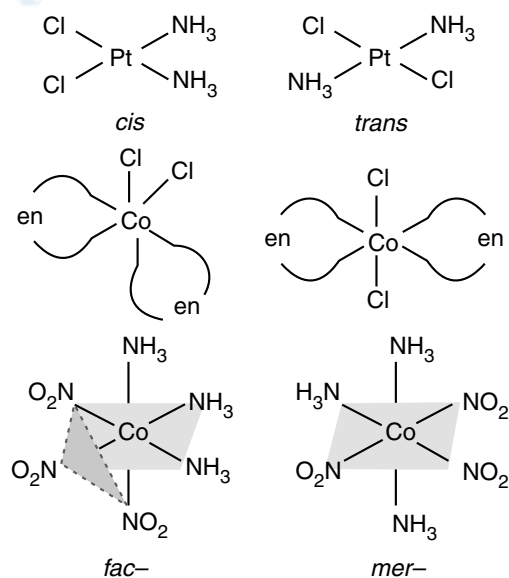
➢ **Optical Isomerism :**

dextro   mirror   Laevo
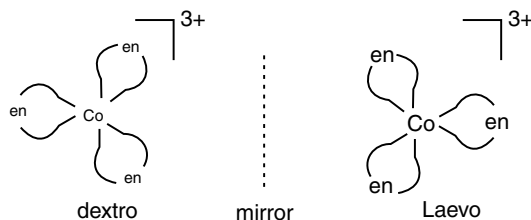
➢ *d*-**orbital splitting in an octahedral crystal field:**
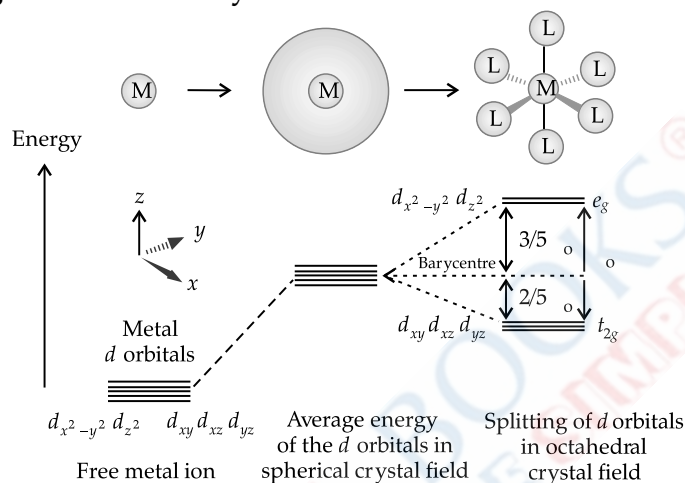
➢ **Valence Bond theory:**
   (i) A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of coordinate bond with the ligands.
   (ii) Central metal ion can use appropriate number of *s*, *p* or *d*-orbitals for hybridisation depending upon total number of ligands.
   (iii) The hybridised orbitals are allowed to overlap with those ligand orbitals that can donate an electron pair for bonding.
   (iv) The outer orbitals or inner orbitals complexes are formed depending upon whether outer *d*-orbitals or inner *d*-orbitals are used.

➢ **Crystal field theory (CFT):**
   (i) The ligands is considered as point charge or point dipole.
   (ii) Interaction between metal ion and ligand is considered as electrostatic in nature.
   (iii) Metal ion is supposed to be present at the origin of the axis. Ligands approach to metal ion along the axis of octahedral complex between the axis of tetrahedral complex and in the case of square planar complex four ligand approach to metal ion along *x*, *y* plane.
   (iv) Due to the electrostatic interaction between ligands electrons and metal *d*-orbital electron degeneracy of *d*-orbital is lost and spliting of *d*-orbitals occurred.
   (v) Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of *d*-orbitals.

➢ *d*-**orbital splitting in a tetrahedral crystal field:**
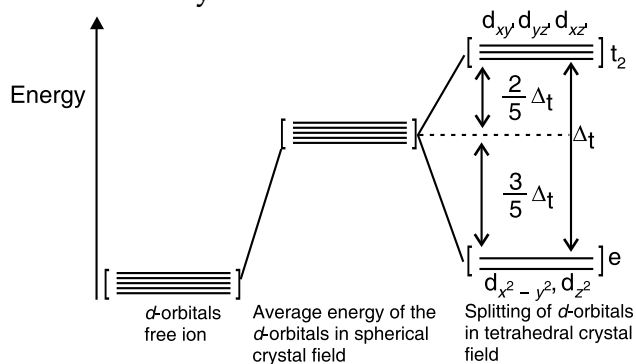
- **Metal carbonyls:** Homoleptic carbonyls are formed by *d*-block elements and contain carbonyl ligands only. *e.g.*, $V(CO)_6$, $Cr(CO)_6$, etc.

- **Number of Orbitals and Types of Hybridisation :**

Coordination number	Type of hybridising	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

- **Bonding in metal carbonyls:** It also involves both *s*-and *p*-bond. *s*-bond is formed by overlapping of lone pair on CO to the vacant *d*-orbitals of metal whereas *p*-bond is formed by the back donation of pair of *d*-electrons to vacant anti bonding orbital of carbonyl.

UNIT-X   HALOALKANES AND HALOARENES

- Hydrogen atom in aliphatic hydrocarbons replaced by halogen are called haloalkanes, while in benzene ring are called haloarenes.

- **Allylic halides :** Halogen is bonded to allylic carbon.
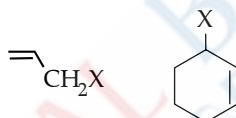
- **Benzylic halides :** Halogen atom is bonded to an sp^3 hybridised carbon atom next to an aromatic ring.

(1°)   R' = CH_3. R''=H(2°)
R' = R''=CH_3(3°)
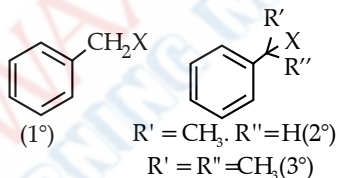
- **Vinylic halides :** Halogen is bonded to one of the carbon atoms of a vinylic carbon.

- **Aryl halides :** Halogen atom is directly bonded to sp^2 hybridised carbon atom of an aromatic ring.
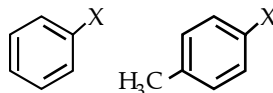
- **Preparation of haloalkanes and haloarenes :**

$R{-}OH + HX \xrightarrow{ZnCl_2} R{-}X + H_2O$ (X = Cl, Br, I)

$R{-}OH + NaBr + H_2SO_4 \longrightarrow RBr + NaHSO_4 + H_2O$

$3R{-}OH + PX_3 \longrightarrow 3R{-}X + H_3PO_3$ (X = Cl, Br)

$R{-}OH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl$

$R{-}OH \xrightarrow[X_2=Br_2, I_2]{Red\ P/X_2} R{-}X$

$R{-}OH + SOCl_2 \longrightarrow R{-}Cl + SO_2 + HCl$

$CH_3CH_2CH_2CH_3 \xrightarrow[Or\ heat]{Cl_2/UV\ light} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$
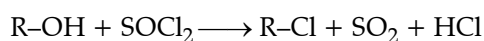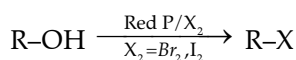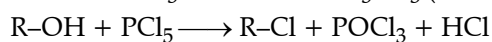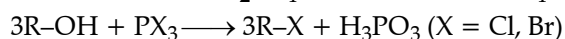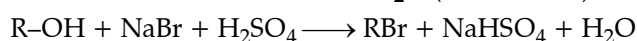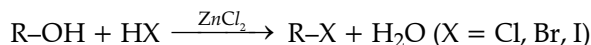
n-Butyl chloride   sec-Butyl chloride (Major product)

$$R — CH = CH_2 + HBr \xrightarrow[\text{Anti-Markovnikov's rule}]{\text{Benzoyl chloride}} R — CH_2 — CH_2 — Br$$

$$R — CH = CH_2 + HX \xrightarrow{\text{Markovnikov's rule}} R — \underset{\underset{X}{|}}{CH} — CH_2$$

$$\underset{H}{\overset{H}{>}}C = C\underset{H}{\overset{H}{<}} + Br_2 \xrightarrow{CCl_4} BrCH_2 — CH_2Br$$

➤ **Sandmeyer's reaction :**

Benzene diazonium
halide

Aryl halide
(X = Cl, Br)

➤ **Finkelstein Reaction :**

$$R–X + NaI \xrightarrow{\text{Dry acetone}} R–I + NaX$$

➤ **Swarts Reaction :**

$$R – X \xrightarrow{\text{AgF, HgF ,CoF or SbF}} R – F$$
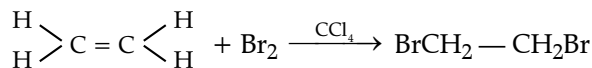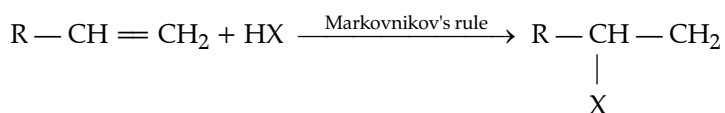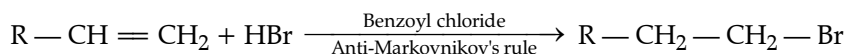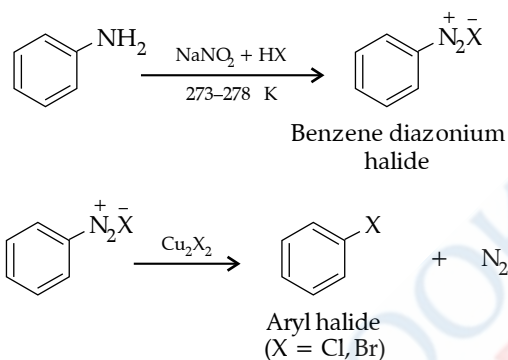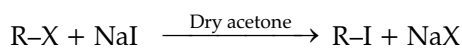
➤ **Properties :**

➤ **Mechanism of Nucleophilic substitution reaction :**

■ Unimolecular nucleophilic substitution reaction (S_N1) :

   STEP I :

(Planar)

   STEP II :

(Planar)

■ Biomolecular nucleophilic substitution reaction (S_N2) :

Transition state
(Trigonal bipyramidal)

S_N^1 reactivity increases →

$$CH_3X \ , \ RCH_2X \ , \ R\!-\!\overset{\displaystyle |}{\underset{\displaystyle R'}{CH}}\!-\!X \ , \ R\!-\!\overset{\displaystyle R''}{\underset{\displaystyle R'}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}\!-\!X$$

1°   2°   3°

← S_N^2 reactivity increases
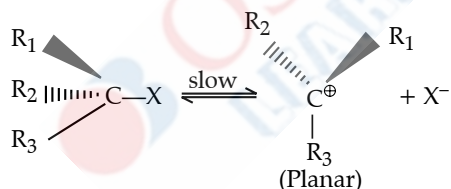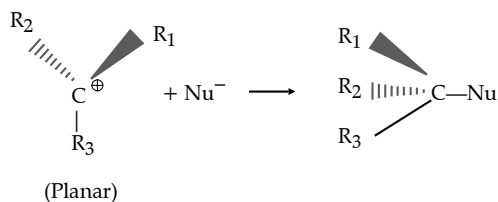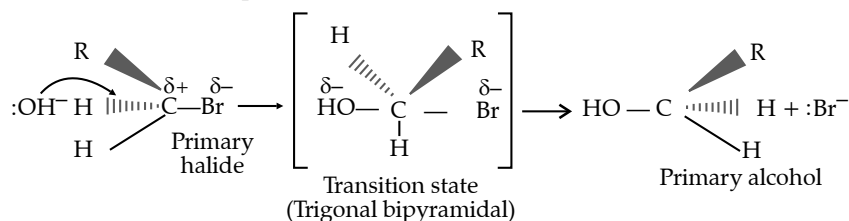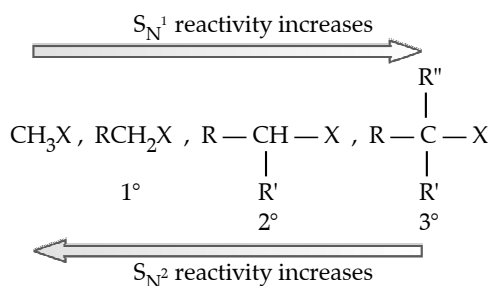
(i) Nucleophilic substitution reactions: When an atom or group of atoms is replaced by nucleophile, the reaction is called nucleophilic substitution reaction. e.g.,

$$\underset{\text{Nucleophile}}{\overset{\delta+ \quad \delta-}{>\!C\!-\!X}} \ + \ :Z^{\ominus} \ \longrightarrow \ \underset{\text{Product}}{\overset{\delta+ \quad \delta-}{>\!C\!-\!Z}} \ + \ \underset{\text{Leaving group}}{:X^{\ominus}}$$

R — X
Alkyl halide

+ KOH (aq) → R — OH + KX   Alcohol

+ NaO⁺R⁻ → R — O — R' + NaX   Ether

+ KCN(alc) → R — CN + KX   Alkyl cyanide

+ AgCN → R — NC + AgX   Alkyl isocyanide

+ KNO$_2$ → R — O — N = O   Alkyl nitrite

+ AgNO$_2$ → R — NO$_2$ Nitroalkane

+ R' — $\overset{O}{\overset{\|}{C}}$ — O — Ag → R — $\overset{O}{\overset{\|}{C}}$ — O — R' + AgX   Ester

+ LiAlH$_4$ → R — H   Alkane

+ NH$_3$ → R — NH$_2$ + H — X   Amine

+ NaSH → R — SH + NaX   Thioalcohol

+ Na$^+$ C≡CH$^-$ → R — C ≡ CH + NaX   Higher alkyne
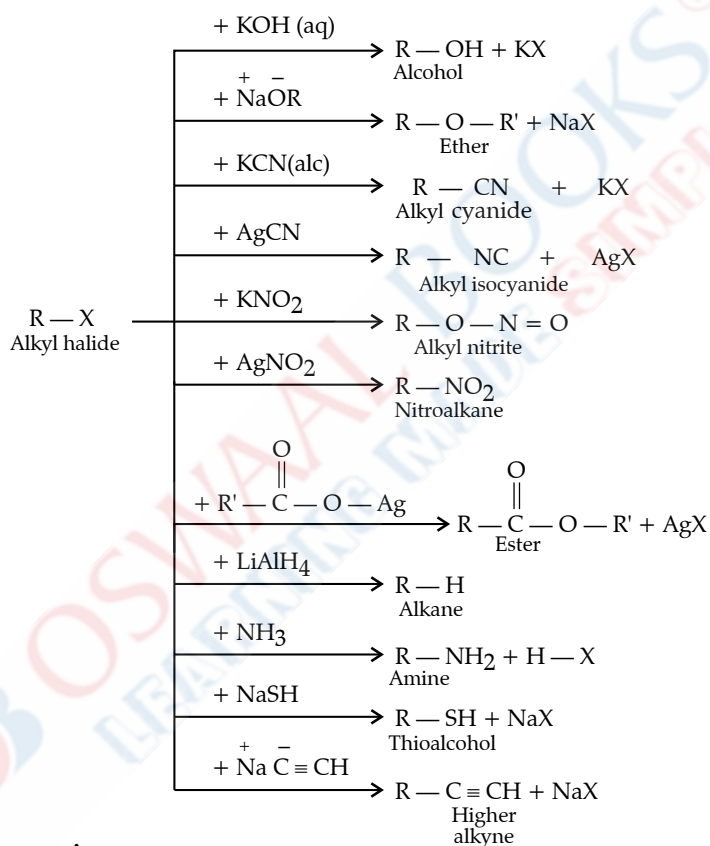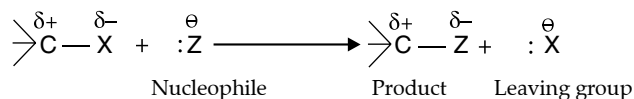
(ii) Elimination reaction:

$$CH_3\!-\!\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}\!-\!Cl + KOH \xrightarrow[\text{heat}]{\text{ethanol}} \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{>}}C = CH_2 \ + KCl + H_2O$$

(iii) Reduction:

$$R - X + 2(H) \xrightarrow{\text{Zn/HCl (conc)}} R - H + H - X$$

(iv) Reaction with metals :

$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} CH_3CH_2MgBr$$

Grignard reagent

$$RMgX + H_2O \longrightarrow RH + Mg(OH)X$$

Wurtz reaction :

$$2RX + 2Na \longrightarrow R\text{–}R + 2NaX$$
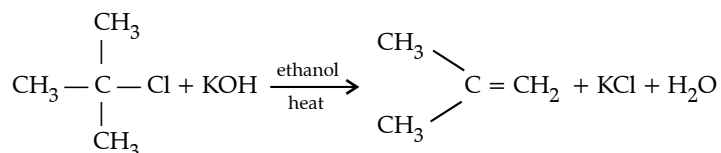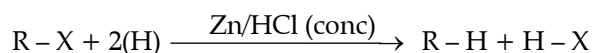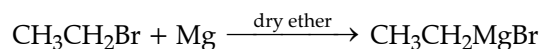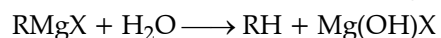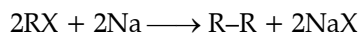
➢ Aryl halides are less reactive towards nucleophilic substitution reaction, due to resonance effect and hybridization.

Halogenation :

1, 4-Dichlorobenzene
(Major)

1, 2-Dichlorobenzene
(Minor)

Nitration :

1-Chloro-2-nitrobenzene
(Minor)

1-Chloro-4-nitrobenzene
(Major)

Sulphonation :

2-Chlorobenzenesulphonic acid
(Minor)

4-Chlorobenzenesulphonic acid
(Major)
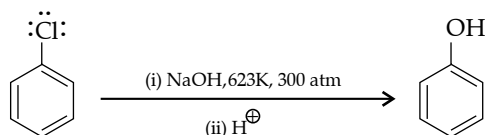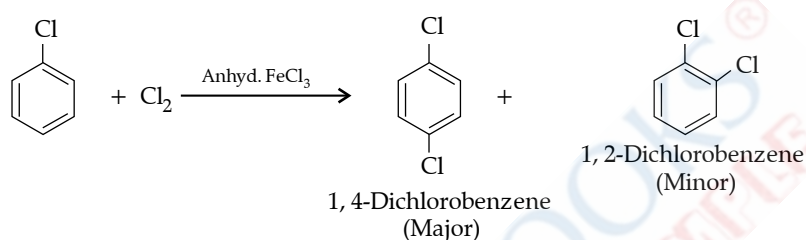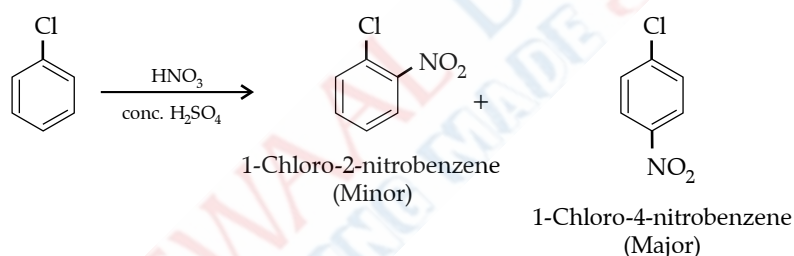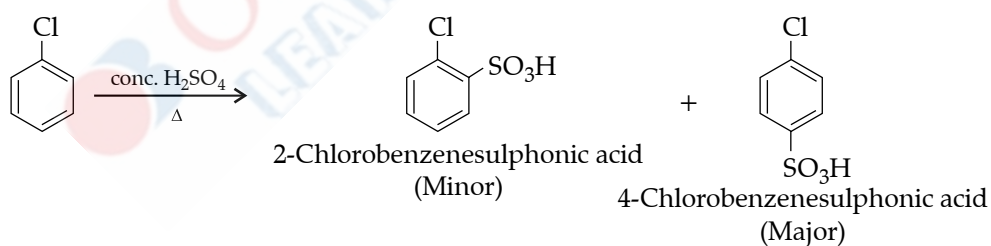
Friedel-Crafts reaction :

1-Chloro-2-methylbenzene
(Minor)

1-Chloro-4-methylbenzene
(Minor)

2-Chloroacetophenone
(Minor)

4-Chloroacetophenone
(Major)
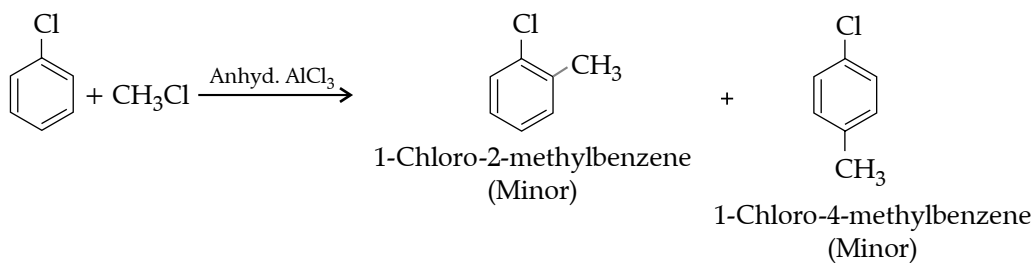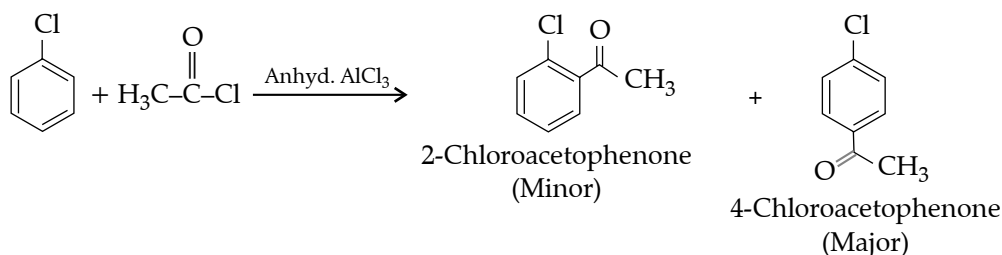
> **Wurtz-Fittig reaction :**

> **Fittig reaction :**

Diphenyl

Chlorobenzene   Phenol
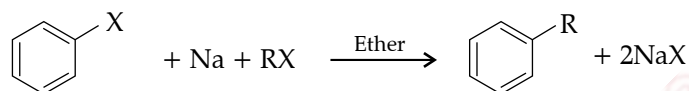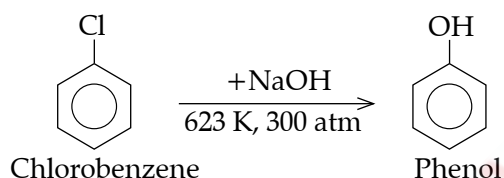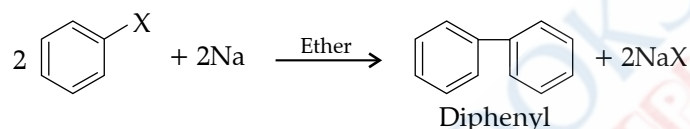
> **Important Terms:**

■ **Stereoisomerism :** Isomerism exhibited by two or more compounds with the same molecular and structural formula, but different spatial arrangements of atoms or groups in space.

■ **Plane-polarised light** is the beam of light whose oscillations or vibrations are confined to one plane only is called plane-polarised light.

■ **Nicol prism** is a special type of prism made from calcite, a special crystalline form of calcium carbonate.

■ **Optical rotation :** Property of rotating the plane of polarisation either towards left or right.

■ **Dextrorotatory :** Those substances which rotate the plane of polarisation of light towards right, *i.e.,* in clockwise, denoted by '*d*' and (+).

■ **Laevorotatory :** Those substances which rotate the plane of polarisation of light towards the left, *i.e.,* in anticlockwise direction are called laevorotatory, denoted by '*l*' and (–)

■ Specific rotation $[\alpha] = \dfrac{\text{observed rotation } (\alpha_{abs})}{\text{length of tube } (dm) \times \text{concentration of solution (g mol}^{-1})}$

■ **Optically active substances** are those substances which rotate the plane of polarisation of plane-polarised light when it is passed through their solutions.

■ **Polarimeter** is the instrument to measure angle of rotation by which the plane-polarised light is rotated.

■ **Chiral :** An object which is non-superimposable on its mirror image.

■ **Achiral :** Achiral objects are those objects which are superimposable on their mirror images.

■ **Asymmetric carbon** is the carbon atom which is attached with four different groups of atoms.

■ **Racemic mixture** is a mixture containing equal amounts of enantiomers which does not show any optical activity.

■ **Racemisation** is the process of conversion of an enantiomer into racemic mixture.

➢ Freon (CCl_2F_2) is a non-toxic gas which can be liquefied easily.

➢ **Polyhalogen compounds :**

■ $CH_4 + 2Cl_2 \xrightarrow{hv} CH_2Cl_2 + 2HCl$

■ $CH_4 + 3Cl_2 \xrightarrow[\text{Sunlight}]{hv} CHCl_3 + 3HCl$

■ $CH_3CH_2OH + 6NaOH + 4I_2 \xrightarrow{\Delta} CHI_3 + 5NaI + HCOONa + 5H_2O$

$CH_3COCH_3 + 4NaOH + 3I_2 \xrightarrow{\Delta} CHI_3 + 3NaI + CH_3COONa + 3H_2O$

■ $CS_2 + 3Cl_2 \xrightarrow[\Delta]{AlCl_3} CCl_4 + SCl_2$

$CH_4 + 4Cl_2 \xrightarrow{hv} CCl_4 + 4HCl$

■
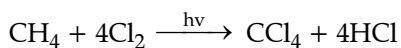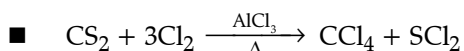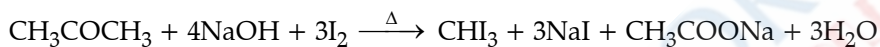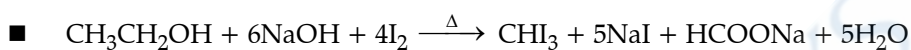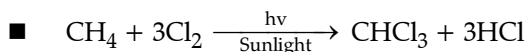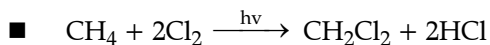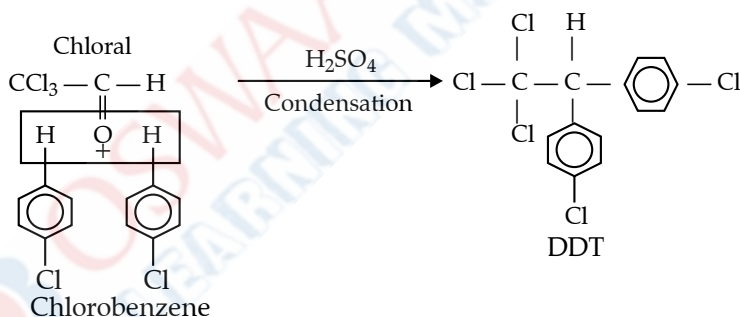
UNIT-XI   ALCOHOLS, PHENOLS AND ETHERS

➢ When one hydrogen atom of alkane is replaced by — OH group, the compounds obtained are called **alcohols**.

➢ General formula $C_nH_{2n+1}OH$

➢ **Allylic alcohols:** —OH group is attached to single bonded sp^3-hybridised carbon next to C=C. e.g., $CH_2 = CH—CH_2—OH$

Vinylic alcohols: —OH group is attached to double bonded sp^2-hybridised carbon atom. *e.g.*
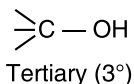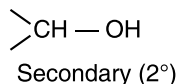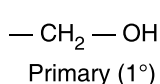
➢ **Preparation of Alcohols :**

■ $CH_3 — Cl + aq.\ KOH \longrightarrow CH_3 — OH + KCl$

■ $CH_3 — \overset{\overset{\textstyle O}{\|}}{C} — H + H_2 \xrightarrow{\text{Ni or Pt}} CH_3 — CH_2 — OH$

■ $CH_3 — \overset{\overset{\textstyle O}{\|}}{C} — CH_3 + H_2 \xrightarrow{\text{Ni}} CH_3 — \overset{\overset{\textstyle OH}{|}}{CH} — CH_3$

■ $H — \overset{\overset{\textstyle O}{\|}}{C} — H + CH_3MgBr \longrightarrow \left[H — \overset{\overset{\textstyle OMgBr}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}} — H \right] \xrightarrow{H_2O/H^+} CH_3CH_2OH + Mg \Big\langle \begin{smallmatrix} OH \\ Br \end{smallmatrix}$

■ $CH_2 = CH_2 + H_2SO_4 \longrightarrow CH_3CH_2OSO_3H \xrightarrow{H_2O} CH_3CH_2OH + H_2SO_4$

■ $3R – CH = CH_2 + (BH_3)_2 \longrightarrow (R – CH_2 – CH_2)_3 B \xrightarrow[OH^-,\ H_2O]{H_2O_2} R – CH_2 – CH_2 – OH + H_3BO_3$

■ $CH_3–CH=CH_2 \xrightarrow[H_2O]{(CH_3–COO)_2Hg} CH_3–\underset{\underset{\textstyle OH}{|}}{CH}–CH_2–HgOOCCH_3$

Propene

$\xrightarrow[\text{NaBH}_4 \,|\, OH^-]{}$

$CH_3–\underset{\underset{\textstyle OH}{|}}{CH}–CH_3$

■ $RCOOH \xrightarrow{\text{LiAlH}_4,\ H_2O} RCH_2OH$
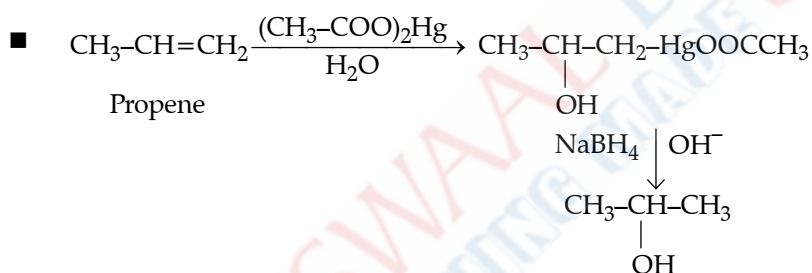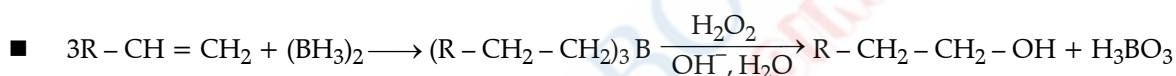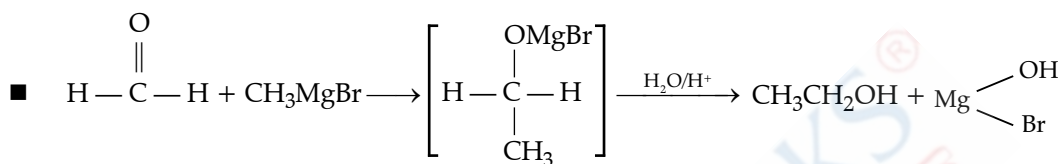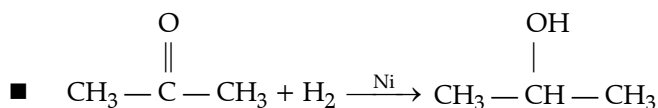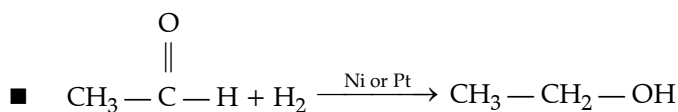
➢ **Preparation of Phenols :**

■

Chlorobenzene   Phenol

■

■
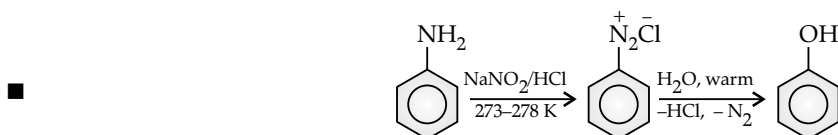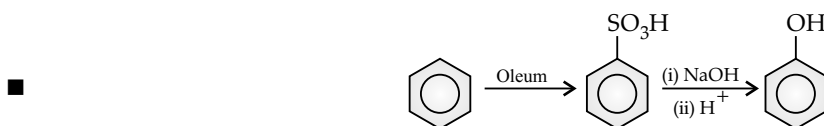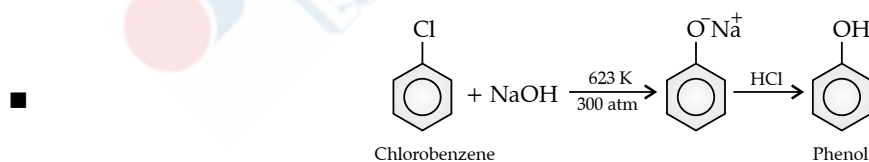
➢   In alcohols and phenols, b.p. increases with increase in C atoms. In alcohols, b.p. decreases with increase in branching chain.

➢

Reactions of Phenol :

Benzoquinone

- **Reactions of Ethanol :**

$$C_2H_5OH \xrightarrow[\text{anhyd. ZnCl}_2]{\text{HCl}} C_2H_5Cl + HCl$$

$$\xrightarrow{\text{HI + Red P}} C_2H_6 + I_2 + H_2O$$

$$\xrightarrow{\text{NH}_3/\text{ThO}_2.630K} C_2H_5NH_2 + \text{Secondary and tertiary amine}$$

$$\xrightarrow{\text{PCl}_5} C_2H_5Cl + POCl_3 + HCl$$

$$\xrightarrow{\text{SOCl}_2} C_2H_5Cl + SO_2 + HCl$$

$$\xrightarrow[\text{ZnCl}_2.2\text{NH}_3]{\text{NH}_3} C_2H_5NH_2 + H_2O$$

$$\xrightarrow{\text{Na}} C_2H_5\overset{\ominus}{O}\overset{\oplus}{N}a$$

$$\xrightarrow[\text{or (CH}_3\text{CO)}_2\text{O}]{\text{CH}_3\text{COOH or CH}_3\text{COCl}} C_2H_5OOCCH_3 + CH_3COOH$$

$$\xrightarrow[520K]{\text{Al}_2\text{O}_3} C_2H_5OC_2H_5 + H_2O$$

$$\xrightarrow[620\ K]{\text{Al}_2\text{O}_3} CH_2 = CH_2 + H_2O$$

$$\xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$$

$$\xrightarrow[410K]{\text{Heat with H}_2\text{SO}_4, \text{C}_2\text{H}_5\text{OH in excess}} C_2H_5-O-C_2H_5$$

$$\xrightarrow[440K]{\text{H}_2\text{SO}_4 \text{ in excess}} CH_2 = CH_2 + H_2O$$

$$\xrightarrow{\text{Cu, 573K}} CH_3CHO + H_2O$$

$$\xrightarrow{[O]} CH_3CHO \xrightarrow{\text{Cl}_2} CCl_3CHO$$

$$\xrightarrow{\text{I}_2 + \text{NaOH}} CHl_3$$

$$\xrightarrow{\text{CH}_3\text{MgI}} CH_4 + Mg\overset{I}{\underset{OC_2H_5}{<}}$$

- **Distinction between Primary, Secondary and Tertiary Alcohols :**
  - **(i)   Lucas Test :** In tertiary alcohol turbidity appears immediately, in secondary alcohol turbidity appears within five minutes and in primary alcohol turbidity appears on heating.
  - **(ii) Iodoform Test:** Given by compounds with a methyl group next to a carbonyl group. Secondary alcohols with a CH_3 on the carbon give a positive iodoform test.
- **Ethers R — O — R' :** General formula : $C_nH_{2n+2}O$
- **Preparation of ethers :**
  - ◼ **Williamson synthesis :**
    $$R — X + Na — O — R' \longrightarrow R — O – R' + NaX$$
  - ◼ $$C_2H_5OH + HOC_2H_5 \xrightarrow[413\ K]{\text{conc. H}_2\text{SO}_4} C_2H_5OC_2H_5 + H_2O$$
  - ◼ $$2C_2H_5Cl + Ag_2O \xrightarrow{\text{heat}} C_2H_5—O—C_2H_5 + 2AgCl$$
    $$CH_3Cl + Ag_2O + C_2H_5Cl \longrightarrow CH_3—O—C_2H_5 + 2AgCl$$
  - ◼ $$CH_3OCH_2Cl + BrMgC_2H_5 \longrightarrow CH_3 — O — CH_2 — C_2H_5 + Mg\overset{Br}{\underset{Cl}{<}}$$
  - ◼ $$C_2H_5OH + CH_2N_2 \xrightarrow{\text{BF}_3} C_2H_5OCH_3 + N_2$$

■

OH + NaOH ⟶ ONa $\xrightarrow{R–X}$ OR

➤ **Kolbe's reaction :**

Sodium phenoxide → Sodium salicylate → Salicylic acid

$\xrightarrow{NaOH}$ $\xrightarrow[+CO_2]{\substack{400\ K \\ 4–7\ atm}}$ $\xrightarrow{+H_2}$

Salicylic acid + $(CH_3CO)_2O$ $\xrightarrow{conc.\ H_2SO_4}$ Acetyl salicylic acid + CH_3COOH (Acetic acid)

➤ **Fries Rearrangement :**

Phenyl acetate $\xrightarrow[AlCl_3]{Heat}$ p – Hydroxy actephenone + o – Hydroxy actephenone

➤ **Properties :**

■ $R — O — R + HX \xrightarrow{373\ K} ROH + RX\ (X = Br, I)$

Ring substitution in aromatic ethers :

Anisole

- $\xrightarrow[\text{(Bromination)}]{Br_2\ \text{in acetic acid}}$ p-Bromoanisole (Major) + (Minor)
- $\xrightarrow[\text{(Friedel-Crafts alkylation)}]{CH_3Cl/anhyd.AlCl_3}$ p-Methoxytoluene (Major) + (Minor)
- $\xrightarrow[\text{(Friedel-Crafts acylation)}]{CH_3–C–Cl\ /\ anhyd.AlCl_3}$ p-Methoxy acetophenone (Major) + (Minor)
- $\xrightarrow[\text{Nitration}]{HNO_3(conc.)/H_2SO_4\ (conc.)}$ p-Nitroanisole (Major) + (Minor)
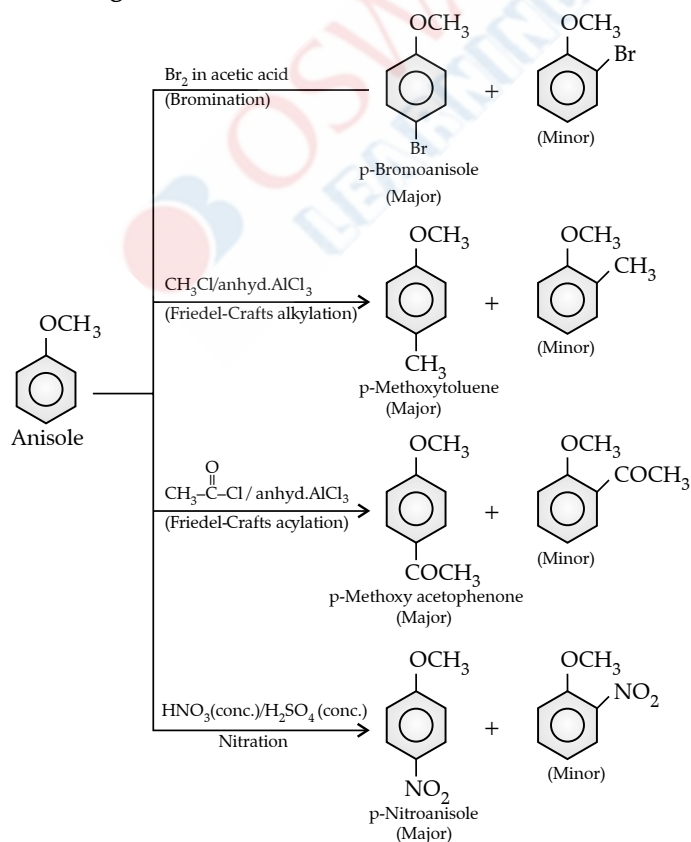
UNIT-XII	ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

- **Carbonyl group:** Functional group $\diagup C = O$

- **Aldehydes:** Carbonyl group is attached to either two hydrogen atoms or one hydrogen atom and one carbon containing group with hydrogen atom.

- **Ketones:** Carbonyl group is attached with two alkyl or two aryl or one alkyl and one aryl group.

- **Preparation of aldehydes:**

- $RCH_2OH + [O] \xrightarrow[\text{or KMnO}_4]{K_2Cr_2O_7/H_2SO_4} R—CHO + H_2O$

- $R—CH_2—OH \xrightarrow[573K]{Cu} RCHO + H_2$

- $R—CH = CH—R' + O_3 \longrightarrow R—CH \diagdiag CH—R' \xrightarrow[-\text{ZnO}]{H_2O,\ Zn} R—CHO + R'—CHO$
  Alkene   Aldehyde

$CH \equiv CH + H_2O \xrightarrow{H_2SO_4/HgSO_4} \left[\begin{array}{c} OH \\ | \\ CH_2 = CH \end{array} \right] \longrightarrow CH_3 — CHO$

Ethyne   Unstable   Ethanal
(Acelylene)   (Acetaldehyde)

- $\underset{\text{Acyl chloride}}{R — \overset{\overset{O}{\|}}{C} — Cl} + H_2 \xrightarrow[\text{Reduction}]{\text{Pd-BaSO}_4,\ S \\ \text{Rosenmund}} \underset{\text{Aldehyde}}{R — \overset{\overset{O}{\|}}{C} — H} + HCl$

  - **Stephen reaction:**

    $RCN + H_2 \ \dfrac{SnCl_2}{HCl} \ RCH = NH \xrightarrow{H_2 + Cl} RCHO + NH_4Cl$

  - **Etard reaction:**

Toluene   Chromium complex   Benzaldehyde
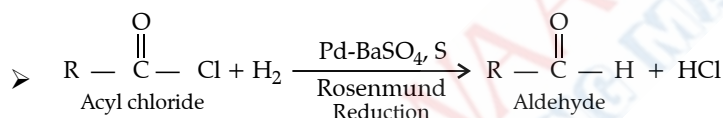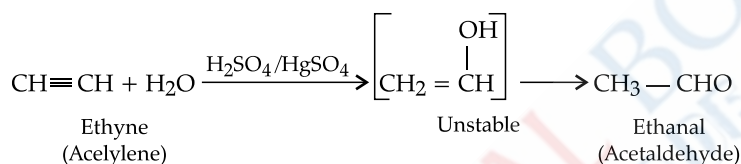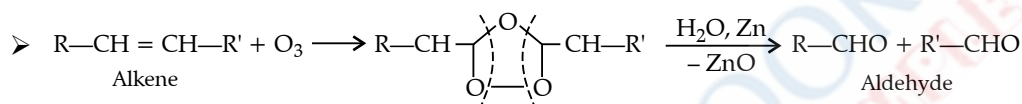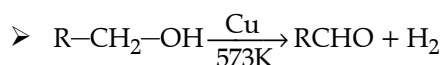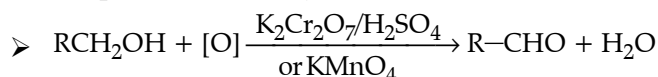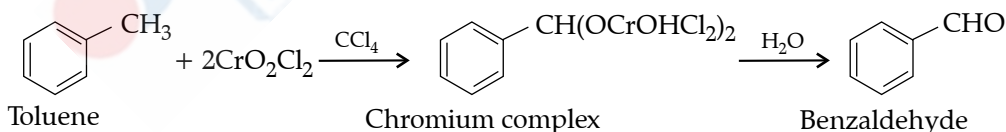
  - **Gattermann Koch reaction:**

Benzene   Benzaldehyde

- **Preparation of ketones:**

  (i) $2R — Mg – X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$

  (ii) $2\ \underset{\underset{O}{\|}}{R' – C – Cl} + R_2Cd \longrightarrow 2\ \underset{\underset{O}{\|}}{R' – C – R} + CdCl_2$

(iii) $CH_2 - CH_2 - C \equiv N + C_6H_5MgBr \xrightarrow{\text{ether}} CH_3CH_2 - \underset{\underset{C_6H_5}{|}}{\overset{\overset{NMgBr}{\|}}{C}} \xrightarrow{H_3O^+} C_2H_5 - \underset{C_6H_5}{\overset{O}{\overset{\|}{C}}}$

Propiophenone
(1-Phenylpropanone)

(iv) $\underset{R'}{\overset{R}{>}}CH—OH + [O] \xrightarrow[\text{or } CrO_3]{K_2Cr_2O_7/H_2SO_4} \underset{R'}{\overset{R}{>}}C = O + H_2O$

    2° Alcohol   Ketone

(v) $\underset{R'}{\overset{R}{>}}CH—OH \xrightarrow{\overset{Cu}{573K}} \underset{R'}{\overset{R}{>}}C = O + H_2$

    2° Alcohol   Ketone

(vi) $\underset{R}{\overset{R}{>}}C = C\underset{R'}{\overset{R'}{<}} + O_3 \longrightarrow \overset{R\searrow\;\;O\;\;\swarrow R'}{\underset{\overset{O-O}{\;}}{C\;\;\;C}}R' \xrightarrow[- ZnO]{H_2O, Zn} RCOR + R'COR'$
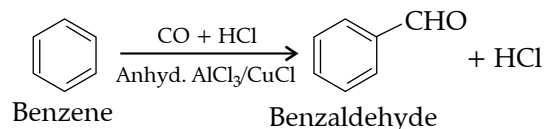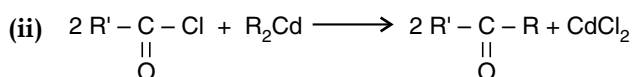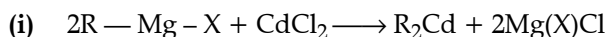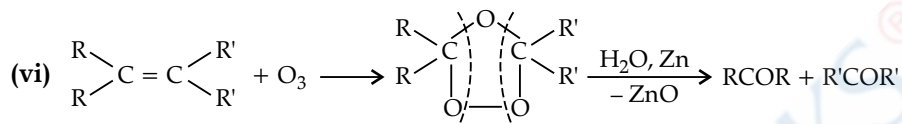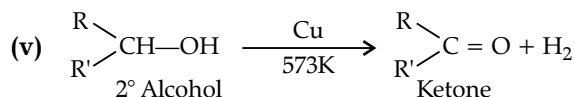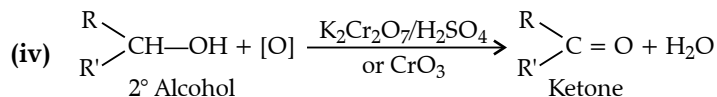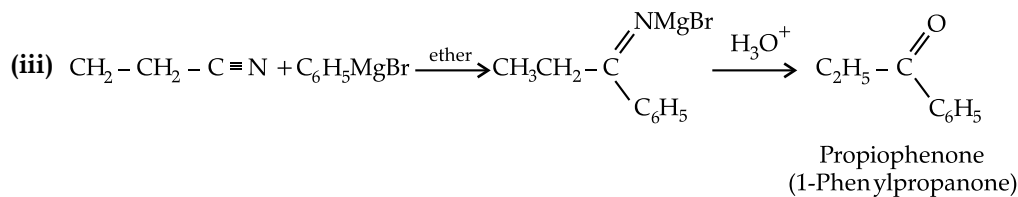
> **Friedel-Crafts acylation reaction:**

$$\bigcirc + Ar/R - \overset{O}{\overset{\|}{C}} - Cl \xrightarrow{\text{Anhyd.AlCl}_3} \bigcirc\!\!-\overset{O}{\overset{\|}{C}}-Ar/R + HCl$$
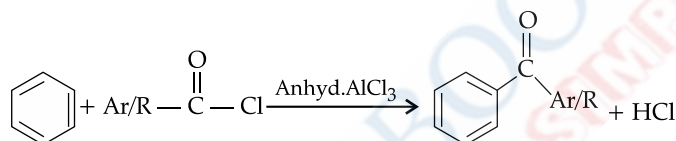
> Aldehydes and ketones generally undergo nucleophilic addition reaction.

> Aldehydes are very reactive than ketones due to more +I effect in ketones.

> **Chemical Properties of Aldehydes and Ketones:**

- $HCN + OH^- \rightleftharpoons :\overline{C}N + H_2O$

$$\underset{}{\overset{\delta^+}{>}C = \overset{\delta^-}{O}} + :\overline{C}N \rightleftharpoons \left[>C\overset{O^-}{\underset{CN}{<}} \right] \overset{H^+}{\rightleftharpoons} >C\overset{CN}{\underset{OH}{<}} \begin{cases} \xrightarrow{H_3O^+} \overset{OH}{\underset{}{-\overset{|}{\underset{|}{C}}-COOH}} \\ \text{Hydroxy acid} \\ \xrightarrow{LiAlH_4} >C\overset{NH_2}{\underset{OH}{<}} \\ \text{amino alcohol} \end{cases}$$

                              Cyanohydrin

- $>C = O + NaHSO_3 \rightleftharpoons >C\overset{SO_3H}{\underset{ONa}{<}} \rightleftharpoons >C\overset{SO_3Na}{\underset{OH}{<}}$

- $>C = O + RMgX \longrightarrow >C\overset{OMgX}{\underset{R}{<}} \xrightarrow{H_2O/H^+} >C\overset{OH}{\underset{R}{<}} + Mg\overset{OH}{\underset{X}{<}}$

- $>C = O + H_2N—Z \rightleftharpoons \left[>C\overset{OH}{\underset{NHZ}{<}} \right] \rightarrow >C = N - Z + H_2O$
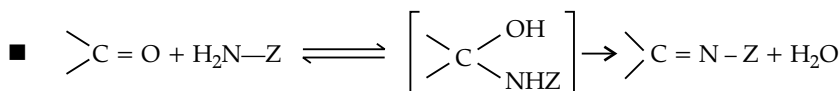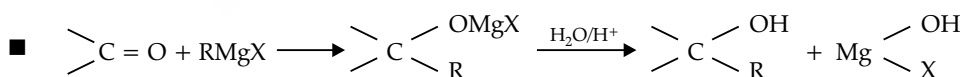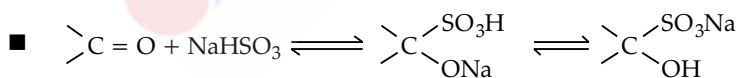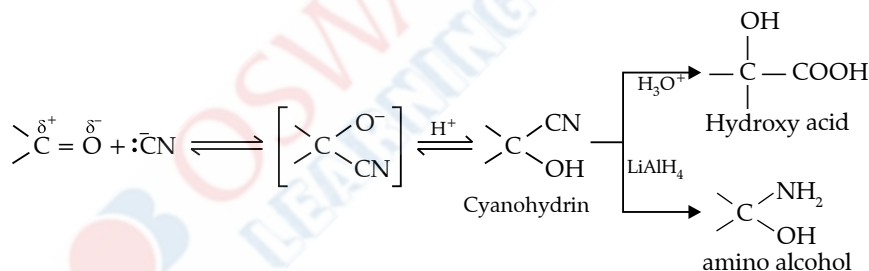
    where Z = Alkyl, aryl, OH, NH_2CONH_2, *etc.*

- $R — CHO + 2[H] \xrightarrow[\text{or } BH_4]{LiAlH_4} R—CH_2OH$

     Aldehyde   1° Alcohol

- $\underset{R}{\overset{R}{>}}C = O + H_2 \xrightarrow{Ni \text{ or } Pt} \underset{R}{\overset{R}{>}}CH—OH$

                    2°Alcohol

■ **Aldol condensation:**

$$2CH_3—CHO \xrightarrow{\text{dil. NaOH}} CH_3—CH—CH_2—CHO \xrightarrow[-H_2O]{\Delta} CH_3—CH=CH—CHO$$
$$\overset{|}{\underset{OH}{}}$$
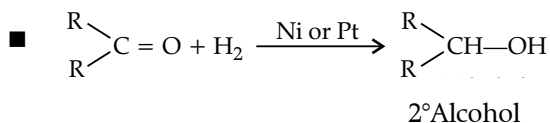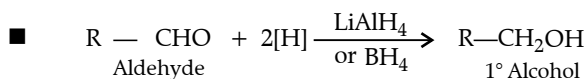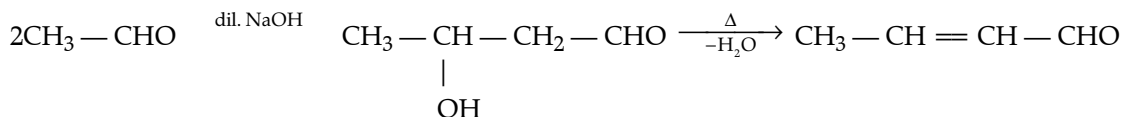
■ **Cross aldol condensation:**

$$CH_3CHO + CH_3CH_2CHO \xrightarrow[\Delta,\ -H_2O]{\text{dil. NaOH}} CH_3—CH=C—CHO + CH_3—CH_2—CH=CHCHO$$
$$\overset{|}{\underset{CH_3}{}}$$
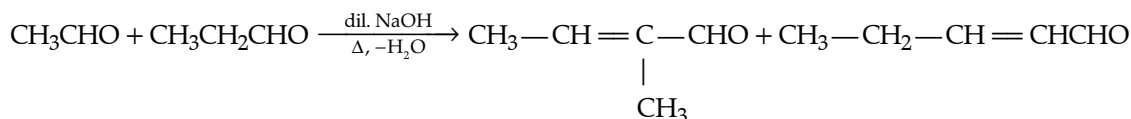
➤ **Clemmensen reduction:**

$$\underset{/}{\overset{\backslash}{}}C=O \xrightarrow[\text{HCl}]{\text{Zn-Hg}} \underset{/}{\overset{\backslash}{}}CH_2 + H_2O$$

➤ **Wolff-Kishner reaction:**

$$\underset{/}{\overset{\backslash}{}}C=O \xrightarrow[-H_2O]{NH_2–NH_2} \underset{/}{\overset{\backslash}{}}C=N–NH_2 \xrightarrow[\text{heat}]{\text{KOH/ethylene glycol}} \underset{/}{\overset{\backslash}{}}CH_2 + N_2$$
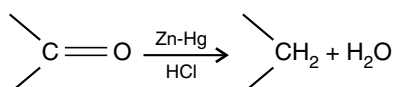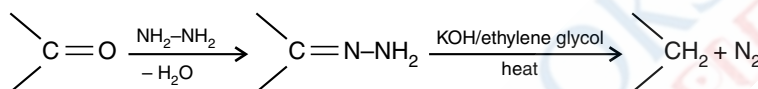
➤ Tollens' and Fehling test are used to distinguish between aldehydes and ketones.

Tollens' test: Ketone does not give this test.
$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCOO^- + 2Ag\downarrow + 2H_2O + 4NH_3$$
$$\text{Silver Mirror}$$
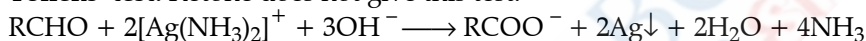
Fehling test: Ketone does not give this test.
$$R–CHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + Cu_2O\downarrow + 3H_2O$$
$$\text{Red ppt}$$
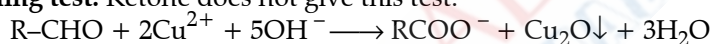
➤ **Cannizzaro reaction**

$$\underset{H}{\overset{H}{}}C=O + \underset{H}{\overset{H}{}}C=O + \text{Conc. KOH} \xrightarrow{\Delta} H-\underset{H}{\overset{H}{C}}-OH + H-C\underset{OK}{\overset{O}{}}$$
$$\text{Formaldehyde} \qquad\qquad\qquad \text{Methanol} \quad \text{Potassium formate}$$

$$2\ \bigcirc\!\!\!\!-CHO + \text{Conc. NaOH} \xrightarrow{\Delta} \bigcirc\!\!\!\!-CH_2OH + \bigcirc\!\!\!\!-COONa$$
$$\text{Benzaldehyde} \qquad\qquad \text{Benzyl alcohol} \quad \text{Sodium benzoate}$$
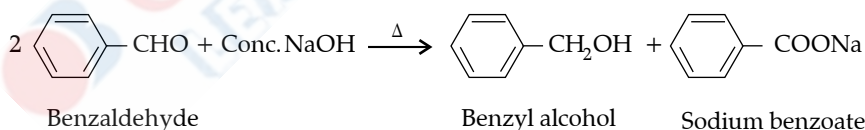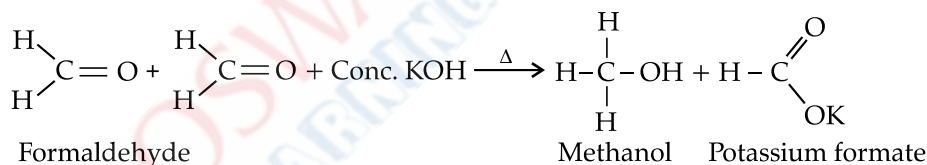
➤ Aldehydes and ketones also react with ammonia derivatives like:

(i) NH_2OH to give amines.

(ii) $NH_2–NH_2$ to give hydrazones.

(iii) Phenyl hydrazine to give phenyl hydrazones.

➤ **Carboxylic acids:** General formula: $C_nH_{2n+1}COOH$

➤ **Preparation:**

■ $$R—CH_2—OH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) Alk. KMnO}_4} R—COOH$$

■ $$R—CHO + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} R—COOH$$

■ $$R—C\equiv N \xrightarrow{H_3O^+} R—\overset{O}{\overset{||}{C}}—NH_2 \xrightarrow{H_3O^+} R—\overset{O}{\overset{||}{C}}—OH$$

■ $R — Mg — X + CO_2 \xrightarrow{\text{Dry ether}} R — \overset{\overset{\text{O}}{||}}{C} — OMgX \xrightarrow{H_3O^+} R — \overset{\overset{\text{O}}{||}}{C} — OH$

■

$$C_6H_5\overset{\overset{\text{O}}{||}}{C} \underset{CH_3\underset{\underset{\text{O}}{||}}{C}}{\diagdown} O \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Ethanoic acid}}{CH_3COOH}$$

Benzoic ethanoic anhydride

■ $CH_3—CH_2—CH_2—\overset{\overset{\text{O}}{||}}{C}—OCH_2—CH_3 \xrightarrow{\text{NaOH}} CH_3—CH_2—CH_2—COONa$

Ethyl butanoate

$+ CH_3CH_2—OH \xrightarrow{H_3O^+} CH_3CH_2CH_2COOH$

Butanoic acid

➢ **Properties:**

■ Carboxylic acids are weak acids. They liberate H^+ ions on ionization.

■ $2R — COOH + 2Na \longrightarrow \underset{\text{Sodium carboxylate}}{2R — CO\overline{O}Na^+} + H_2$

■ $R — COOH + NaOH \longrightarrow R — CO\overline{O}Na^+ + H_2O$

■ $R — COOH + NaHCO_3 \longrightarrow R — CO\overline{O}Na^+ + H_2O + CO_2 \uparrow$

■

$$H_3C—\overset{\overset{\text{O}}{||}}{C}\underset{OH}{\diagdown} + \underset{HO}{\overset{\overset{\text{O}}{||}}{C}}— CH_3 \xrightarrow[\text{or } P_2O_5, \Delta]{H^+, \Delta} CH_3 – \overset{\overset{\text{O}}{||}}{C}\underset{O}{\diagup \diagdown}\overset{\overset{\text{O}}{||}}{C}– CH_3 + H_2O$$

Ethanoic acid　　　　　　　　　　　　　　　Ethanoic anhydride

■ **Esterification:**

$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$

■ **Reaction with PCl_5, PCl_3 and $SOCl_2$:**

$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$

$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 \uparrow + HCl \uparrow$

■ **Reduction:**

$R — COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) LiAlH}_4 / \text{ether or B}_2H_6} R — CH_2OH$

■ $\underset{\text{Carboxylic acid}}{R — COOH} + NH_3 \rightleftharpoons R — COO – NH_4 \xrightarrow[-H_2O]{\Delta} \underset{\text{Amide}}{R — CONH_2}$

■

$$\underset{\text{Benzoic acid}}{\overset{\text{COOH}}{\bigcirc}} + NH_3 \rightleftharpoons \underset{\text{Ammonium benzoate}}{\overset{C\overline{O}O\overset{+}{N}H_4}{\bigcirc}} \xrightarrow{\Delta} \underset{\text{Benzamide}}{\overset{\text{CONH}_2}{\bigcirc}} + H_2O$$

■

Phthalamide   Phthalimide

■ **Hell Volhard Zelinsky reaction:**

$$R-CH_2-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red phosphorus}} R-\underset{\underset{X}{|}}{C}H-COOH$$

X = Cl, Br

α -Halocarboxylic acid

■   **Nitration**   **Bromination**

m-nitrobenzoic acid   *m*-bromobenzoic acid
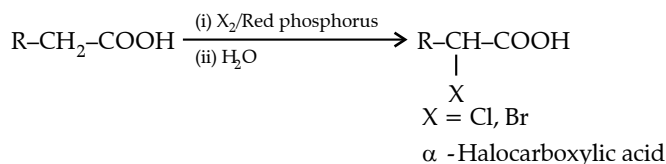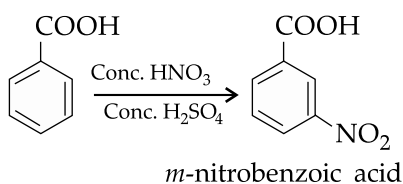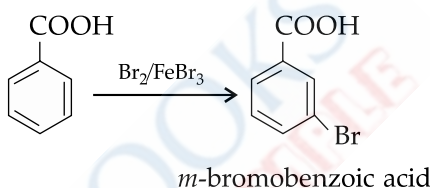
➤ **Order of strength of Acids:**

HCOOH > CH_3COOH > CH_3CH_2COOH > C_3H_7COOH

CCl_3COOH > $CHCl_2COOH$ > $CH_2ClCOOH$ > CH_3COOH
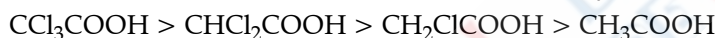
➤ **Uses:** Hexanedioic acid is used in the manufacture of nylon-6, 6. Esters of benzoic acid are used in perfumery. Sodium benzoate is used as a food preservative. Higher fatty acids are used for the manufacture of soaps and detergents.

UNIT-XIII	ORGANIC COMPOUNDS CONTAINING NITROGEN

➤ Amines are considered as derivatives of ammonia by replacement of hydrogen atoms with alkyl or aryl groups.

$$CH_3-NH_2, \ C_6H_5-NH_2, \ CH_3-NH-CH_3, \ CH_3-N\begin{smallmatrix} \diagup CH_3 \\ \diagdown CH_3 \end{smallmatrix}$$
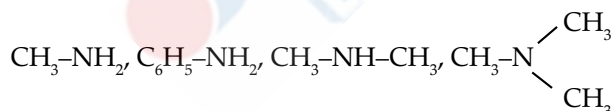
➤ Amines exhibit hydrogen bonding which influence their physical properties.

➤ **Identification of primary, secondary and tertiary amines:**

S.No.	Test	Primary amine	Secondary amine	Tertiary amine
1.	Action with HNO_2	Alcohol is formed and nitrogen is evolved.	Nitroso-amine is formed which with phenol and conc. H_2SO_4 gives green colour (Liebermann Test).	In cold, nitrite salt is formed which on heating gives nitroso-amine. This nitroso-amine gives Liebermann test.
2.	Action with $CHCl_3$ and alc. KOH.	Isocyanide with offensive odour is formed.	No reaction.	No reaction.

3.	Action with CS_2 and $HgCl_2$ (Mustard oil reaction).	Forms N-substituted isothiocyanate which has smell like that of mustard oil.	No reaction.	No reaction.
4.	Action with acetyl chloride.	Acetyl derivative is formed.	Acetyl derivative is formed.	No reaction.
5.	Action with CH_3I.	Three molecules of CH_3I on reaction with primary amine give quaternary salt.	Two molecules of CH_3I on reaction with secondary amine give quaternary salt.	Only one molecule of CH_3I reacts with tertiary amine and formation of quaternary salt takes place.
6.	Action with Hinsberg ($C_6H_5SO_2Cl$) reagent.	Mono alkyl sulphonamide derivative is formed which is soluble in KOH.	Dialkyl sulphonamide derivative is formed which is insoluble in KOH.	No reaction.

➢ **Gabriel phthalimide synthesis:**

Phthalimide   N–Alkylphthalimide

Phthalic acid   +RNH_2 (1° amine)
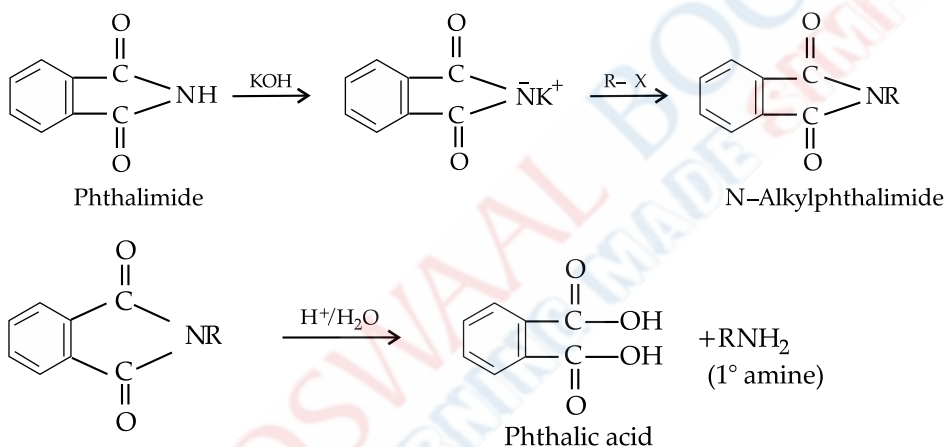
➢ **Hoffmann bromamide degradation reaction:**

$$R - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2 + Br_2 + 4NaOH \longrightarrow R - NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

➢ **Carbylamine reaction:**

$$R - NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} R - NC + 3KCl + 3H_2O$$

➢ **Diazotisation:**

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278 \text{ K}} C_6H_5N_2{}^+Cl^- + NaCl + 2H_2O$$

➢ **Coupling reactions:**

p-hydroxyazobenzene (orange dye)

p-Aminoazobenzene (yellow dye)
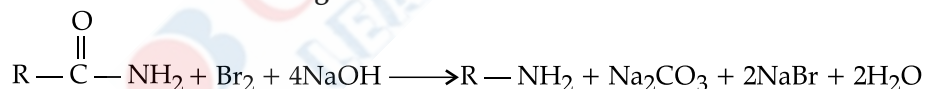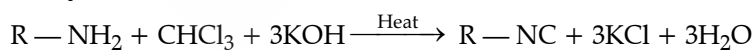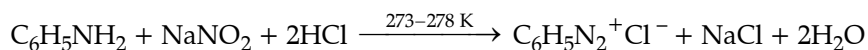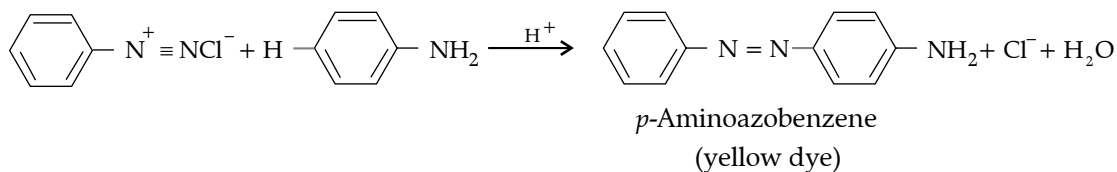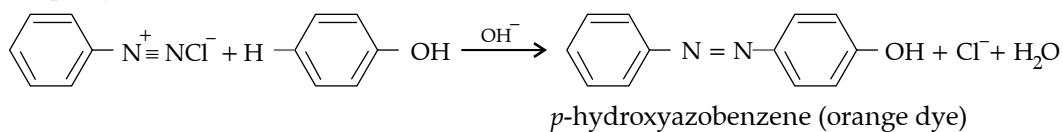
➢ **Methods of preparation and reactions of ethyl amine**

$$C_2H_5I + NH_3 \longrightarrow$$

$$C_2H_5OH + NH_3 \xrightarrow{Al_2O_3}$$

$$C_2H_5NO_2 \xrightarrow{Sn + HCl}$$

$$CH_3CN \xrightarrow{Na(Hg)+ C_2H_5OH} \boxed{C_2H_5NH_2}$$

$$C_2H_5CONH_2 \xrightarrow[\text{Hoffmann's reaction}]{Br_2 + KOH}$$

Gabriel phthalimide reaction — $\begin{array}{c} CO \\ \\ CO \end{array} NK + C_2H_5I \longrightarrow$, $\xrightarrow{H_2O}$

$$CH_3CONH_2 \xrightarrow{LiAlH_4}$$

From $C_2H_5NH_2$:

$$\xrightarrow{H_2O} C_2H_5NH_3^+ + OH^-$$

$$\xrightarrow{HCl} C_2H_5NH_2.HCl$$

$$\xrightarrow{H_2SO_4} (C_2H_5NH_2)_2.H_2SO_4$$

$$\xrightarrow{2HCl + PtCl_4} (C_2H_5NH_2)_2.H_2PtCl_6$$

$$\xrightarrow{C_2H_5I} (C_2H_5)_2NH \xrightarrow{C_2H_5I} (C_2H_5)_3N$$

$$(C_2H_5)_3N \xrightarrow{C_2H_5I} (C_2H_5)_4\overset{+}{N}I$$

$$\xrightarrow[\text{or} \atop (CH_3CO)_2O]{CH_3COCl} C_2H_5 \, NHCOCH_3$$

$$\xrightarrow{C_6H_5COCl} C_2H_5NHCOC_6H_5$$

$$\xrightarrow{HNO_2} C_2H_5OH$$

$$\xrightarrow[\text{Carbylamine reaction}]{CHCl_3 + KOH} C_2H_5NC$$

$$\xrightarrow[\text{Mustard oil reaction}]{CS_2 + KOH} C_2H_5NCS$$

$$\xrightarrow{Na} C_2H_5NHNa$$

$$\xrightarrow[{[O]}]{KMnO_4} CH_3CHO$$

$$\xrightarrow{CH_3CHO} C_2H_5N = CHCH_3$$

UNIT-XIV	BIOMOLECULES

➢ **Biomolecules** are naturally occurring organic compounds present as essential constituents of living organism in different cells. *e.g.*, polysaccharides, proteins, etc.

➢ **Carbohydrates**

▪ **Carbohydrates** are optically active polyhydroxy aldehydes or ketones or compound which produce such units on hydrolysis. *e.g.*, cellulose, glycogen, starch etc.

▪ They are classified as monosaccharides, disaccharides, oligosaccharides and polysaccharides on the basis of their behaviour on hydrolysis.

▪ All monosaccharides and disaccharides are sweet in taste, so called sugars.

▪ **Reducing sugars :** Carbohydrates which contain free aldehydic or ketonic group and reduce Fehling's solution and Tollens' reagent. *e.g.*, all monosaccharides, maltose.

Non-reducing sugars : Carbohydrates which do not have free aldehydic or ketonic group and do not reduce Fehling's solution or Tollens' reagent. *e.g.,* sucrose.

- All reducing carbohydrate undergoes mutarotation in aqueous solution.

- Glucose and fructose are examples of monosaccharides.

- **Preparation of Glucose:**

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$(C_6H_{10}O_5)n + nH_2O \xrightarrow[393 \text{ K, 2-3 bar}]{H^+} nC_6H_{12}O_6 \text{ Glucose}$$

- **Reactions of glucose:**

$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{HI, \Delta} CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

(*n*-Hexane)

$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{NH_2OH} \begin{array}{c} CH{=}N{-}OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{-NO} \begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{HCN} \begin{array}{c} CH{\overset{CN}{\underset{OH}{<}}} \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

Glucose monoxime   Glucose cyanohydrin

$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{Br_2 \text{ water}} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

Gluconic acid

$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{5 \text{ (Acetic anhydride)}} \begin{array}{c} CHO \\ | \\ (CHO{-}\overset{O}{\overset{||}{C}}{-}CH_3)_4 \\ | \\ CH_2O{-}\overset{O}{\overset{||}{C}}{-}CH_3 \end{array} + 5CH_3COOH$$

$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow[\text{conc. HNO}_3]{\text{Oxidation}} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ COOH \\ \text{Saccharic} \\ \text{acid} \end{array} \xleftarrow[\text{conc. HNO}_3]{\text{Oxidation}} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \\ \text{Gluconic} \\ \text{acid} \end{array}$$
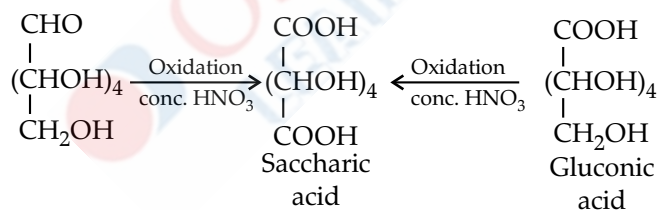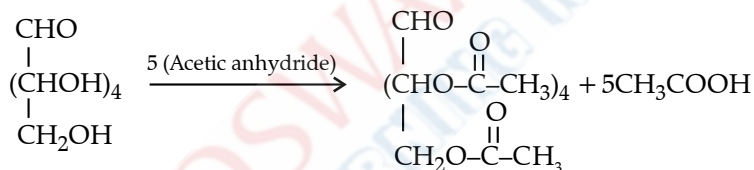
- Sucrose, maltose and lactose are examples of disaccharides. Maltose molecule is composed of two α-D-glucose units in which C_1 of one glucose (I) is linked to C_4 of another glucose unit (II).

- Amylose is a long unbranched chain with 200 – 1000 α-D-(+)-glucose units held by $C_1 - C_4$ glycosidic linkage. Amylopectin is a branched chain polymer of α-D-glucose units in which the chain is formed by $C_1 - C_4$ glycosidic linkage whereas branching occurs by $C_1 - C_6$ glycosidic linkage.

- Starch and cellulose are examples of polysaccharides.

- Cellulose is a polysaccharide whose fundamental structural unit is β-D-glucose joined by glycosidic linkage between C_1 of one glucose unit and C_4 of the next glucose unit.

- D-ribose and deoxyribose are sugars present in RNA and DNA respectively.

➢ **PROTEINS, VITAMINS AND NUCLEIC ACIDS**

- Proteins are condensation polymers in which monomeric units are the α-amino acids.

- The compounds which contain carboxylic acid (–COOH) group and an amino group ($-NH_2$) are called **amino acids.**

- On the basis of structure, proteins are classified as **fibrous and globular proteins**.

- Fibrous proteins are thread like molecules which tend to lay side by side while globular proteins are folded molecular to form compact units of spheroidal shape.

Amino acids
(Contain –COOH and $-NH_2$ group)

Essential | Non-essential | Acidic | Basic | Neutral
(Not synthesized | (Synthesized
by the body) | by the body)
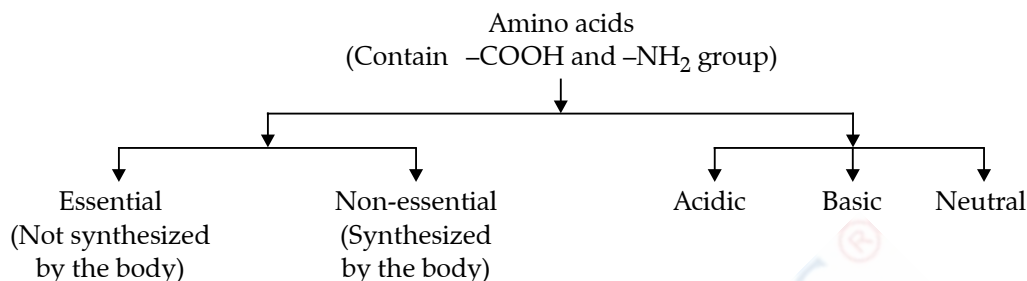
- **Based on structure and shape :**

(i) **Primary structure :** Each polypeptide in a protein has amino acids linked with each other in a specific sequence.

(ii) **Secondary structure :** It refers to the shape in which a long polypeptide chain exists i.e., α-helix and β-pleated sheet.

(iii) **Tertiary structure :** It represents overall folding of polypeptide chains by H-bonds, disulphide linkages, van der Waals and electrostatic form of attraction.

(iv) **Quaternary structure :** The spatial arrangement of two or more polypeptide chains with respect to each other.

- α-amino acids exist as dipolar ions or Zwitter ions.

- Proteins help as transporting agent, as enzymes, as metabolic regulators, as antibodies and as structural materials.

- **Vitamins** are required in small quantities for the growth, life and health of human beings.

- Vitamins can be water soluble (B and C) and fat soluble (A, D, E and K).

- **Nucleic acids** are the polymers of nucleotides help in synthesis of protein and transfer genetic traits.

- Monomeric unit of nucleic acid is a nucleotide.

- Nucleotide is made up of a pentose sugar, a heterocyclic base and phosphoric acid unit.

- **Nucleic acids** are of 2 types : (i) DNA (deoxyribonucleic acid)

(ii) RNA (ribonucleic acid)

- DNA has a double helical structure.

- RNA has a single strand.

- Nucleic acid helps in replication and protein synthesis.

- **RNA :** (i) *m*-RNA (Messenger RNA)

(ii) *r*-RNA (Ribosomal RNA)

(iii) *t*-RNA (Transfer RNA)

➢ **Differences between**

■ **DNA and RNA**

S. No.	RNA	DNA
(i)	The sugar is D-ribose.	The sugar is D-2-deoxyribose.
(ii)	It exists as a single chain structure.	It has a double helix structure.

(iii)	The base units are : * Adenine (A) and guanine (G) as purine bases. * Cytosine (C) and uracil (U) as pyrimidine bases.	The base units are : * Adenine (A) and guanine (G) as purine bases. * Cytosine (C) and thymine (T) as pyrimidine bases.
(iv)	It is responsible for protein synthesis.	It is responsible for inheritance of characters.

■ **Fibrous and Globular protein**

S. No.	Globular proteins	Fibrous proteins
(i)	These are water soluble proteins.	These are water insoluble proteins.
(ii)	These are spherical in shape.	These are linear in shape.
(iii)	Globular proteins are highly unstable.	Fibrous proteins are stable to moderate change in temperature and pH.

■ **Reducing and Non-reducing sugar**

S. No.	Reducing sugar	Non-reducing sugar
(i)	Carbohydrates which can reduce Tollens' reagent or Fehling solution.	Carbohydrates which cannot reduce Tollens' reagent or Fehling solution.
(ii)	Have free aldehyde or ketone groups.	Do not have free aldehyde or ketone groups.
(iii)	Osazone formation takes place.	Osazone formation does not take place.
(iv)	E.g., maltose, glucose.	E.g., sucrose, raffinose.

➢ Hormones are the chemical substances produced by ductless glands called endocrine gland.

➢ **Various hormones, gland of secretion and their functions :**

S. No.	Hormones	Gland	Function
1.	**Steroid hormones :** (i) Testosterone (androgens) (ii) Estrogen and progesterone (iii) Cortisone	 Testes Ovary Adrenal cortex	 Responsible for development of male sex organs. Influences development of sex organs maintains pregnancy. Regulates metabolism of water, mineral salts.
2.	**Amine hormones :** (i) Adrenalin (ii) Thyroxine	 Adrenal medulla Thyroid	 Increases blood pressure and pulse rate. It also releases glucose from glycogen and fatty acids from fats. Stimulates rate of oxidative metabolism and regulates general growth and development.
3.	**Peptide hormones :** (i) Oxytocin (ii) Vasopressin (ADH) (iii) Insulin (iv) Glucagon	 Posterior pituitary Posterior pituitary Pancreas Pancreas	 Causes constriction of some smooth muscles. It causes contraction of uterus during child birth. Controls the reabsorption of water in kidneys. Controls blood glucose level. Increases blood glucose level.

➤ **Different Vitamins :**

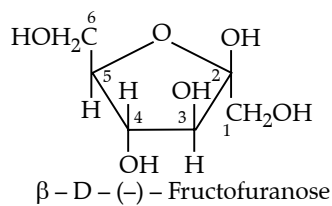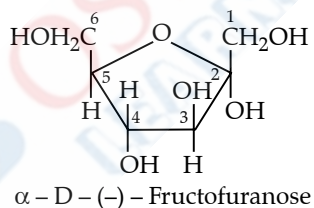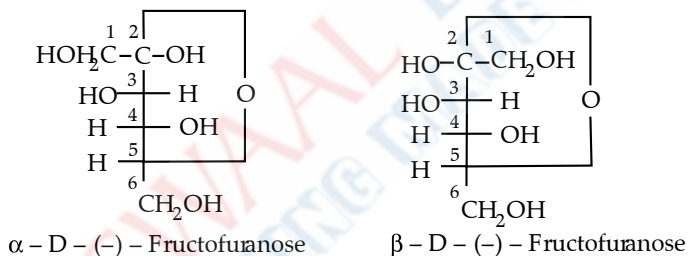| Vitamin	Name and Formula	Sources	Function	Deficiency Diseases
Vitamin A	Retinol or Axerophthol $C_{20}H_{30}O$	Milk, butter, egg, fish, spinach, green vegetables, carrot, etc.	Essential for vision and growth. Develops resistance against diseases.	Night blindness, xerophthalmia, retarded growth and decreases the immunity of body towards various diseases.
Vitamin B_1	Thiamine or Aneurin $C_{12}H_{17}N_4OS$	Egg, fish, meat, rice, wheat, yeast, etc.	For proper functioning of nervous system.	Beri-beri, anaemia, weakness of muscles, etc.
Vitamin B_2	Riboflavin or Lactoflavin $C_{17}H_{20}N_4O_6$	Milk, cheese, egg, meat, green vegetables, liver, etc.	Essential for growth of body.	Cracking skin particularly at the corners of mouth (Cheilosis), glossitis, dermatitis.
Vitamin B_6	Pyridoxine $C_8H_{11}O_3N$	Wheat, maize, husk of rice, meat, fish, egg, etc.	In blood formation	Convulsions, paralysis.
Vitamin B_{12}	Cyanocobalamin $C_{63}H_{88}CoN_{14}O_{14}P$	Liver, egg, fish, meat, etc.	In blood formation	Macrocytic anaemia or pernicious anaemia.
Vitamin C	Ascorbic acid $C_6H_8O_6$	Citrus fruits such as lemon, orange, tomatoes, amla, etc.	For bones, teeth and healing of wounds, healthy skin.	Scurvy, pyria, pain in joints, loosening of teeth, mental depression, anaemia, bleeding of gums.
Vitamin D	Calciferol or Ergo-calciferol or Vitamin D_2, $C_{27}H_{44}O$	Egg, meat, fish, liver oil, butter, etc.	Control of metabolism of calcium and phosphorus in the formation of bones.	Rickets, osteomalacia.
Vitamin E	α-Tocopherol $C_{29}H_{50}O_2$	Milk, egg, meat, pulses, green vegetables, seeds, beans etc.	Anti sterility or reproduction.	Loss of reproductive ability or infertility.
Vitamin K (Vitamin K_1 or K_2)	Vitamin K_1 or Phylloquinone $C_{31}H_{46}O_2$, Vitamin K_2, $C_{41}H_{56}O_2$	Cabbage, spinach, green vegetables, egg, fish, etc.	Helps in clotting of blood.	Delay in blood clotting (Haemophilia).

➢ **IMPORTANT STRUCTURES**

Glucose :

α – D – (+) – Glucose   β – D – (+) – Glucose

α – D – (+) – Glucopyranose   β – D – (+) – Glucopyranose

Fructose :

α – D – (–) – Fructofuranose   β – D – (–) – Fructofuranose

α – D – (–) – Fructofuranose   β – D – (–) – Fructofuranose

Sucrose :

α – D – Glucose   Glycosidic linkage   β – D – Fructose
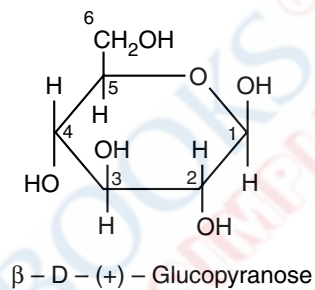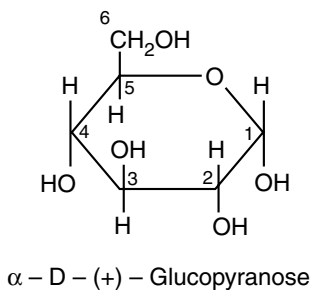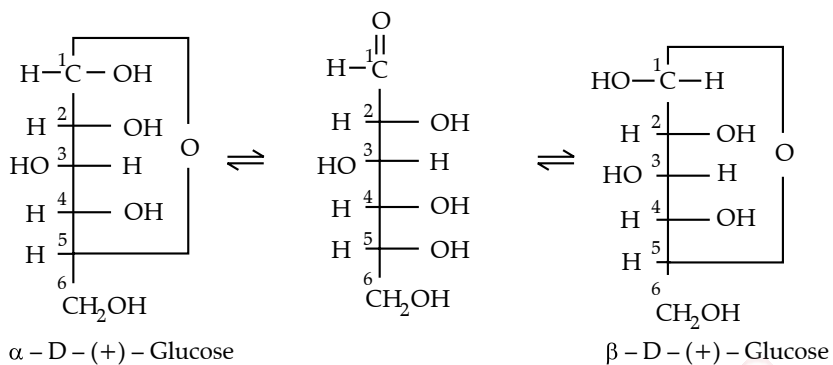
Zwitter ion :
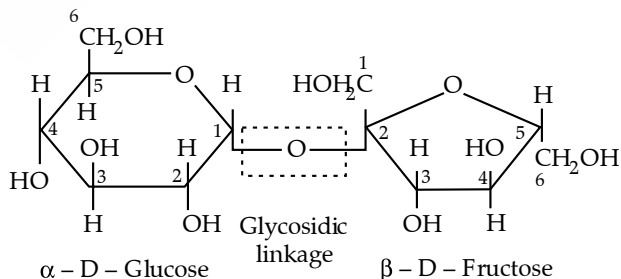
Amino acid   (Zwitter ion)
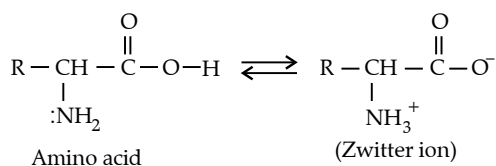
UNIT-XV	POLYMERS

➢ Polymers are high molecular mass macromolecules consisting of repeating structural units derived from corresponding monomers.

➢ **On the simple basis of origin of polymers , they are classified as :**
   (i)   Natural polymers : Obtained from plants and animals. *E.g.*, protein, natural rubber.
   (ii)   Synthetic polymers : Man made *i.e.*, synthesized in laboratory factory. *E.g.*, polythene, PVC.

➢ On the basis of structure, they are classified as **linear, branched and cross linked polymers.**

➢ On the basis of polymerization, they are classified as **addition and condensation polymers.**

➢ On the basis of types of monomers , they are classified as **homopolymers and copolymers.**

➢ On the basis of molecular forces , they are classified as
   (i)   Elastomers : Polymer chains are held by van der Waals forces.
   (ii)   Fibres : Polymers chains are held by strong forces like H-bonding and dipole interactions.
   (iii) Thermoplastics : Intermolecular forces are intermediate between elastomers and fibres.
   (iv)   Thermosetting polymers : Cross linked structure.

➢ The polymers that can be broken down rapidly by enzyme catalyzed reaction are called biodegradable polymers.

➢ **Differences between**

■ **Chain Growth and Step Growth Polymerization :**

S. No.	Chain Growth Polymerization	Step Growth Polymerization
(i)	Concentration of monomers disappears early in the reaction.	Concentration of monomers decreases steadily throughout the reaction.
(ii)	Reaction is fast and polymer is formed at once.	The polymer is formed in gradual steps.
(iii)	There is very little change in the molecular mass throughout the reaction.	The molecular mass of polymer increases throughout the reaction.
(iv)	Increase in reaction time increases the yield but molecular weight is affected a little.	Long reaction time is required to get high molecular mass polymer.
(v)	Only one repeating unit is added at a time.	Any two species present can react.
(vi)	Reaction mixture contains only monomer, polymer and growing chain.	All molecular species are present at any stage.

■ **Addition and Condensation polymerization :**

S. No.	Addition Polymerization	Condensation Polymerization
(i)	They are formed by adding monomers to a growing polymer chain without loss of any molecule.	Monomers combine together with the loss of small molecules like H_2O, NH_3, CO_2, CH_3OH, etc.
(ii)	They are formed from unsaturated compounds.	Monomers have di or poly functional groups.
(iii)	It involves chain reaction. *E.g.*, polyethene, polypropene, PVC, teflon, etc.	It does not involve chain reaction. *e.g.*, nylon-66, nylon-6, terylene, glyptal, bakelite, etc.

■ **Natural, Synthetic and Condensation Polymers :**

Natural Polymers

S. No.	Polymer	Monomer	Class	Uses
(i)	Cellulose	β-Glucose	Biopolymer	Occurs in cotton, cell wall

(ii)	Starch	α-Glucose	Biopolymer	Food material storage in plants
(iii)	Proteins	Amino acids	Biopolymer	Essential for growth
(iv)	Nucleic acid	Nucleotides	Biopolymer	Essential for life perpetuation
(v)	Rayon (Artificial silk)	β-Glucose	Processed cellulose	Fabrics, surgical dressings
(vi)	Natural rubber	*cis*-Isoprene (cis-2-methyl-1, 3-butadiene)	Natural polymer Elastomer	Used for tyres after vulcanisation
(vii)	Gutta percha	*trans*-Isoprene	Natural Polymer	Rubber like material

Synthetic Polymers

S. No.	Polymer	Monomer	Class	Uses
(i)	Polyethene	Ethene ($CH_2 = CH_2$)	Addition and Chain growth	Electrical insulator, packing materials, films, bottles, etc.
(ii)	Polypropene	Propene ($CH_3—CH=CH_2$)	Addition and Chain growth	Storage battery tanks
(iii)	Polystyrene	Styrene ($C_6H_5–CH=CH_2$)	Addition and Chain growth	In combs, plastic handles, toys
(iv)	Polyvinyl chloride (PVC)	$CH_2 = CHCl$ Vinyl chloride	Addition and Chain growth	Pipes, raincoats, vinyl floorings
(v)	Polytetrafluoroethene PTFE (Teflon)	$CF_2 = CF_2$ Tetrafluoroethene	Addition and Chain growth	Non-stick kitchenwares, electrical insulator
(vi)	Polymonochlorotrifluoro-ethene	$F—\overset{\overset{\displaystyle Cl}{\vert}}{C} = CF_2$ Monochlorotrifluoroethene	Addition and Chain growth	Non-stick kitchenwares
(vii)	Polymethyl methacrylate (PMMA) (Perspex, Lucite or Acrylite)	$CH_3—\overset{\overset{\displaystyle \|}{}}{\underset{\underset{\displaystyle CH_2}{}}{C}}—COOCH_3$ Methyl methacrylate	Addition and Chain growth	Substitute of glass and decorative material
(viii)	Polyethyl acrylate	$CH_2 = CH—COOC_2H_5$ Ethyl-2-propenoate	Addition and Chain growth	Lacquers, films, house piping
(ix)	Polyvinyl acetate	$CH_2 = CH—O—COCH_3$	Addition and Chain growth	Floor coverings and fibres
(x)	Vinylite	Vinyl chloride and Vinyl acetate	Addition and Chain growth	Vinyl floorings
(xi)	Polyacrylonitrile or Acrylane (orlon)	$CH_2 = CH—C \equiv N$ Vinyl cyanide (Acrylonitrile)	Addition and Chain growth	It closely resembles wool
(xii)	Buna-S	1, 3-Butadiene and styrene	Addition and Chain growth	Automobile tyres
(xiii)	Buna-N	1, 3-Butadiene and Acrylonitrile	Addition and Chain growth	Used for storing oil and solvents

(xiv)	Neoprene	2-Chloro-1, 3-butadiene (Chloroprene)	Addition and Chain growth	Insulation, conveyor belt
(xv)	Thiokol	1, 2-Dichloroethene and sodium polysulphide	Condensation polymer	Rocket propellent
(xvi)	Poly-β-hydroxybutyrate-co-β-hydroxyvalerate (PHBV)	$\underset{\overset{\|}{OH}}{CH_3—CH—CH_2—COOH}$ $\underset{\overset{\|}{OH}}{CH_3—CH_2—CH—CH_2—COOH}$	Condensation Polymer	As packaging, orthopaedic and in controlled drug release.
(xvii)	Nylon-2-Nylon-6	Glycine (H_2NCH_2COOH) and aminocaproic acid $H_2N(CH_2)_5COOH$	Condensation polymer	Biodegradable polymer

Condensation Polymers

S. No.	Polymer	Monomer	Class	Uses
(i)	Polyesters (Terylene) Dacron	Terephthalic acid and ethylene glycol	Condensation and step growth	Ropes, safety belts, tyre cards.
(ii)	Glyptal (Alkyd resin)	Phthalic acid and ethylene glycol	Condensation and step growth	Binding material, paints and Lacquers
(iii)	Nylon-6	Caprolactam (cyclic amide)	Condensation and step growth	Fibre, plastic, tyre-cords and ropes
(iv)	Nylon-6, 6	Adipic acid and hexa-methylenediamine	Condensation and step growth	Stockings, shirts, ropes
(v)	Bakelite	Phenol and formaldehyde	Condensation and step growth	Electric switches and switch-boards
(vi)	Melamine formaldehyde resin	Melamine and HCHO	Condensation and step growth	Crockery
(vii)	Urea formaldehyde resin	Urea and HCHO	Condensation and step growth	Crockery and laminated sheets

UNIT-XVI   CHEMISTRY IN EVERYDAY LIFE

- ➢ **Drugs** are the chemical substances of low molecular mass, interacting with macromolecular targets and produce a biological response.
- ➢ **Medicines** are drugs which produce a therapeutic and useful response.
- ➢ **Classification of drugs**
  - **(i) On the basis of pharmacological effect**—For a particular type of problem. *E.g.*, analgesic (pain relieving).
  - **(ii) On the basis of drug action**—*E.g.*, antihistamine (inhibit the action of a compound) and histamine (causes inflammation).
  - **(iii) On the basis of chemical action**—Drugs having similar structure. *E.g.*, sulpha drugs.
  - **(iv) On the basis of molecular targets**—Drugs interacting with biomolecules as lipids, proteins.
- ➢ **Antagonists** are drugs that bind to the receptor site and inhibit its natural function.
- ➢ **Agonists** are drugs that mimic the natural messenger by switching on the receptor.
- ➢ **Analgesics** are drugs that give relief from pain.
  - **(i) Non-narcotic :** *E.g.*, Aspirin, paracetamol.
  - **(ii) Narcotic :** Drugs which produce sleep and unconsciousness. *E.g.*, Opium, morphine.

- ➤ **Antiseptics** are chemicals that prevent microbial growth. *E.g.*, Dettol.
- ➤ **Disinfectant** are chemicals which kill micro-organisms. *E.g.*, 0.2 % solution of phenol.
- ➤ **Tranquilizers** are chemical substances used for treatment of stress, mild or even severe mental diseases. *E.g.*, Luminal, seconal.
- ➤ **Antimicrobials :** To cure diseases caused by variety of microbes such as bacteria, fungi, virus, etc.
- ➤ **Antibiotics :** In low concentration, either kill or inhibit are growth of micro-organisms. *E.g.*, Penicillin, ampicillin.
- ➤ **Sulpha drugs :** Derivatives of sulphanilamide with antibacterial powers. *E.g.*, sulphadiazine, sulpha-thiazole.
- ➤ **Antifertility drugs :** To control pregnancy in woman. *E.g.*, norethindrone, ethinylestradiol.
- ➤ **Antihistamines :** To treat allergy. *E.g.*, chlorpheniramine.
- ➤ **Antioxidants :** Retard the action of oxygen on the food and help in preservation. *E.g.*, butylated hydroxy toluene (BHT).
- ➤ **Antacid :** Removes excess of acid and raise the pH of stomach to appropriate level. *E.g.*, magnesium hydroxide, sodium bicarbonate.
- ➤ **Chemicals in food :**
- ➤ **Artificial Sweeteners :** *E.g.*, saccharin, aspartame, sucralose.
- ➤ **Food preservatives :** *E.g.*, sodium benzoate, sodium metabisulphite.
- ➤ **Soaps** are sodium or potassium salts of long chain fatty acids.
- ➤ **Synthetic detergent :**
    - **(i) Anionic :** Sodium salts of sulphonated long chain alcohols. *E.g.*, sodium dodecylbenzene sulphonate.
    - **(ii) Cationic :** Quaternary ammonium salts of amines with acetates, chlorides or bromides. *E.g.*, cetyltrimethyl ammonium bromide.
    - **(iii) Non-ionic :** Do not contain any ion in their constitution. *E.g.*, liquid dish wash detergents.
- ➤ **Biodegradable detergents -** can be decomposed by micro-organisms.
    Non-biodegradable detergents - cannot be decomposed.
- ➤ **Saponification :** Hydrolysis of oils and fats with aqueous alkali.

❑❑❑