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MIND MAP-1

Frenkel defect:
- Ions (cations) missing from their lattice site occupy interstitial sites
- No effect on density.
- There is a large difference in the size of the ions (cation or anions).

Interstitial defect:
- When some of the atoms occupy interstitial sites.
- It increases the density of a substance.

Vacancy defect:
- When some of the lattice sites are vacant.
- Decreases the density of the substances
- It develops on heating.

Schottky defect:
- Cations and anions are missing equally
- Density decreases
- It is shown by ionic substances in which ions (cations or anion) having almost similar sizes.

Due to presence of extra cations at interstitial sites e.g.,

$$ZnO \xrightarrow{\Delta} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Zn^{2+} ions and the electrons occupy interstitial sites.

Due to anionic vacancy (F-centres) When holes created by anions are occupied by electrons, these sites are called F-centres and are responsible for colour in the crystal. e.g., NaCl

Metal deficiency defects: It is due to missing of a cation from its lattice site and the presence of a cation having higher charge in the adjacent lattice site e.g., FeO

Non-ionic solids

Ionic solids

Metal excess defects

Stoichiometric defects: This defects do not disturb the stoichiometry of the solid
- They are also called intrinsic defects
- It increases with the increase in temperature (thermodynamic defects)

Impurity defects: Foreign atoms are present at the lattice site in place of host atoms or at vacant interstitial sites.

Non-Stoichiometric defects: The ratio of (+)ve and (–)ve ions present in the compound differs from that required by ideal formula.

Line defects: Deviation in entire rows of lattice point.

Point defects: Deviation around a point or an atom in a solid

Unit cell: Smallest repeating pattern

Type of solids

Imperfection in solids

Properties of solids

Structure of solids

SOLIDS

Close packed structure

Crystalline solids :
- Definite characteristic
- geometrical shape
- Long range order
- Anisotropic in nature e.g., NaCl, KNO_3, LiF etc.

Amorphous solids :
- Irregular in shape
- Short range order
- Isotropic in nature e.g. plastic, glass etc.

Type of solid	Intermolecular forces	Properties
Ionic	Ion-Ion forces	Brittle, hard, high melting point, insulator in solid but conductors in both fused and aqueous solution. e.g., NaCl.
Molecular	Dispersion forces/dipole dipole/H-bonds	Soft, low melting point, Insulators e.g H_2O, Br_2, CO_2, CH_4
Covalent	Covalent bonds	Hard, very high melting point e.g C-diamond, SiO_2
Metallic	Metallic bonds	Variable hardness and melting point, malleable and ductile, conducting e.g Na, Zn, Cu, Fe

Doping: The conductivity of an intrinsic semiconductor increases by adding an impurity which is electron rich or electron deficient as compared to Si or Ge. This process is called doping.

Radius ratio rules:
- The coordination number is a function of the sizes of the ions.
- Ionic radius ratios of cation and anion is very important in the determination of the crystal structures of an ionic substances.

Radius ratio = Radius of cation (r_+)/Radius of anion ($r\_$)

Radius ration	C.N.	shape	Example
0.155–0.255	3	Planar triangle	B_2O_3
0.255–0.414	4	Tetrahedral	ZnS
0.414–0.732	6	Octahedral	NaCl
0.732–1.0	8	Body-centred cubic	CsCl

Unit cell dimensions:

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

Z = no. of atoms per unit cell
d = density of solid
a = edge length
M = molar mass
N_A = Avogadro's number

Body-centred: It contains one constituent particle at its body centre, besides the ones that are at its corners.

Face centred: One constituent particles is present at the centre of each face.

End-centred: One constituent particles is present at the centre of any two opposite faces.

Primitive unit cell: Constituent particles (atom, molecules or ions) are present on the corner positions only

Centred unit cell: Constituent particles are present on the corner position alongwith some other positions.

Number of atoms per unit cell:

Primitive cubic $\Rightarrow 8 \times \frac{1}{8} = 1$

Body-centred cubic

$\Rightarrow 8 \times \frac{1}{8} + 1 = 2$

Face-centred cubic

$\Rightarrow 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

Crystal system e.g.	Axial distances or edge lengths	Axial angles	Examples
Cubic	a = b = c	$\alpha = \beta = \gamma = 90°$	Zinc blend, KCl, NaCl, Cu
Tetragonal	a = b ≠ c	$\alpha = \beta = \gamma = 90°$	Sn (white tin), TiO_2, $CaSO_4$, SnO_2
Orthorhombic	a ≠ b ≠ c	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $CaSO_4$
Monoclinic	a ≠ b ≠ c	$\alpha = \gamma = 90°; \beta \neq 90°$	Monoclinic sulphur, $PbCrO_4$, $Na_2SO_4.10H_2O$
Hexagonal	a = b ≠ c	$\alpha = \gamma = 90°; \beta = 120°$	Graphite, CdS, ZnO
Rhombohedral or Trigonal	a = b = c	$\alpha = \gamma = \beta \neq 90°$	$CaCO_3$ (calcite), HgS (cinnabar)
Triclinic	a ≠ b ≠ c	$\alpha \neq \gamma \neq \beta \neq 90°$	$CuSO_4.5H_2O$, H_3BO_3, $K_2Cr_2O_7$

Close packing in one dimension : Lattice point arranged in a row C.N. = 2

Close packing in two dimensions :
(a) Square close packing : (A–A–A) ....type C.N. = 4
(b) Hexagonal close packing: (A – B – A – B type) C.N. = 6

Close packing in three dimensions :
(a) Primitive cubic unit cell: AAA ... type arrangement, CN = 6, P.F. = 52.4%
(b) *hcp* : ABAB ... type pattern, C.N. = 12 PF = 74 %
(c) *ccp* or *fcc* : ABCABC ... type pattern, CN = 12 PF = 74%

Magnetic Properties :
- Paramagnetic substances are weakly attracted by a magnetic field. e.g., O_2, Cu^{2+}, Cr^{3+}.
- Diamagnetic substances are weakly repelled by a magnetic field. e.g., H_2O, C_6H_6 and NaCl.
- Ferromagnetic substances are those which show permanent magnetism even in the absence of magnetic field e.g., Fe, Ni, Co, CrO_2 etc.
- Anti-ferromagnetic substances are those which are expected to possess paramagnetism or ferromagnetism but actually have zero net magnetic magnetic moment due to equal number of domains in opposite directions, e.g., MnO.
- Ferrimagnetic substances are those expected to have large magnetism but actually have small net magnetic moment

↑ ↑ ↑ ↑ ↑ ↑ Ferromagnetic ↑ ↓ ↑ ↓ ↑ ↓ Antiferromagnetic ↑ ↑ ↓ ↑ ↑ ↓ Ferrimagnetic

Electrical Properties
- Conductors: Valence band is partially filled or it overlaps with a higher energy unoccupied conduction band
- Semiconductors: Small energy gap between valence and conduction band
- Insulators: Large energy gap between valence and conduction band

p-type semiconductor (by doping electron deficient impurities)
n-type semiconductor (by doping electron rich impurities)

MIND MAP-2

SOLUTIONS

- **Relative Lowering of v.p :** In terms of molecular weight of solute

$$= \frac{P^o - P_s}{P^o} = \chi_A = \frac{n_A}{n_A + n_B} \qquad M_A = \frac{W_A \times M_B}{W_B \left[\frac{P^o - P_s}{P^o}\right]}$$

Where, P^o & P_s = vapour pressure of pure solvent and solution
n_A, n_B = moles of solute & solvent
W_A, W_B & M_A, M_B = W_A, W_B are the masses and M_A, M_B are the molar masses of the solute and solvent respectively.

- **Elevation in b.p.** $\Delta T_b = K_b m$

K_b = boiling point elevation constant or molal elevation constant **(ebullioscopic constant)** having unit K kg mol^{-1}

m = molality $[m = \frac{W_A}{M_A \times W_B} \times 1000]$; $\Delta T_b = \frac{K_b W_A}{M_A \times W_B} \times 1000$

$$\Delta T_b = T_s - T_b$$

T_s & T_b are the boiling point of solution and pure solvent.

- **Depression in f.p.** $\Delta T_f = K_f m$

K_f = freezing point depression constant or molal depression constant or **cryorcopic constant.**

$$\Delta T_f = \frac{K_f W_A}{M_A \times W_A} \times 1000 \quad ; \quad \Delta T_f = T_f - T_s$$

T_s & T_f are the freezing point of solution and pure solvent.
The values of K_f and K_b, which depend upon nature of the solvent can be determined from the following relations.

$$K_f = \frac{M_B R T_f^2}{1000\, \Delta_{fus} H} \quad ; \quad K_b = \frac{M_B R T_b^2}{1000\, \Delta_{vap} H}$$

Here, R & M_B stand for the gas constant and molar mass of solvent in g·mol^{-1}, T_f & T_b = freezing point and the boiling point. $\Delta_{fus}H$ & $\Delta_{vap}H$ = enthalpies for the fusion and vaporisation of the solvent, respectively.

Colligative properties :
These properties of a solution depend on the total concentration of all solute particles, regardless of their ionic or molecular nature, charge, or size.

∝ No. of particles
∝ No. of molecules (In the solution of non-electrolytes)
∝ No. of ions (In the solution of electrolytes)

Osmotic Pressure (π) :

- Osmotic pressure is the hydrostatic pressu produced when a solution is separated from t solvent by a semipermeable membrane.
- Osmotic pressure may be defined as the exce pressure which must be applied to a solution order to prevent flow of solvent into the soluti through the semipermeable membrane.

Osmotic pressure $(\pi) = \frac{n}{V} RT = CRT$

For dilute solutions, osmotic pressure is found t follow the equation $(\pi) = \frac{n}{V} RT = CRT$

(Gay-Lussac-van't Hoff law)

when w g of solute are dissolved in V litre of solutions and M is the molar mass of the solute, then $(\pi) = \frac{wRT}{MV} \left[\because n = \frac{w}{M}\right]$

van't Hoff Factor (*i*)
Certain solutes which undergo dissociation or association in solutions are found to show abnormal molecular mass. Thus, in order to know about the extent of association or dissociation of solutes in solution van't Hoff in 1886 introduced a factor (*i*). It is defined as the ratio of the normal mass to the observed molecular mass of the solute i.e.

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} \quad ; \quad \text{since, molecular mass} \propto \frac{1}{\text{Colligative property}}$$

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}} \quad \therefore\ i = \frac{\text{Total number of particles after association/dissociation}}{\text{No. of particles before association/dissociation}}$$

The value of *i* depends upon the state of solute in the solution. Following cases may become possible.

- when $i = 1$, then the solute remains unaffected (i.e., normal) in solution.
- when $i > 1$, then the solute undergoes dissociation in solution.
- when, $i < 1$, then the solute undergoes association in solution.
  Modified equation for colligative properties.

$$\frac{P^\circ - P_S}{P^\circ} = i\chi_A = \frac{n_A}{n_A + n_B}; \Delta T_b = iK_b m; \Delta T_f = iK_f m; \quad \pi = i\frac{n}{V}RT$$

Solubility : Maximum amount of a substance that can be dissolved in a specified amount of solvent at a specified temperature it depends upon
• Nature of solute • Nature of solvent • Temperature • Pressure

Solubility of a solid in liquid	Solubility of a gas in liquid
• Effect of nature of solute and solvent ⇒ like dissolves like • Effect of temp ⇒ Exothermic process - increase with rise in temp. • Endothermic process - decrease with rise in temp. . Effect of pressure ⇒ No effect	• Effect of temp. ⇒ Follow same order as in case of solid. • Effect of pressure ⇒ Henry's law states that the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution" $p = K_H x$ K_H ⇒ Henry's law constant solubility $\propto \frac{1}{K_H}$

Raoult's Law
$(P_s = P_A^o + (P_B^o - P_A^o)\, x_B$
$P_s = P_A^o + (P_B{}^o + P_A{}^o) x_B$ where P_s = Total pressure, P_A^o & P_B^o = vapour pressure in pure state of two constituents A and B in solution

Types of solution

Classification based on physical state:

- Gas in gas (Air)
- Gas in liquid (Soda water)
- Gas in solid (Hydrogen in Pd)
- Liquid in gas (Fog)
- Liquid in liquid (Alcohol in water)
- Liquid in solid (Amalgams)
- Solid in gas (Smog)
- Solid in liquid (Sugar in water)
- Solid in solid (Alloys)

Classification based on concentration

- Dilute solutions
- Concentrated solutions
- Saturated solutions
- Supersaturated solutions

Concentration of solutions

- Mass percentage (w/W) = $\frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 100$
- Molarity (M) = $\frac{\text{No. of moles of solute}}{\text{Volume of solution (L)}}$
- Molality (m) = $\frac{\text{No. of moles of solute}}{\text{Weight of the solvent in kg}}$
- Normality (N) = $\frac{\text{No. of grams equivalent of solute}}{\text{Volume of solution (L)}}$
- Mole fraction (x) = $\frac{\text{No. of moles of solute}}{\text{Total moles in solution}}$
- Volume percentage (v/V) = $\frac{\text{Volume of solute}}{\text{Total volume of solution}} \times 100$
- ppm = $\frac{\text{No. of parts of solute}}{\text{Total no. of parts of all components of solution}} \times 10^6$
- Mass by volume percentage (w/V) = $\frac{\text{mass of solute}}{\text{Total volume of solution (mL)}} \times 100$
- **Mass %, ppm, mole fraction and molality are independent of**

Ideal solution	Non-ideal solutions	
	Positive deviation from Raoult's law	Negative deviation from Raoult's law
(i) Obey Raoult's law at every range of concentration. (ii) $\Delta V_{mix} = 0$; total volume of solution is equal to the sum of volumes of the components. (iii) $\Delta H_{mix} = 0$; neither heat is evolved nor absorbed during dissolution. (iv) A – A, A – B, B – B molecular interactions present in the two liquids should be same, i.e., A and B are identical in shape, size and character. (v) $P_{Total} = p_A + p_B = p_A^o\, x_A + p_B^o\, x_B$ i.e., $p_A = \overset{\circ}{p}_A x_A$; $p_B = \overset{\circ}{p}_B \times_B$ (vi) Escaping tendency of A and B is same in pure liquids as well as in the solution **Examples** Dilute solutions Ethyl bromide + Ethyl iodide n-Butyl chloride + n-Butyl bromide	(i) Do not obey Raoult's law. (ii) $\Delta V_{mix} > 0$. Volume is increased after dissolution. (iii) $\Delta H_{mix} > 0$. Endothermic dissolution; heat is absorbed. (iv) A–B force of attraction are less than A – A and B – B attractive forces. A and B have different shape, size (v) $p_A > \overset{\circ}{p}_A x_A$; $p_B > \overset{\circ}{p}_B x_B$ $\therefore P_{Total} > \overset{\circ}{p}_A x_A + \overset{\circ}{p}_B x_B$ (vi) Escaping tendency of A and B is very high (showing higher vapour pressure than expected) **Examples** Acetone + Ethanol $CCl_4 + CHCl_3$	(i) Do not obey Raoult's law. (ii) $\Delta V_{mix} < 0$. Volume is decreased during dissolution. (iii) $\Delta H_{mix} < 0$. Exothermic dissolution; heat is evolved. (iv) A – B force of attraction are greater than A – A and B – B attractive forces. A and B also have different shape, size and character. (v) $p_A < \overset{\circ}{p}_A x_A$; $p_B < \overset{\circ}{p}_B x_B$ $\therefore P_{Total} < \overset{\circ}{p}_A x_A + \overset{\circ}{p}_B x_B$ (iv) Due to lower escaping tendency it shows lower vapour pressure than expected **Examples** Acetone + Aniline Chloroform + Diethyl ether

MIND MAP-3

ELECTROCHEMISTRY

Corrosion

Batteries

Faraday's Laws of Electrolysis

In corrosion, a metal is oxidised by loss of electrons to oxygen and forms metal oxide. Corrosion of iron (which is commonly known as rusting) occurs in presence of water and oxygen (air).

Rusting of Iron : According to electrochemical theory, rusting can be represented as :

Oxidation at Anode: $Fe \rightarrow + Fe^{2+} + 2e^{-} ; E^{\circ}_{oxi} = -0.44\ V$

Reduction at Cathode : $CO_2 + H_2O \rightarrow H^{+} + HCO_3^{-}$

$$2H^{+}(aq) + 2e^{-} \rightarrow 2H$$

$$2H + \frac{1}{2}O_2 \rightarrow H_2O$$

$$2H^{+} + \frac{1}{2}O_2 + 2e^{-} \rightarrow H_2O ; E^{\circ}_{red} = 1.23V$$

Overall reaction of corrosion cell :

$$Fe + 2H^{+} + \frac{1}{2}O_2 \rightarrow Fe^{2+} + H_2O ; E^{\circ}_{cell} = 1.67\ V$$

The ferrous ions so formed move through water and come at the surface of iron object where these are further oxidised to ferric state by atmospheric oxygen and constitute rust which is hydrated iron (III) oxide.

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H_2O \rightarrow Fe_2O_3 + 4H^{+}$$

$$Fe_2O_3 + xH_2O \rightarrow \underset{\text{Rust}}{Fe_2O_3.xH_2O}$$

Prevention of Corrosion

- The metal surface is coated with paint which keeps it out of contact with air, moisture etc.
- By applying film of oil and grease on the surface of the iron tools and machinery
- The iron surface is coated with non-corroding

Faraday's First Law: When an electric current is passed through an electrolyte, the amount of substance deposited or liberated at an electrode is proportional to the quantity of electric charge passed through the electrolyte.

If W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation. $W \propto Q$

A coulomb is the quantity of charge when a current of one ampere is passed for one second.

$$Q = \text{current in amperes} \times \text{time in seconds} = I \times t$$

$$W \propto I \times t$$

$$W = Z \times I \times t$$

where Z is a constant, known as electro-chemical equivalent, and is characteristic of the substance deposited.

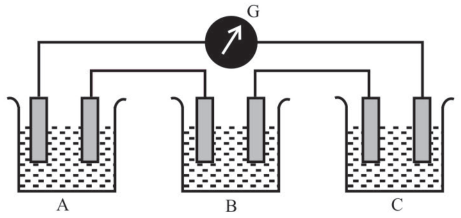
Electro-chemical equivalent (Z) =

$$\frac{\text{equivalent wt. of element}}{96500}$$

Faraday's Second Law: It states that when same quantity of electricity is passed through different electrolytes, then the quantity of deposit is directly proportional to respective equivalent weight. (Equivalent wt. of electrolytes).

$$W \propto E$$

$$\frac{W_A}{E_A} = \frac{W_B}{E_B} = \frac{W_C}{E_C}$$



Regardless whether a cell is a voltaic or an electrolytic-cell,

— The anode is the electrode at which oxidation occurs

— The cathode is the electrode at which reduction occurs

	Voltaic cell	**Electrolytic-cell**
Anode	Oxidation, Negative (–) terminal	Oxidation positive (+) terminal
Cathode	Reduction Positive (+) terminal	Reduction negative (–) terminal

- Electrode potential

$E_{cell} = E^{o}_{right} - E^{o}_{left}$

For SHE, $E^{o}_{cell} = 0$

- Nernst equation :

For reaction, $M^{n+} + ne^{-} \rightarrow M(s)$

$$E = E^{o} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}]}$$

- **For reaction :**

$aA + bB \rightarrow cC + dD$

$$Ec_{cell} = E^{o}_{cell} - \frac{2.303RT}{nF}\log\frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

At equilibrium $E_{cell} = 0$

$$E^{o}_{cell} = \frac{2.303RT}{nF}\log K_c$$

$\Delta_r G = -nFE_{cell}$ or $\Delta_r G = -nFE^{o}_{cell}$

- **Electrochemical series:** Arrangement of elements in order of increasing value of E^{o} red. Reducing nature decreases form top

Name of cell/Battery	**Anode (–)**	**Cathode (+)**	**Electrolyte**	**Reactions at electrodes**	E_{cell}
• Dry cell (primary cell)	Zn container	Graphite rod	Powdered MnO_2+C +Paste of NH_4Cl+ $ZnCl_2$	**Anode:** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ **Cathode:** NH_3 forms complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$ $MnO_2 + 2NH_4^{+} + e^{-} \rightarrow MnO(OH) + NH_3$. NH_3 Forms Complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$	1.25 to 1.5 V
• Mercury cell (primary cell)	Zn-Hg amalgam	Paste of HgO and C	Paste of KOH + ZnO	**Anode:** $Zn(Hg) + 2OH^{-} \rightarrow ZnO + H_2O + 2e^{-}$ **Cathode:** $HgO + H_2O + 2e^{-} \rightarrow Hg(1) + 2\bar{O}H$	1.35 V
• Lead storage Battery (secondary cell)	Pb	Pb + PbO_2	38% by mass H_2SO_4 (d=1.30 g cm^{-3})	**Anode:** $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^{-}$ **Cathode :** $PbO_2(s) + SO_4^{2-}(aq) + 4H^{+}(aq) + 2e^{-} \rightarrow PbSO_4(s) + 2H_2O(1)$ On applying a potential slightly greater than the potential of battery, battery can be recharged.	12 V consists of 6 cell each producing 2 V
• Ni-Cd Secondary cell Or Ni-Cd cell (Rechargeable	Cd	NiO_2	Moist KOH	**Anode:** $Cd(s) + 2\bar{O}H(aq) \rightarrow Cd(OH)_2(s) + 2e^{-}$ **Cathode :** $NiO_2(s) + 2H_2O + 2\bar{e} \rightarrow Ni(OH)_2(s) + 2\bar{O}H(aq)$	1.4 V
• Fuel cell (H_2–O_2)	Porous carbon containing catalyst (finely divided Pt and Pd)	Porous carbon containing catalyst (finely divided Pt and Pd)	Concentrated NaOH solution	**Anode:** $2H_2(g) + 4OH^{-}(aq)$ $4H_2O(1) + 4e^{-}$ Cathode : $O_2(g) + 2H_2O(1) + 4e^{-} \rightarrow 4OH^{-}(aq)$	0.09 V

Conductance of Electrolytic Solutions:

- Conductance (G) = $\frac{1}{\text{Resistance}}$

  Unit : ohm^{-1} or Siemens
- Specific conductivity (κ) = $G\frac{l}{a}\left(\frac{l}{a} = \text{cell constant}\right)$

  Unit = $ohm^{-1}\ cm^{-1}$ or $S\ cm^{-1}$
- Molar conductance (Λ_m) = $\frac{1000 \times \kappa}{M}$

  Unit = $S\ cm^{2}\ mol^{-1}$
- Equivalent conductance (Λ_{eq}) = $\frac{1000 \times \kappa}{N}$

  Unit = $cm^{2}\ ohm^{-1}\ g\text{-}eq^{-1}$

  Conductance (G), molar conductance (Λ_m) and equivalent conductance (Λ_{eq}) increase with dilution where as specific conductance (κ) decrease with dilution

  Effect of concentration on Λ_m:
- **For strong electrolytes,** Λ_m increases slowly with dilution and can be represented by the equation : $\Lambda_m = \Lambda^{o}_m - AC^{1/2}$

  (Debye–Huckel Onsager equation)

Plot of Λ_m against $C^{1/2}$ is a straight line with intercept equal to $\Lambda_m{}^{o}$ and slope equal to '$-A$.'

Thus, Λ_m decreases linearly with $\sqrt{C}$, when C = 0, $\Lambda_m = \Lambda^{o}_m$ and Λ^{o}_m can be determined experimentally.

- **For weak electrolytes,** Λ_m increases as C decreases but does not reach a constant value even at infinite dilution. Hence, there Λ^{o}_m cannot be determined experimentally.
- **Kohlrausch's Law :**

$$\Lambda^{\infty}_{eq} = \lambda^{o}_{+} + \lambda^{o}_{-}$$

Where $= \lambda^{o}_{+}$ is the limiting equivalent conductivity of the cation and λ^{o}_{-} is the limiting equivalent conductivity of the anion. These contributions are called limiting equivalent conductances at infinite dilution. The above equation is, however, correct only for binary electrolyte like NaCl, $MgSO_4$ etc.

Applications of Kohlrausch's Law:

- **Calculation of Molar Conductivity at Infinite Dilution for Weak Electrolytes :**

In order to calculate Λ^{∞}_m or Λ^{∞}_m of a weak electrolyte say CH_3COOH, we determine permentally Λ_{mo} values of the strong electrol

$\Lambda^{\infty}_{m(CH_3COOH)} = \lambda^{\circ}_{CH_3COO^-} + \lambda^{\circ}_{H^+}$ ....(i)

for strong electrolytes :

$\Lambda^{\circ}_{m(CH_3COOK)} = \lambda^{\circ}_{CH_3COO^-} + \lambda^{\circ}_{K^+}$ ......(ii)

$\Lambda^{\circ}_{m(HCl)} = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{Cl^-}$ .....(iii)

$\Lambda^{\circ}_{m(KCl)} = \lambda^{\circ}_{K^+} + \lambda^{\circ}_{Cl^-}$ .....(iv)

∴ eqn (ii) + eqn. (iii) – eqn (iv) = eqn (i)

i.e., $\Lambda^{\infty}_{m(CH_3COOK)} + \Lambda_m{}^{\infty}_{(HCl)} - \Lambda_m{}^{\infty}_{(KCl)} = \Lambda^{\infty}_{m(CH_3COOH)}$

- **Calculation of the Degree of Dissociation :**

Λ^{c}_m is the molar conductivity of a solution at any concentration C and Λ°_m the molar conductivity at infinite dilution (i.e., zero concentration), we will have $\alpha = \frac{\text{no.of dissociat edions}}{\text{no.of totalions present}}$; Degree of dissociation $(\alpha) = \frac{\Lambda^{c}_m}{\Lambda^{\circ}_m}$

- **Calculation of Dissociation Constant of a Weak Electrolyte :**

$$K_c = \frac{C\alpha^2}{1-\alpha}$$

MIND MAP-4

CHEMICAL KINETICS

Rate of reaction a chemical

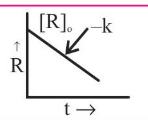
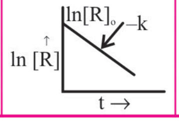
Instantaneous rate : The rate of reaction at any particular instant during the course of reaction is called as instantaneous rate of reaction. Mathematically, instantaneous rate = (Average rate)$_{\Delta t \to 0}$

Average rate (denoted by r_{av})

- $r_{av} = -\frac{\Delta R}{\Delta t} = -\frac{[R_2]-[R_1]}{(t_2-t_1)}$
- Average rate depends upon the change in conc. of reactants or products and the time taken for the change to occur.

Integrated Rate Equations

Integrated rate law and linear plots for reactions of different orders.

Reaction type	Order	Differential rate law	Integrated rate law	Linear plots	Half life
R→P	0	$d[R]/dt = -k$	$kt = [R]_o - [R]$		$[R]_o/2k$
R→P	1	$\frac{d[R]}{dt} = -k[R]$	$kt = \ln \frac{\{[R]_o}{[R]\}}$		0.693/k

- Rate constant for zero order reaction k $= \frac{[R]_o - [R]}{t}$
- Rate constant for 1st order reaction k $= \frac{2.303}{t}\log\frac{[R]_o}{[R]}$
- Rate constant for 1st order reaction k $= \frac{2.303}{t}\log\frac{P_i}{(2P_i - P_t)}$ (for gas phase reaction)

(where P_i = initial pressure,

Collision Theory of chemical reactions :

The important points of this theory are :

- If two molecules are to react together they must collide together.
- **Threshold Energy (Energy Barrier):** The minimum energy which the molecules should possess so that their mutual collision result in chemical reaction is called threshold energy.
- **Effective Collisions:** Only those collisions which result in the formation of product are called effective collisions.
- **Collision Frequency:** The number of collisions that take place per second per unit volume of the reaction mixture is called collision frequency.

For a bimolecular elementary reaction $A + B \to$ Products

rate of reaction can be expressed as Rate $= Z_{AB}e^{-Ea/RT}$

where Z_{AB} represents the collision frequency of reactants, A and B and $e^{-Ea/RT}$ represents the fraction of molecules with energies equal to or greater than E_a.

To account for effective collisions, another factor P, called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e., Rate $= PZ_{AB}e^{-Ea/RT}$

Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

Temperature Dependence of Rate of Reaction

For a chemical reaction with rise in temp. by 10°C, the rate constant is nearly doubled.

Arrhenius Equation :

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

$\ln k = \ln A - \frac{E_a}{RT}$

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

At two different temperatures

$\log = \frac{k_2}{k_1} = \frac{E_a}{2.303}\left(\left(\frac{T_2 - T_1}{T_2T_1}\right)\right)$

where k_1, k_2 are the values of rate constant at temp, T_1 and T_2 respectively.

The plot of logk vs 1/T gives a straight line with slope $= \frac{-E_a}{2.303R}$ and intercept = logA

Rate expression and rate constant :

The mathematical expression, which practically relates the rate of a chemical reaction and concentration of reactants is called rate law equation e.g. for a hypothetical reaction.

$aA + bB \rightleftharpoons cC + dD$ (Where a, b, c and d are the stoichiometric coefficients)

Rate $\propto [A]^a[B]^b$.

Rate $\propto [A]^x[B]^y$ .... (i)

Rate $= k[A]^x[B]^y$ .... (ii)

$\frac{-d[R]}{dt} = k[A]^x[B]^y$ .... (iii)

(Where x and y may or may not be equal to the a and b)

Molecularity of reaction :

"The minimum number of molecules, atoms or ions of reactants required for an elementary reaction to occur which is indicated by the sum of the stoichiometric coefficients of the reactant(s) in the chemical equation, is known as molecularity of the reaction".

Thus for an elementary reaction represented by the general chemical equation.

$aA + bB \to$ products

molecularity = a + b

Ex. Reactions	Molecularity
$PCl_5 \rightleftharpoons PCl_3 + Cl_2$	1
$H_2 + I_2 \rightleftharpoons 2HI$	2

Factors Influencing Rate of a reaction :

- **Concentration of the Reactants:** Greater the concentrations of the reactants, faster is the reaction.
- **Temperature:** The rate of reaction increases with increase of temperature.
- **Presence of Catalyst:** A catalyst generally increases the speed of a reaction without itself being consumed in the reaction.

Order of reaction :

Order of reaction is defined as the sum of the powers of the concentration terms appearing in experimentally observed rate law.

In general, let a reaction be represented by the chemical equation:

$aA + bB \to$ Products

obeys the following rate law.

Rate $\propto [A]^m[B]^n$, or Rate $= k[A]^m[B]^n$

Pseudo First order Reaction :

A bimolecular reaction conforms to the first-order when one of the reactants is taken in large excess and the reaction is said to be pseudo unimolecular or pseudo first order.

An example of this is the hydrolysis of ester by dil. acid i.e.

$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

The reaction is originally obeying the second-order kinetics.

Rate $= k[CH_3COOC_2H_5][H_2O]$

But the reaction is usually carried out taking dilute aqueous solution of ester and acid (HCl) such that in the reaction mixture water exists in large excess as compared to ester

Hence reactions obeys the following 1st order kinetics.

Rate $= k[CH_3COOC_2H_5]$

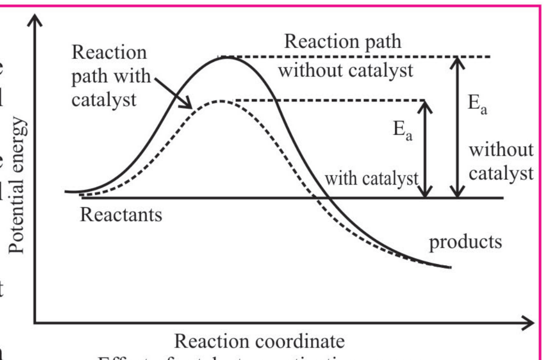
Thus, the molecularity of the above reaction is 'two' but its order is 'one'.

Units of rate constant :

S.No.	Reaction	Order	Units of rate constant
(i)	Zero order reaction	0	$\frac{(molL^{-1})}{s}\times\frac{1}{(molL^{-1})^0} = molL^{-1}\ s^{-1}$
(ii)	First order reaction	1	$\frac{(molL^{-1})}{s}\times\frac{1}{(molL^{-1})^1} = s^{-1}$
(iii)	second order reaction	2	$\frac{(molL^{-1})}{s}\times\frac{1}{(molL^{-1})^2} = mol^{-1}\ Ls^{-1}$
(iv)	nth order reaction	n	$\frac{(molL^{-1})}{s}\times\frac{1}{(molL^{-1})^n} = mol/L^{1-n}\ s^{-1}$

Effect of Catalyst on Rate of Reaction

- A catalyst is a foreign substance which influence the rate of a reaction without itself undergoing any chemical change.
- It provides an alternate pathway by reducing the activation energy and hence lowering the potential energy barrier as shown in figure.
- It does not alter Gibbs energy, ΔG and ΔH of a reaction.
- It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.
- It catalyses the forward as well as the backward reaction to the same extent so that the equilibriun state remains same.



Effect of catalyst on activation energy

MIND MAP-5

SURFACE CHEMISTRY

Catalysis

Type of Catalysis

- Homogeneous: Reactants and catalyst in same physical state e.g.,
  $2SO_2(g) + O_2(g) \xrightleftharpoons{NO(g)} 2SO_3(g)$
- Heterogeneous: Reactants and catalyst in different physical state e.g.,
  $2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$

Enzyme catalysis

Mechanism of enzyme catalysed reaction

- Lock and key theory
- Induced fit theory

Thermodynamic Feasibility of Adsorption :

- The phenomenon of adsorption arises because of attraction between the particles or molecules of adsorbent and adsorbate. Therefore, it is exothermic in nature and is accompanied by release in energy known as enthalpy of adsorption (heat of adsorption).
- When a gas is adsorbed, the freedom of movement of its molecules become restricted. This accounts to decrease in the entropy of the gas after adsorption, i.e., ΔS is negative.
- Thus adsorption is accompanied by decrease in enthalpy as well as decrease in entropy of the system.
- For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, ΔG must be negative,
- On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if, ΔH has sufficiently high negative value as $-T\Delta S$ is positive.

Adsorption theory of heterogeneous catalysis :

The mechanism involves five steps :

i. Diffusion of reactants to the surface of the catalyst

ii. Adsorption of reactant molecules on the surface of the catalyst

iii. Occurrence of chemical reaction on the catalyst's surface through the formation of an intermediate

iv. Desorption of reaction products from the catalyst surface, and thereby, making the surface available again for more reaction to occur

v. Diffusion of reaction products away from the catalyst's surface.

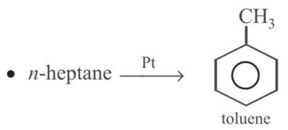
Shape selective catalysis by zeolites : Zeolites are Microporous alumino silicates with Al–O–Si frame work. It is widely used as catalysts in petrochemical industries (ZSM-5)

Activity and selectivity of catalyst

(a) **Activity :** Activity is the ability of catalysts to accelerate chemical reactions.

The degree of acceleration can be as high as 10^{10} times in certain reactions. For example : Reaction between H_2 and O_2 to form H_2O in presence of platinum as catalyst takes place with explosive violence. In absence of catalyst, H_2 and O_2 can be stored indefinitely without any reaction.

(b) **Selectivity :** It is the ability of catalysts to direct reaction to yield particular products (excluding other). For example



- $CH_3CH=CH_2 \xrightarrow[\text{(bismuth molybdate)}]{BiMoO_4} \underset{\text{acrolein}}{CH_2=CHCHO}$
- $HC \equiv CH + H_2 \xrightarrow[\text{Catalyst}]{Pt} CH_3-CH_3$
  $HC \equiv CH + H_2 \xrightarrow[\text{Catalyst}]{\text{Lindlar's}} CH_2=CH_2$

Adsorption

Adsorption Isotherms

Difference between Absorption and Adsorption

	Absorption	Adsorption
(i)	It is phenomenon as a result of which the species of one of substance get distributed uniformly throughout the body of the other substance.	It is the phenomenon as a result of which the species of one substance get concentrated mainly at the surface of the other substance which adsorbs these.
(ii)	The concentration is the same throughout the material.	The concentration on the surface of the adsorbent is different from that in the bulk.
(iii)	It is a bulk phenomenon since it occurs throughout the bulk of the material.	It is only a surface phenomenon since it occurs only at the surface.
(iv)	Absorption proceeds at uniform rate.	Adsorption is rapid in the beginning and its rate slowly decreases with the non-availability of the surface.

Types of adsorption

Comparison of physisorption and chemisorption :

Physisorption	Chemisorption
It is reversible in nature.	It is irreversible.
It is not specific in nature.	It is highly specific in nature.
It arises because of van der Waal's forces.	It is caused by chemical bond formation
It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
It depends on the surface area. It increases with an increases of surface area.	It also depends on the surface area. It too increases with an increase of surface area.
Low temperature is favourable for adsorption. It decreases with increases of temperature.	High temperature is favourable for adsorption. It increases with the increase of temperature.
No appreciable activation energy is needed.	High activation energy is sometimes needed.
Enthalpy of adsorption is low (20-40 kJ mol^{-1}).	Enthalpy of adsorption is high (80-240 KJ mol^{-1}).
It results into multimolecular layers on adsorbent	It results into unimolecular layer.

Freundlich adsorption isotherm

Adsorption from solution phase :

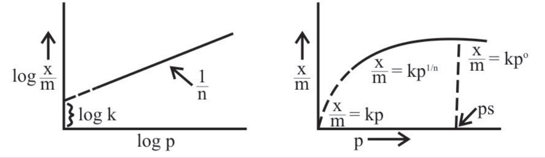
- The extent of adsorption depends on the nature of the adsorbent and adsorbate.
- The extent of adsorption depends on the concentration of solute.
- The extent of adsorption increase with an increase of surface area of adsorbent while decrease with an increase in temp.
- Instead of pressure equilibrium conc. of adsorbates in the solution is considered.

Thus, $\frac{x}{m} = kC^{1/n}$

$\log\frac{x}{m} = \log k + \frac{1}{n}\log C$ Plotting $\log\frac{x}{m}$ against log 'C' a straight line is obtained similar to one shown for x/m and P for gases on solid.

$\frac{x}{m} = k.p^{1/n}\ (n>1)$ $\left[\begin{array}{l}x \Rightarrow \text{mass of the gas adsorbed, } m = \text{mass of the adsorbent at pressure (p)}\\ \text{k \& n are the constant, depend on the nature of the adsorbent and the gas at a particular temp.}\end{array}\right]$

$\log\frac{x}{m} = \log k + \frac{1}{n}\log p$ T = constant



At low pressure $\frac{x}{m} \propto$ (when $\frac{1}{n} = 1$)

At high pressure $\frac{x}{m} \propto p^{\circ}$ (when $\frac{1}{n} = 0$)

At intermediate pressure $\frac{x}{m} = kp^{1/n}$ where n > 1

Emulsions

- Oil in water (disparsed phase is oil) e.g. milk
- Water in oil (disparsed phase is water) e.g. butter

Colloids

Types of Colloids

Based on Physical state of dispersed phase and dispersion medium

Dispersed phase	Dispersion medium	Type of colloid	Examples
Gas	Liquid	Foam	Shaving cream
Gas	Solid	Solid sol	Pumice stone
Liquid	Gas	Liquid Aerosol	Fog
Liquid	Liquid	Emulsion	Milk
Liquid	Solid	Gel	Butter
Solid	Gas	Solid Aerosol	Dust
Solid	Liquid	Sol	Ink
Solid	Solid	Solid sol	Alloys

Based on dispersed phase

Multimolecular colloids	Macromolecular colloids	Associated colloids
1. They consist of aggregates of atoms or molecules which generally have diameter less than 1 nm.	They consist of large molecules (generally polymers)	They behave as colloidal size particles at higher concentrations.
2. The atoms or molecules are held by weak van dar Waal's forces.	The molecules are flexible and can take any shape.	They behave as normal electrolytes at low concentrations
3. They have usually lyophilic character.	They have usually lyophobic character.	Their molecules contain both lyophilic and lyophobic groups.

Based on nature of interaction

- Lyophilicsols (reversible)
- Lyophobic sols (irreversible sols)

Methods of Preparation

Dispersion methods
- Mechanical
- Bredig's Arc

Condensation methods
- Peptisation
- Exchange of solvent
- Excessive

Chemical methods
- Oxidation
- Reduction
- Hydrolysis
- Double

Purification methods

Dialysis
- Electrodialysis
- Ultrafiltration

Properties of colloids

- **Colour:** depends on the size of colloidal particles
- **Brownian movement:** Random and rapid motion of particles
- **Tyndall effect:** Path of light passing through the colloid
- **Colligative properties:** Smaller than true solution
- **Electro-osmosis:** Migration of dispersion medium through a semipermeable membrane.
- **Electrophoresis:** Migration of colloidal sol particles towards electrode of opposite charge.
- **Coagulation:** Precipitation of colloidal sol.
  Coagulation occurs (i) by addition of electrolyte, (precipitation ∝ valency of flocculating ion) (ii) by electrophoresis, (iii) by mixing oppositely charged sols, (iv) by prolonged dialysis, and (v) by boiling

MIND MAP-6

GENERAL PRINCIPLES AND PROCESS OF ISOLATION OF ELEMENTS

Electrochemical principles of metallurgy:

- Highly reactive metals cannot be obtained from their compounds (or ores) by carbon reduction method. This is because these metals have more affinity for oxygen than carbon has. Such highly electropositive metals can be obtained by electrolytic reduction method.
- For an electrochemical reaction, $\Delta G^\circ = -nFE^\circ$ where n is the number of electrons involved in the reactions, E° is the standard electrode potential of the redox pair.
- For a reaction to become spontaneous, E° should be positive. For more reactive metals, E° are highly negative.
- To make the net emf positive, an external emf greater than E° is applied in the direction opposite to that of the cell.
- The ions in the solution or melt can be reduced by applying external emf, that is, by electrolysis, (or by electrolytic reduction method). In electrolytic reduction, the ions of the metal get reduced to the corresponding metal at the cathode, (negative electrode).

Thermodynamic principle of metallurgy
Ellingham diagram :

- Provides a basis for the choice of reducing agent for reduction of a particular metal oxide.
- Temperature is chosen such that the sum of ΔG° in two combined redox process is negative.
- There is a point in curve below which ΔG° is negative and above this point metal oxide decompose automatically.

Applications of Ellingham diagram

- Iron oxides ores are reduced by using coke (carbon-reduction method) in a blast furnace.
  The net reaction for the reduction of FeO by carbon is
  $$FeO(s) + C(s) \rightarrow Fe(s) + CO(g)$$
  The change in the free energy for this reaction is given by
  $$\Delta_r G^\circ = \Delta_f G^\circ(C, CO) + \Delta_f G^\circ(FeO, Fe)$$
  The reduction reaction will be feasible if $\Delta_r G^\circ$ is negative.
  From Ellingham diagram $\Delta_f G^\circ$ (C, CO) vs T plot goes downwards, and $\Delta_r G^\circ$ (Fe, FeO) vs T plot goes upwards.
  At temperature above 700 K, the C, CO line falls below Fe, FeO line. Therefore above, 700 K, carbon should be able to reduce FeO to Fe, and itself gets oxidised to CO.
  From the Ellingham plots it can be seen that below 980 K, carbon monoxide (CO) is a better reducing agent and above it, haematite is reduced by carbon.
- From the $\Delta_r G^\circ$ vs T plots the $Cu - Cu_2O$ plot is almost at the top. Both C – CO and C – CO_2 plots are much lower particularly beyond 500-600 K. Therefore, Cu_2O can be easily reduced by heating with coke.
- From the $\Delta_r G^\circ$ vs T plot, it can be seen that the Zn – ZnO curve lies above the C – CO line beyond 1100 K. Therefore ZnO can be easily reduced to Zn by carbon.

Concentration of ore:

- **Hydraulic washing :** Based on difference in specific gravities of the gangue and ore particles. It is mainly used for oxides ores.
- **Electromagnetic separation :** When one of the component either ore or impurities is magnetic in nature e.g., iron ores.
- **Froth floatation method :** This method is generally applied to sulphide ores. It is based on the fact that surface of sulphide ores is preferentially wetted by oils while that of the gangue is preferentially wetted by water.
- **Chemical method (leaching) :** Consists of treating powdered ore with suitable reagent which can selectively dissolve the ore but not the impurity.
  It is used for Al, Ag, Au etc e.g., bauxite ($Al_2O_3.xH_2O$)

Principal ores of some important metals :

Metal	**ores**
Al	Bauxite
Fe	Haematits, Magnetite, Iron pyrite, Siderite
Cu	Copper pyrite, Malachite Cuprite, Copper glance
Zn	Zinc blende, Calamine, Zincite

Reduction of metal oxide into metal:

- **Carbon reduction :**
  Metal oxides are heated with coke.
- **Reduction by Aluminium :**
  Used for metals which have high melting points.
- **Self reduction :**
  No external reducing agent is used. Metal ore is heated with air.
- **Electrolytic refining :**
  Metal is obtained by the electrolysis of fused metal ore.

Conversion of concentrated ore into metal oxide:

- **Calcination :** Heating carbonate ore below its fusion temperature in absence of air. e.g.,
  $$ZnCO_3(s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$
- **Roasting:** Heating sulphide ores in presence of air below their fusion temperature. e.g.,
  $$2ZnS + 3O_2 \longrightarrow 2ZnO_2 + 2SO_2$$

Refining of metal:

- **Distillation :** The metals with low boiling points can be purified by distillation. The impure metal is evaporated to obtain the pure metal as distillate. Examples – Zn, Cd, Hg etc.
- **Liquation :** This process is used when the impurity is less fusible than the metal itself. The impure metal is placed on the sloping floor of the furnace and heated. The metal melts and drains away leaving behind the impurities. For e.g. tin, lead etc.
- **Oxidation method :** This method is employed when the impurity have greater affinity with oxygen as compared to metal. The impurities are oxidized to form scum. The scum is skimmed off. Sometimes metal oxides are used as oxidizing agents. For example, copper oxide is added to impure copper.
- **Vapour-phase refining :** In this method, the crude metal is free from impurities by first converting it into a suitable volatile compound by heating it with a specific reagent at a lower temperature and then decomposing the volatile compound at some higher temperature to give the pure metal. This method is illustrated by two processes :

* **Mond process :** It is used for the refining of Ni. The impure Ni is heated with CO. Nickel carbonyl thus formed is then decomposed to get pure Ni and CO.

$$\underset{\text{Impure}}{Ni} + 4CO \xrightarrow{330-350\text{ K}} Ni(CO)_4 \xrightarrow{450-470\text{ K}} \underset{\text{Pure nickel}}{Ni} + 4CO$$

* **van Arkel method :** The crude metal is converted into volatile compound, while impurities remain unaffected during compound formation. The resulting compound is then decomposed to get pure metal . The method is used for refining of Ti and Zr.

$$Ti(s) + 2I_2(s) \xrightarrow{523\text{ K}} TiI_4(g) \xrightarrow{1700\text{ K}} Ti(s) + 2I_2(g)$$

$$Zr(s) + 2I_2(g) \xrightarrow{870\text{ K}} ZrI_4(g) \xrightarrow[\text{Tungsten filament}]{2075\text{ K}} Zr(s) + 2I_2(g)$$

- **Electrolytic refining :** Most of the metals like Ag, Au, Pb, Ni, Sn, Zn, etc., are refined by this method.
- **Zone refining method :** The method is based upon the principle that the impurities are more soluble in the molten state (melt) than in the solid state of the metal. It is employed for obtaining metals in ultrapure state.
- **Chromatographic methods :** This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The mixture is put in a liquid or gaseous medium which is moved through the adsorbent. Different components are adsorbed at different levels on the column. Later the adsorbed components are removed (eluted) by using suitable solvents (eluant).
  This is very useful for purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified.

MIND MAP-7

THE *p*-BLOCK ELEMENTS (GROUP 15, 16, 17 AND 18)

Group 15 Elements

- **Elements:** N, P, As, Sb and Bi
- **Electronic configuration:** ns^2np^3
- **Physical properties :**

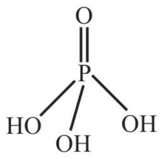
* Melting point : N < P < Bi < Sb < As (exceptional case)

* Ionization enthalpy is much greater than group 14 elements due to extra stability of half filled *p*-orbitals.

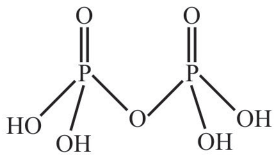
* All elements except Bi show allotropy.

- **Oxidation states**: Common oxidation states are –3, + 3 and + 5
- **Hydrides:** Form hydrides of type MH_3
  NH_3, PH_3, AsH_3, SbH_3 and BiH_3
  Basic character : $NH_3 > PH_3$ (other are not basic)
  Melting point : $PH_3 < AsH_3 < SbH_3 < NH_3$
  Boiling point : $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$
  Reducing character: $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
- **Oxides :** Form oxides of type M_2O_3, M_2O_4 and M_3O_5. Acidic character of oxides decreases down the group
- **Halides**: Form halides of type EX_3 and EX_5
- In case of nitrogen, only NF_3 is known to be stable. It does not form pentahalides due to non-availability of the *d*-orbitals in its valence shell.
- **Reactivity towards metals**: All form binary compound (such as Ca_3N_2, Ca_3P_2, Na_3As, Zn_3Sb_2, Mg_3Bi_2) exhibiting - 3 oxidation state.

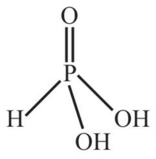
Oxoacids of phosphorus :



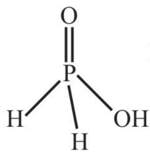
H_3PO_4
Orthophosphoric acid



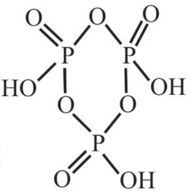
$H_4P_2O_7$
Pyrophosphoric acid



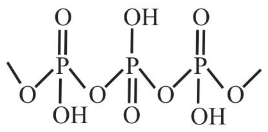
H_3PO_3
Orthophosphorous acid



H_3PO_2
Hypophosphorous acid



$(HPO_3)_3$
Cyclotrimetaphosphoric acid



$(HPO_3)n$
Polymetaphosphoric acid

Group 18 Elements

Elements: He, Ne, Ar, Kr, Xe and Rn

- **Electronic configuration :** ns^2, np^4 except He ($1s^2$)
- **Physical properties**
- **Atomic radii** increase down the group

* **I.E.** decrease down the group and it is very high due to stable electronic configuration.

* **Electron gain enthalpy** is positive because they have no tendency to accept the electron.

- Least reactive due to stable inert gas configuration and due to high I. E. and more positive electron gain enthalpy.
- Xe Forms 3 binary fluorides XeF_2, XeF_4 and XeF_6

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

excess

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

(1:5 ratio)

$$Xe(g) + 3F_2(g) \xrightarrow{573\,K,\ 60–70\,bar} XeF_6(s)$$

(1: 20 ratio)

These are powerful fluorinating agents.

$XeF_2 + PF_5 \rightarrow [XeF]^+ [PF_6]^-$

$XeF_6 + MF \rightarrow M^+ [XeF_7]^-$ (M = Na, K, Rb or (s)

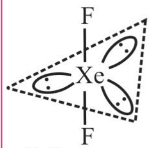
* The oxides of Xe are XeO_3, $XeOF_4$ and XeO_2F_2

$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

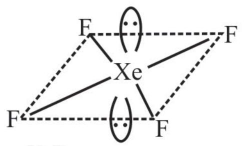
$XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

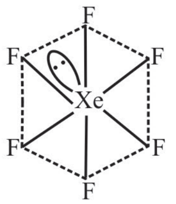
Str. of xenon compounds :



XeF_2
(linear)

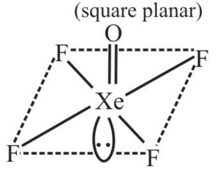


XeF_4
(square planar)

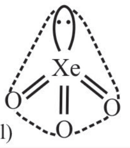


XeF_6
(distorted octahedral)

$XeOF_4$
(square pyramidal)



XeO_3
(pyramidal)



Group 16 Elements

Elements: O, S, Se, Te and Po

- **Electronic configuration:** ns^2, np^4
- **Physical properties** :

* **Electron gain enthalpy** : O < S > Se > Te > Po

* M.P & B.P : O < S < Se < Te > Po

* All these elements exhibit allotropy. For ex,
oxygen ⇒ O_2 & O_3
Sulphur ⇒ Rhombic & monoclinic

Chemical properties :

- **Oxidation states :** 'O' ⇒ –2, –1,1, 2
  S, Se, Te ⇒ –2, 4, 6; Po ⇒ 2, 4

* + 4 and + 6 are more common oxidation state due to inert pair effect. The stability of + 6 decreases down the group while + 4 increases.

- **Hydrides :** Form Hydrides of type H_2E
  Boiling point : $H_2S < H_2Se < H_2Te < H_2O$
  Reducing power : $H_2Te > H_2Se > H_2S > H_2O$
  Acidic character : $H_2O < H_2S < H_2Se < H_2Te$
- **Oxides :** Form oxides of type EO_2, and EO_3
  Both type of oxides are acidic in nature.
  Reducing property decreases from SO_2 to TeO_2.
- **Halides :** Form halides of type EX_6, EX_4, EX_2, and E_2X_2

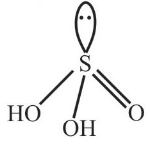
* Stability of halides decreases in order
$F^- > Cl^- > Br^- > I^-$
Monohalides exist as dimer.

* Tetra fluorides, such as SF_4 (gas), SeF_4 (l) and TeF_4 (s) have sp^3d hybridization (see – saw) geometry

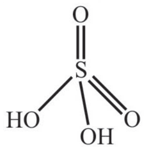
- Amongst hexahalides hexafluorides are the only stable halides

Oxo-acids of sulphur :

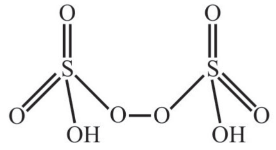
Sulphur forms a number of oxo-acids. Some of these are unstable and cannot be isolated. They are known only in aqueous solutions or in form of their salts. The structures of some important oxoacids are given as follows :



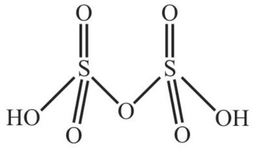
(i) Sulphurous acid (H_2SO_3)



(ii) Sulphuric acid (H_2SO_4)



(iii) Peroxodisulphuric acid or Marshall's acid ($H_2S_2O_8$)



(iv) Pyrosulphuric acid (oleum, $H_2S_2O_7$)

Group 17 Elements

- **Elements:** F, CI, Br, I,At
- **Electronic configuration:** ns^2, np^4
  Physical properties : Exceptional properties
  Electron gain enthalpy F< Cl > Br > I [small size & inter electronic repulsions of 'F']
  Bond dissociation enthalpy $F_2 < Cl_2 > Br_2 > I_2$ [large repulsions of the lone pairs of F_2]
- **Oxidation states**: Fluorine show–1,+1 (except. case) other shows –1, + 1, + 3, + 5 and + 7
  Oxidising power :

* $F_2 > Cl_2 > Br_2 > I_2$

* Relative oxidising power can be illustrated by their reaction with water.

$2F_2(g) + 2H_2O(l) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$

$X_2(g) + H_2O(l) \rightarrow HX(aq) + HOX(aq)$

(where X = Cl, Br)

$4I^-(aq) + 4H^+(aq) + O_2(g) \rightarrow 2I_2(s) + 2H_2O(l)$

Hydrogen halides :
Boiling point HF > HI > HBr > HCl
Melting point HI > HF > HBr > HCl
Acidic strength HI > HBr > HCl > HF

- **Reaction with metals:**
- Ionic character: MF > MCl > MBr> MI
- **Displacement reaction:**

F replaces Cl, Br and I, Cl replaces Br and I

Oxo-acids of halogens:

* Due to high electronegativity and small size 'F' forms only one oxoacid (HOF, hypofluorous acid) while other hologens form oxoacids of the type
HOX, HXO_2, HXO_3 and HXO_4

Cl	Br	I	
HOCl	HOBr	HOI	Hypohalous acid
$HClO_2$	$HBrO_2$	–	Halous acid
$HClO_3$	$HBrO_3$	HIO_3	Halic acid
$HClO_4$	$HBrO_4$	HIO_4	Perhalic acid

* Acid-character of oxo-acids of same halogen increases with increase in O.S. e.g.,
$HOCl < HClO_2 < HClO_3 < HClO_4$

* **Oxidising power** : HOCl > HOBr > HOI

* **Thermal stability**
$HOCl < HClO_2, < HClO_3 < HClO_4$

Interhalogen compounds:

* Compounds of halogens themselves.

* These are covalent compounds
(XX', XX'_3, XX'_5, XX'_7,)
X⇒ large size halogen, X' ⇒small large size halogen,

* More reactive than halogens except 'F' due to weaker A–X bond than X–X bond.

XX'_3 (ClF_3, BrF_3, IF_3 I_2Cl_6) ⇒ Bent T-shaped

XX'_5 (IF_5, BrF_5, ClF_5) ⇒ Square pyramidal

XX'_7 (IF_7) ⇒ Pentagonal bipyramidal

MIND MAP-8

THE *d*-& *f*-BLOCK ELEMENTS

The *d*- Block elements

Some important *d*-block elements compound

$KMnO_4$:

- Prepared from the mineral pyrolusite

$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

commercial method :

$MnO_2 \xrightarrow[\text{Oxidised with air or } KNO_3]{\text{Fused with KOH}} MnO_4^{2-}$

Maganate ion

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

Permaganat ion

- **Oxidising properties:**

In acidic medium:

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

It oxidises I^- to I_2, NO_2^- to NO_3^-, Fe^{2+} to Fe^{3+}, $C_2O_4^{2-}$ to CO_2

In neutral or faintly alkaline medium,

$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4H_2O$

It oxidises $S_2O_3^{2-}$ to SO_4^{2-}, Mn^{2+} to MnO_2, I^- to IO_3^- etc.

$K_2Cr_2O_7$:

- Prepared from chromite ore ($FeCr_2O_4$)

$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

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

The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution.

$2CrO_4^{2-} + 2H^+ \rightarrow \underset{\text{(orange)}}{Cr_2O_7^{2-}} + H_2O$

$Cr_2O_7^{2-} + 2OH^- \rightarrow \underset{\text{(yellow)}}{CrO_4^{2-}} + H_2O$

- **Oxidising properties:**

Ionic equation :

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$; $2I^- \rightarrow I_2 + 2e^-$

$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$; $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$

The full equation is obtained by adding the half reaction for potassium dichromate to the half reaction for the reducing agent

for e.g. $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow \underset{\text{Green}}{2Cr^{3+}} + 7H_2O + 3I_2$

- **Chromly chloride Test :**

$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \rightarrow \underset{\text{(chromyl chloride)}}{2CrO_2Cl_2} + 6KHSO_4 + 3H_2O$

- **Four transition series:**

(i) 3*d* series: From Sc (21) to Zn (30)
(ii) 4*d* series : From Y (39) to Cd (48)
(iii) 5*d* series: La (57), Hf (72) to Hg (80)
(iv) 6*d* series : Ac (89), Rf (104) to Cn (112)

- **Electronic configuration:** $(n - 1)\, d^{1-10}\, ns^{1-2}$
- **Atomic Size :** Atomic and ionic radii of d-block elements is smaller than s-block elements. Atomic radii depends on effective nuclear charge (Z_{eff}) and screening effect (SE).

  In 3*d* series : $Sc \rightarrow Cr$ ($Z_{eff} > SE$) $\therefore$ radius decreases

  $Mn \rightarrow Ni$ ($Z_{eff} = SE$) $\therefore$ radius remains constant; $Cu \rightarrow Zn$ ($Z_{eff} < SE$) $\therefore$ radius increases

  Decrease in the radii with increase in atomic number is not regular. Atomic radii tend to reach minimum near at the middle of the series and increase slightly towards the end of the series.
- **Melting and boiling points :** M.P. and B.P. of *d*-block elements is greater than of s-block (the reason is stronger metallic bond and presence of covalent bond formed by unpaired *d*-electrons.).
- **Ionisation potentials :** The ionisation potentials of *d*-block elements increase as we move across each series from left to right, although the increase is not quite regular, e.g., in the first series, the values for Sc, Ti, V and Cr differ very slightly. Similarly the values Fe, Co, Ni and Cu are fairly close to one another. The value for Zn is appreciably higher due to the additional stability associated with completely filled 3*d*-level in Zn ($Zn \rightarrow 3d^{10}4s^2$).
- **Standard electrode potential :** $E^\circ_{M^{2+}/M}$ values are more negative than $E^\circ_{2H^+/H_2}$ values (except Cu). These metals (except Cu) evolve $H_2(g)$ and hence are oxidised easily when reacted with acid solutions is $E^\circ_{Cu^{2+}/Cu}$ highest (+ 0.34) in first transition series and does not liberate $H_2(g)$ from acids.
  is highest (+ 0.34) in first transition series and does not liberate $H_2(g)$ from acids.
- Cr is unreactive although high negative $E^\circ_{Cr^{2+}/Cr}$ value due to the formation of non-reactive invisible layer of Cr_2O_3
- $E^\circ_{M^{3+}/M^{2+}}$ of Co and Ni is exceptionally high positive value due to high (negative) hydration enthalpy.
- **Oxidation state:** Shows variable oxidation states due to involvement of (*ns*) and (*n*–1)*d* electrons in bonding.
- **Magnetic property:** Transition elements and many of their compounds are paramagnetic. The magnetic moment (μ) can be calculated by using $\mu = \sqrt{n(n+2)}$ where '*n*' is the number of unpaired electrons in the metal ion
- **Coloured compounds:** Forms coloured compounds due to *d*-*d* transition.
- **Forms complexes:** Due to small highly charged ions and vacant *d*-orbitals
- **Forms interstitial compounds:** As they are able to entrap atoms of elements having small atomic size like H, C, N, B etc.
- **Oxides:** Oxides in lower oxidation states are basic, whereas those with higher. oxidation state are acidic or amphoteric

The *f*- block Elements

Lanthanoids: 14 elements from Ce to Lu General E.C: $6s^2\, 5d^{0-1}\, 4f^{1-14}$

Atomic and Ionic Sizes

In the lanthanoid series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutetium (La^{3+} to Lu^{3+}). This contraction in size is known as lanthanoid contraction. In these elements the added electron enters in the deep seated f-orbitals and therefore experiences considerable pull by the nucleus. Such an electron cannot add to the size of the element and also because the intervening $5s^2p^6d^1$ electronic shells, have very little screening effect on the outermost $6s^2$ electrons. Hence with increasing atomic number, the enhanced nuclear charge leads to contraction in the size of atoms and ions.

Oxidation states : All the lanthanoids attains +3 oxidation state and only cerium, praseodymium, terbium, and dysprosium exhibit higher oxidation state (+4).

Oxidation states + 2 and +4 occur particularly when they lead to

(a) A noble gas configuration e.g. Ce^{4+} (f^0)
(b) A half filled '*f*' orbital e.g. Eu^{2+}, Tb^{4+}, (f^7)
(c) A completely filled '*f*' orbital e.g. Yb^{2+} (f^{14})

Colour : The lanthanoid ions have unpaired electrons in their 4*f*- orbitals. Thus these ions absorbs visible region of light an undergo *f*-*f* transition and hence exhibit colour.

- They are highly dense metals with high m.pts.
- **Ionisation Energies** - The first I.E.'s are around 600 kJ mol^{-1} and second about 1200 kJ mol^{-1} which are comparable with those of calcium. The 3rd I.E. is low if it leads to stable empty, half-filled or completely filled configuration. This is the reason for very low 3rd I.E. of La, Gd and Lu.
- **Electropositive character**- High due to low I.P.
- Complex formation- Do not have much tendency to form complexes due to low charge density because of their large size.
- **Reducing Agent** - They readily lose electrons so they act as good reducing agents.

  Due to lanthanide contraction, pairs of elements such as Zr/Hf, Nb/Ta and Mo/W are almost identical in size.

  They are used in the production of alloy steel known as mirsch metal (Ln–95%, Fr–5% traces of S, C, Ca & Al) which is used in making Mg – based alloy to produce bullets, shell and lighter flint.

Chemical properties:

Lanthanoids
- Burn in O_2 — Ln_2S_3
- with S — Ln_2S_3
- heated with N_2 — LnN
- with C 273 K — LnC_2
- with H_2O — H_2 is liberated
- with halogens — LnX_3
- with acids — H_2 is liberated

Actinoids

- General E.C: $5f^{1-14}\, 6d^{0-1}\, 7s^2$

Ionic Sizes: The general trend in lanthanoids is observable in the actinoids as well. There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the actinoid contraction (like lanthanoid contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by 5*f* electrons.

Most stable O.S. is + 3. Also shows O.S like +4, + 5, +6 and +7

- These are mostly radioactive
- Have much greater tendency to form complexes than lanthanides.
  Their magnetic properties are more complex than those of lanthanoids
- Their IE's are lower than for the early lanthanoids. This is because the 5*f* electrons are more effectively shielded from the nuclear charge than the 4*f* electrons of the corresponding lanthanoids.

MIND MAP-9

Some important terms:

Denticity: The number of ligating (linking) atoms present in ligand is called denticity.

* **Unidentate ligands:** The ligands whose only one donor atom is bonded to metal atom are called unidentate ligands. Examples: H_2O, NH_3, CO, CN^-

* **Bidentate ligands:** The ligands which contain two donor atoms or ions through which they are bonded to the metal ion.

Examples: Ethylene diamine $H_2NCH_2CH_2NH_2$ has two nitrogen atoms, oxalate ion has two oxygen atoms which can bind with the metal atom.

* **Polydentate ligand:** When several donor atoms are present in a single ligand, the ligand is called polydentate ligand.

Examples: In $N(CH_2CH_2NH_2)_3$, the ligand is said to be polydentate and $EDTA^{4-}$ is an important hexadentate ligand.

* **Chelate:** An inorganic metal complex in which there is a close ring of atoms caused by attachment of a ligand to a metal atom at two points e.g., $[Cu(NH_2(CH_2)_2NH_2)_2]^{2+}$.

* **Ambidentate ligand:** Ligands which can linked through two different atoms present in it are called ambidentate ligand.

Example: NO_2^- and SCN^-. Here, NO_2^- can link through N as well as O while SCN^- can link through S as well as N atom.

COORDINATION COMPOUNDS

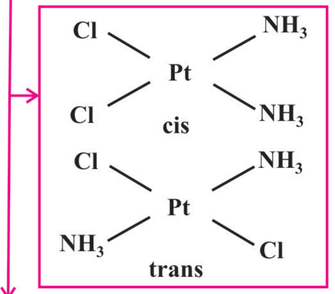
Isomerism

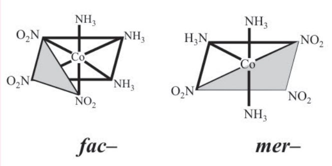
Stereoisomerism

Structural isomerism

Geometrical

Optical





- **Linkage isomerism:**
  $[Co(NH_3)_5(NO_2)]Cl_2$,
  $[Co(NH_3)_5(ONO)]Cl_2$
  Nitrite ion bound through either oxygen or nitrogen.
- **Coordination isomerism:**
  $[Co(NH_3)_6][Cr(CN)_6]$,
  $[Cr(NH_3)_6][Co(CN)_6]$
  Interchange of ligands between cationic and anionic entities.
- **Ionisation isomerism:**
  $[Co(NH_3)_5(SO_4)]Br$,
  $[Co(NH_3)_5Br]SO_4$
  These give different ion in solution
- **Solvate isomerism:**
  $[Cr(H_2O)_6]Cl_3$
  $[Cr(H_2O)_5Cl]Cl_2.H_2O$

Werner's coordination theory:

- The postulates of Werner's theory are:

* Metal shows two different kinds of valences: primary valency and secondary valency.

* The ions/ groups bound by secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

* The most common geometrical shapes in coordination compounds are octahedral, square planar and tetrahedral.

- **Primary valency**

* This valency is normally ionisable.

* It is equal to positive charge on central metal atom.

* These valencies are satisfied by negatively charged ions.

- **Secondary valency**

* This valency is non – ionisable.

* The secondary valency equals the number of ligand atoms coordinated to the metal.

* It is also called coordination number of the metal.

* It is commonly satisfied by neutral and negatively charged, sometimes by positively charged ligands.

Naming of coordination compounds: The following rules are used for naming coordination compounds:

- The cation is named first in both positively and negatively charged coordination entities.
- The ligands are named in an alphabetical order before the name of the central atom/ion.
- Names of the anionic ligands end in–o, those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO. While writing the formula of coordination entity, these are enclosed in brackets.
- Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, bis, tris, tetra, kis are used, the ligand to which they refer being placed in parentheses e.g., $[NiCl_2(PPh_3)_2]$ is named dichloridobis (triphenylphosphine) nickel (II).
- Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.
- If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix – ate.
- The neutral complex molecule is named similar to that of the complex cation.

Stability of coordination compounds: The stability of complex in solution refers to the degree of association between the two species involved in the state of equilibrium. It is expressed as stability constant (K).

$$M^+ + nL^{x-} \rightleftharpoons [MLn]^{y-}; K = \frac{[(MLn)^{y-}]}{[M^+][L^{x-}]^n}$$

- The factors on which stability of the complex depends :

* **Charge on the central metal atom:** As the magnitude of charge on metal atom increases, stability of the complex increases.

* **Nature of metal ion:** The stability order is $3d < 4d < 5d$ series.

* **Basic nature of ligands:** Strong field ligands form stable complex.

Colour in coordination compounds: The crystal field theory attributes the colour of the coordination compounds to *d*-*d* transition of the electron, i.e., electron jump from t_{2g} level to higher e_g level.

In the absence of ligands, crystal field splitting does not occur and hence the substance is colourless.e.g.,

$[Ti(H_2O)_6]^{3+}$ - Violet in colour

$[Cu(H_2O)_4]^{2+}$ - Blue in colour, etc.

Metal carbonyls: Metal carbonyls are homoleptic complexes in which carbon monoxide (CO) acts as the ligand e.g., $Ni(CO)_4$

- The metal-carbon bond in metal carbonyls possess both *s* and *p* character.
- **The M–C σ bond** is formed by the donation of lone pair of electrons from the carbonyl carbon into a vacant orbital of the metal.
- **The M–C π bond** is formed by the donation of a pair of electrons from a filled *d* orbital of metal into the vacant antibonding π orbital of carbon monoxide.
- The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

Crystal field theory (CFT): In this theory, ligands are treated as point charges in case of anions and dipoles in case of neutral molecules.

- The five *d*-orbitals are classified as

* Three *d*-orbitals i.e., d_{xy}, d_{yz} and d_{zx} are oriented in between the coordinate axes and are and d_{zx} are oriented in between the coordinate axes and are called t_{2g} – orbitals.

* The other two *d*-orbitals, i.e., $d_{x^2-y^2}$ and d_{z^2} oriented along the x, y axes are called e_g – orbitals.

- A series in which ligand are arranged in order of increasing magnitude of crystal field splitting, is called **spectrochemical series**.

  $I < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$
- In case of octahedral complexes, Energy of e_g set of orbitals > energy of t_{2g} set of orbitals.
- The energy of e_g orbitals will increase by (3/5) Δ_0 and t_{2g} will decrease by (2/5) Δ_0.
- Ligands for which $\Delta_0 < P$ are known as weak field ligands and form high spin complexes.
- If $\Delta_0 > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital which produce this effect are known as strong field ligands and form low spin complexes.
- In tetrahedral complexes, Energy of t_{2g} set of orbitals > Energy of e_g set of orbitals.
- Pairing of electrons is not possible in tetrahedral complexes, so these are high spin complexes.

Valence bond theory (VBT):

The salient features of the theory are :

(i) The central metal ion a number of empty orbitals for accommodating electrons donated by the ligands. The number of empty orbitals is equal to the coordination number of the metal ion for the particular complex.

(ii) The atomic orbitals (s, *p* or *d*) of the metal ion hybridize to form hybrid orbitals with definite directional properties. These hybrids orbitals now overlap with the ligand orbitals to form strong chemical bonds.

Number of orbitals and types of hybridisation :

Coordination number	**Type of hybridisation**	**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

- The *d*-orbitals involved in the hybridization may be either inner (*n*-1) *d* orbitals or outer *nd*-orbitals. The complexes formed in these two ways are referred to as low spin and high spin complexes, respectively.
- If the complex contains unpaired electrons, it is paramagnetic in nature, while if it does not contain unpaired electron, it is diamagnetic in nature.

MIND MAP-10

HALOALKANES AND HALOARENES

Haloalkanes

Preparation:

- **From alcohols:**

$ROH + HX \longrightarrow RX + H_2O$

$ROH + PCl_5 \longrightarrow PCl + POCl + HCl$

$ROH + SOCl_2 \longrightarrow RCl + SO_2 + HCl$

From hydrocarbons:

$CH_2{=}CH_2 + HX \longrightarrow CH_3CH_2X$

Order of reactivity HI > HCl > HF In case of unsymmetrical alkenes addition occurs according to Markownikoffs rule only in case of Hbr in presence of peroxides addition occures according to anti Markowinkoffs rule

$CH_2{=}CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2CH_2Br$

$CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$

From halogen exchange

With NaI **(Finkelstein reaction)**

$\underset{(X=Cl,\,Br)}{R-X} + NaI \xrightarrow{Acetone} \underset{\text{Iodoalkane}}{R-I} + NaX$

with AgF (**Swarts reaction)**

$C_2H_5Cl + AgF \longrightarrow \underset{\text{Fluoroethane}}{C_2H_5F} + AgCl$

Properties:

Physical properties

- Lower alkyl halides are colourless with sweet smell or pleasant oily liquid, except CH_3F, CH_3Cl, CH_3-CH_2-F, CH_3-CH_2-Cl which are gaseous in nature.
- Alkyl halides having 18-carbon or more than it are solid in nature.
- These are completely soluble in organic solvents but insoluble in H_2O
- Reactivity order is RI > RBr > RCl > RF
- For same halide group, reactivity order is 3° (halide) > 2° (halide) > 1° (halide)
- Polarity order is RF > RCl > RBr > RI
- Melting & Boiling points, for same alkyl group the order is RI > RBr > RCl > RF
- Fluorides and chlorides are lighter than water whereas bromides and iodides are heavier than H_2O due to higher density of bromine than oxygen.

Chemical properties:

- **Nucleophilic substitution:**

$RX + KOH \longrightarrow ROH + KX$

$RX + H_2O \longrightarrow ROH + HX$

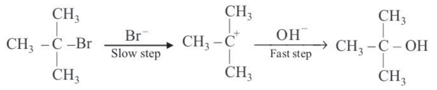
$RX + NaOR \longrightarrow ROR + NaX$

$RCl + NaI \xrightarrow{Acetone} RI + NaCl$

$RX + LiAlH_4 \longrightarrow RH + LiX + AlX_3$

- **These reactions** are of two types:

* **S_N1 type** (Unimolecular nucleophilic reactions) proceeds in two steps:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \xrightarrow[\text{Slow step}]{Br^-} CH_3-\underset{CH_3}{\overset{CH_3}{C^+}} \xrightarrow[\text{Fast step}]{OH^-} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

* Rate, r = k[RX]. It is a first order reaction.

* Reactivity order of alkyl halide towards S_N1 mechanism 3° > 2° > 1°

* Polar solvents, low concentration of nucleophiles and weak nucleophiles favour S_N1 mechanism.

* In S_N1 reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack on planar carbocation

- **S_N2 type** (Bimolecular nucleophilic substitution), these reactions proceed in one step.

* It is a second order reaction with r = k[RX] [Nu].

* During S_N2 reaction, inversion of configuration occurs

* Reactivity of halides towards S_N2 mechanism is 1° > 2° > 3°

* Rate of reaction in S_N2 mechanism depends on the strength of the attacking nucleophile.

* Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour S_N2 mechanism.

$CH_2CH_2Br \xrightarrow{OH^-} CH_2CH_2 + H_2O + Br^-$

$CH_3CH_2Br + Mg \xrightarrow{Dry\ Ether} CH_2CH_2 + MgBr$

Grignard reagents are highly reactive and react with any source of proton (H_2O, alcohols, amines etc. to give hydrocarbons.)

$2RX + 2Na \longrightarrow RR + 2NaX$

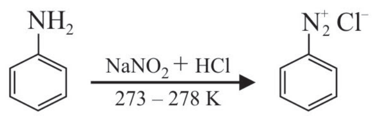
Haloarenes

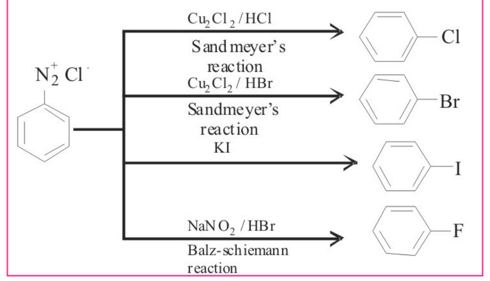
Preparation:

From arenes:

$C_6H_6 + Cl_2 \xrightarrow[dark]{Fe} C_6H_5Cl$

From benzene diazonium chloride:





Polyhalogen compound:

- **Dichloromethane (CH_2Cl_2):** It is useful as solvent in industries. Mostly it is used as solvent in the production of chemicals used in removal of colour.

*It is Harmful to nervous system. If it comes in direct contact with eye it damages the cornea. In addition, if it comes in direct contact with skin, red rashes are formed.

- **Tetrachloromethane (CCl_4):** It is used in the manufacture of refrigerants and propellants for aerosol cans.

*Used as a cleaning solvent, degreasing agent and as fire extinguisher.

*It causes permanent damage to nerve cells.

*In atmosphere, it depletes the ozone layer.

- **Freons:** Chlorofluorocarbon compounds of methane and ethane are collectively known as freons and it is manufactured by **swarts reaction** using tetrachloromethane.

* Freon 12 (CCl_2F_2) is one of the most common freons in industrial use.

* Freon is able to initiate radical chain reactions that can disturb the natural ozone balance.

- **DDT:** It is a powerful insecticide.

* It is a persistent organic pollutant that is readily adsorbed to soils and sediments, which can act both as sinks and as long-term sources of exposure affecting organisms.

* It is not metabolised very rapidly by animals.

Properties :

Physical properties:

* Aryl halides are colourless liquids or colourless solids with characteristic odour.

* Boiling point generally increases with increase in the size of aryl group or halogen atom. Boiling point order Ar–I > Ar–Br > Ar–Cl > Ar–F

* The melting point of *p* -isomer is more than *o*- and *m*-isomer. This is because of more symmetrical nature of *p*-isomer.

* Due to resonance in chlorobenzene, C-Cl bond is shorter and hence, its dipole moment is less than that of cyclohexyl chloride.

Chemical properties :

- **Nueleophilic substitution reactions:**

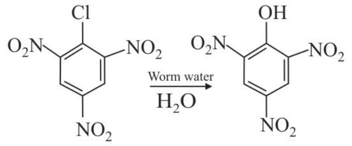
Aryl halides are less reactive towards nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

* Due to resonance, C-X bond has partial double bond character.

* Stabilisation of the molecule by delocalisation of electrons.

* Instability of phenyl carbocation.

However, aryl halides having electron withdrawing groups (like – NO_2, $-SO_3H$, etc.) at ortho and para positions undergo nucleophilic substitution reaction easily.

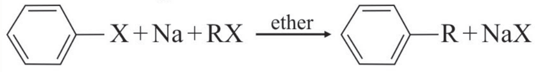


- **Electrophilic substitution reactions:**

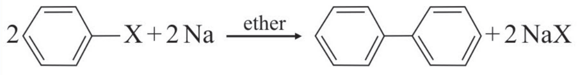
Haloarenes are *o*, *p*-directing, due to + I effect of halogen group electrondensity increases at ortho and para positions e.g., halogenation, nitration, sulphonation, Friedel-crafts reaction etc.

Reaction with metals:

* Wurtz fitting reaction :



Fitting reaction :



MIND MAP-11

ALCOHOLS, PHENOLS AND ETHERS

Alcohols

Preparation:

- **By acid catalysed hydration**: Alkanes reacts with H_2O in presence of acid (as catalyst).

$$CH_3CH=CH_2+H_2O\xrightarrow[\text{(markovnikov's addition)}]{H^+}CH_3CH(OH)CH_3$$

- **By Hydroboration-Oxidation:** Diborane with alkene gives trialkyl boride which gives alcohol with H_2O_2/OH^-

$$CH_3CH=CH_2\xrightarrow[\substack{\text{(ii) } H_2O_2,\, OH^- \\ \text{anti–markovnikov's} \\ \text{addition}}]{\text{(i) } B_2H_6/THF}CH_3CH_2CH_2OH$$

- **Reduction of Aldehydes and Ketones**

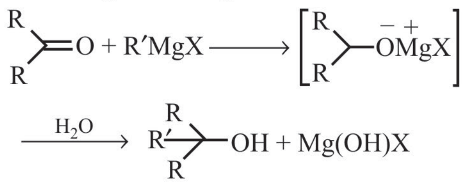
$$\text{Aldehyde}\xrightarrow{H_2/Pd}1°\text{Alcohol}$$

$$\text{Ketone}\xrightarrow{NaBH_4}2° \text{ Alcohol}$$

- **Reduction of carboxylic acids:**

$$RCOOH\xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4}RCH_2OH$$

- **From Grignard Reagent:**



- **Physical Properties of Alcohols:**
- Alcohols are colourless with characteristic smell (alcoholic).
- They are soluble in water due to H–bonding.
- These are partially soluble in organic solvents.
- They are liquid in nature up to 12–carbon.
- Melting point and boiling point ∝ molecular mass $\propto \dfrac{1}{\text{No. of branches}}$
- Boiling point of alcohols are higher than the corresponding ether due to H–bonding.
- **Chemical Properties:**
- $2ROH+2M\longrightarrow 2R\text{–}\overset{-}{O}\overset{+}{M}+H_2\ (M=Na, K, Cl)$
- $RCOOH+H-OR'\longrightarrow RCOOR'+H_2O$
- $RCOCl+H-OR'\longrightarrow RCOOR'+HCl$
- $ROH+R'MgX\longrightarrow R'-H+ROMgX$

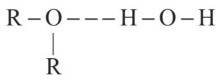
Commercially important alcohols:

- **Methanol**: Methanol, CH_3OH, also known as 'wood spirit', was produced by destructive distillation of wood. Methanol is used as a solvent in paints, varnishes and for making formaldehyde.
- **Ethanol**: Ethanol is a colourless liquid with boiling point 351 K. It is used as a solvent in paint industry and in the preparation of a number of carbon compounds. The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.

Preparation:

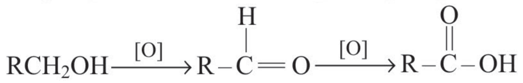
Physical Properties of Ethers

- Dimethyl ether and ethyl methyl ether are gases. All other are colourless liquids with pleasant odour.
- They are sparingly soluble in water but readily soluble in organic solvents. Solubility of ether in water is due to hydrogen bonding between ether and water molecule.



$$\underset{\substack{|\\R}}{R-O}---H-O-H$$

- Boiling points of ether show a gradual increase with increase in molecular weight. Ethers have low boiling points than isomeric alcohols as there is no association with hydrogen bonding between ether molecules. The boiling points of ethers are close to the boiling points of alkanes.
- They are lighter than water.
- Lower ethers are highly volatile and inflammable.

- $R-OH+HCl\xrightarrow{\text{anh. } ZnCl_2}R-Cl+H_2O$
- $CH_3CH_2OH\xrightarrow{\text{conc. } H_2SO_4}CH_2=CH_2+H_2O$
- 

$$RCH_2OH\xrightarrow{[O]}R-\overset{\substack{H\\|}}{C}=O\xrightarrow{[O]}R-\overset{\substack{O\\\|}}{C}-OH$$

Ethers

Preparation:

- **Dehydration of alcohol**:

$$2CH_3CH_2OH\xrightarrow[413\text{ K}]{H_2SO_4}C_2H_5OC_2H_5+H_2O$$

- **Williamson's synthesis**:

  $R-X+R'-ONa\longrightarrow ROR'+NaX$

  Here, alkyl halide should be primary because secondary and tertiary alkyl halides give elimination reaction rather than substitution.

  Thus, the reactivity order is 1° > 2° > 3°

Chemical Properties:

- Cleavage of C–O bond:

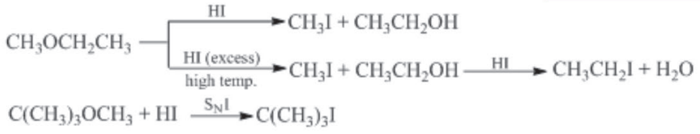
  $ROR+HX\longrightarrow RX+ROH$

  $ROH+HX\longrightarrow RX+H_2O$

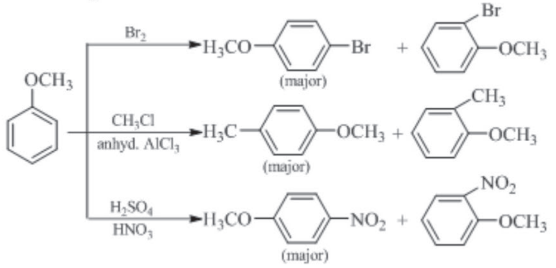
  $PhOR+HX\longrightarrow PhOH+RX$

- Reactivity with HX:

  Reactivity order of HX is HI > HBr >> HCl.



- **Electrophilic substitution:**



Phenols

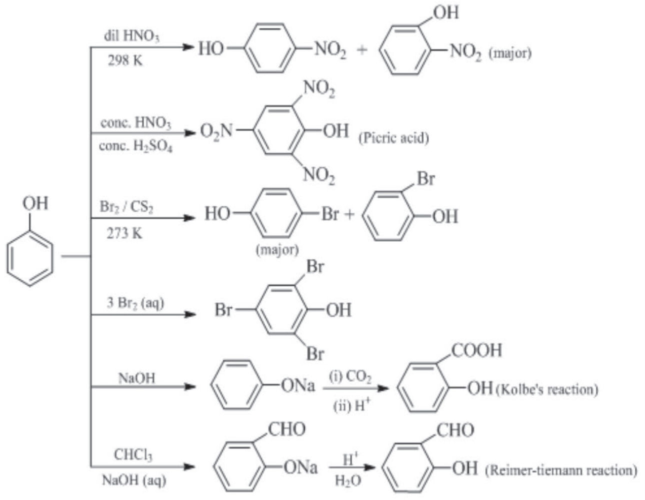
Preparation:

- $\text{Chlorobenzene}+NaOH\xrightarrow[\text{(ii) } HCl]{\text{(i) 623 K, 300 atm.}}\text{Phenol}$
- $\text{Benzene}\xrightarrow[\text{(ii) } NaOH,\, H^+]{\text{(i) Oleum}}\text{Phenol}$
- $\text{Aniline}\xrightarrow[272–278K]{NaNO_2+HCl}\text{Diazonium salt}\xrightarrow{H_2O}\text{Phenol}$
- $\text{Cumene}\xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) } O_2}\text{Phenol}$

Physical properties:

- Phenols are colorless crystalline solid or liquid having characteristic odour.
- Due to hydrogen bonding phenols has higher boiling point and more solubility compared to arene compounds which contains approximately same molecular mass.

Chemical Properties:



MIND MAP-12

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Preparation of aldehydes and ketones:

- **Oxidation of alcohols:**

$1^\circ \text{ Alcohol} \xrightarrow{K_2Cr_2O_7+H_2SO_4} \text{Aldehyde}$

$2^\circ \text{ Alcohol} \xrightarrow{K_2Cr_2O_7+H_2SO_4} \text{Ketone}$

- **Dehydrogenation of alcohols:**

$1^\circ \text{ Alcohol} \xrightarrow{Cu,\ 573\ K} \text{Aldehyde}$

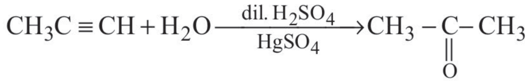
$2^\circ \text{ Alcohol} \xrightarrow{Cu,\ 573\ K} \text{Ketone}$

- **Ozonolysis of alkenes:**

$CH_3CH = CHCH_3 + O_3 \xrightarrow{H_2O,\ Zn} 2CH_3CHO$

- **Hydration of alkynes:**

$CH \equiv CH + H_2O \xrightarrow[HgSO_4]{dil.\ H_2SO_4} CH_3 - CHO$



$CH_3C \equiv CH + H_2O \xrightarrow[HgSO_4]{dil.\ H_2SO_4} CH_3 - \underset{\underset{O}{\|}}{C} - CH_3$

- **Preparation of aldehydes only:**

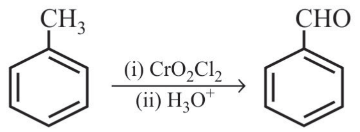
* **Rosenmund reduction**:

$\text{Acyl chloride} \xrightarrow{H_2Pd-BaSO_4} \text{Aldehyde}$

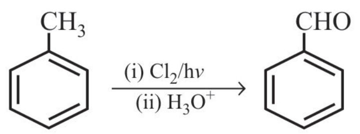
* **Stephen reaction**:

$RCN + SnCl_2 + HCl \xrightarrow{H_3O^+} RCHO$

* **Etard Reaction**:



* **Side chain chlorination**:

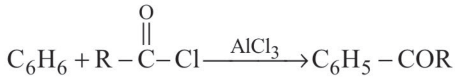


* **Gatterman-Koch reaction**:

$\text{Benzene} \xrightarrow[anhy.\ AlCl_3/CuCl]{CO,\ HCl} \text{Benzaldehyde}$

- **Preparation of Ketones only:**

* **Friedel crafts acylation:**



$C_6H_6 + R - \overset{\overset{O}{\|}}{C} - Cl \xrightarrow{AlCl_3} C_6H_5 - COR$

* **From nitriles:**

$C_2H_5CN \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr} C_2H_5COC_6H_5$

* **From acyl chloride:**

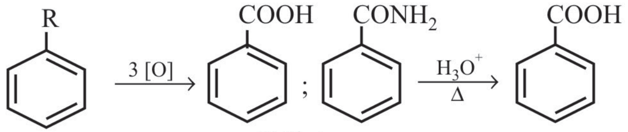
$2\,RMgX + CdCl_2 \longrightarrow R_2Cd + 2\,Mg(X)Cl$

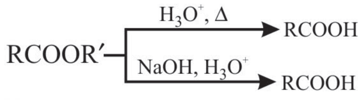
$2\,R'COCl + R_2Cd \longrightarrow 2\,R'COR + CdCl_2$

Carboxylic acids

Preparation:

- $RCH_2OH \xrightarrow[(ii)\ H_3O^+]{(i)\ alk.\ KMnO_4} RCOOH$
- $RCN \xrightarrow[H_2O]{H^+/OH^-} R - C(O) - NH_2 \xrightarrow[OH^-]{H^+\ or} RCOOH$
- $R - Mg - X + CO_2 \xrightarrow[(ii)\ H_3O^+]{(i)\ dry\ ether} RCOOH$
- $RCOCl \xrightarrow{H_2O} RCOOH + Cl^-$





Properties:

- **Physical State** :
  C_1 to C_3 = Colourless pungent smelling liquids
  C_4 to C_9 = Oily liquids having goat's butter like smell.
  C_{10} + = Colourless and odourless waxy solids.
  These are polar substances and can form H-bonds with each other to form dimer structures.
- **Acidity of Carboxylic Acids** : The acidic character of carboxylic acids is due to resonance in the acidic group which imparts electron deficiency (positive charge) on the oxygen atom of the hydroxyl group.

Non-equivalent structures (Resonance less important)

- Gives CO_2 with carbonates and $NaHCO_3$
- $2 \text{ Ethanoic acid} \xrightarrow[or\ P_2O_5,\ \Delta]{H^+,\ \Delta} \text{Ethanoic anhydride}$
- **Esterification**
- $RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$
- $RCOOH + PCl_5 \longrightarrow RCOCl + PCl_3 + HCl$
- $RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$
- $RCOOH \xrightarrow[\Delta,\ H_2O]{NH_3} RCONH_2$
- $RCOOH \xrightarrow[(ii)\ H_3O^+]{(i)\ LiAlH_4} RCH_2OH$
- $RCOONa \xrightarrow[(decarboxylation)]{NaOH\ \&\ CaO/\Delta} RH + Na_2CO_3$
- **Hell–Volhard Zelinsky reaction**:

$RCH_2COH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/Red\ P} RCH(X)COOH$

Aldehydes and Ketones

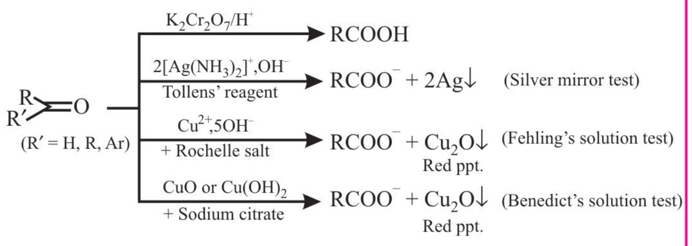
- **Clemmensen reduction**:

$\rangle C = O \xrightarrow[HCl]{Zn-Hg} \rangle CH_2 + H_2O$

- **Wolff–kishner reduction**:

$\rangle C = O \xrightarrow[(ii)\ KOH/ethylene\ glycol]{(i)\ NH_2 - NH_2} \rangle CH_2 + N_2$

- **Oxidation**:



- Aldehydes give positive test with Tollen's reagent Benedict's reagent and Fehling solution while ketones do not give such test.

$RCOCH_3 \xrightarrow{NaOX} RCOONa + CHX_3\ (X = Cl,\ Br,\ I)$

- **Aldol condensation**:
  Condensation of aldehydes and ketones having atleast one α–H atom.

$2\,CH_3CHO \xrightarrow[Aldol\ reaction]{dil.\ NaOH}$

$CH_3CH(OH)CH_2CHO \xrightarrow[\substack{Aldol\\condensation}]{\Delta} CH_3CH{=}CHCHO$

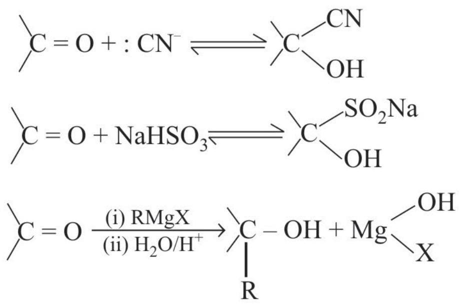
- **Cannizzaro reaction:**
  Aldehydes with no α-hydrogen undergoes, self oxidation and reduction.

$\underset{(No\ \alpha-hydrogen)}{2\,HCHO} \xrightarrow{conc.\ KOH} CH_3OH + HCOOK$

$C_6H_5CHO + HCHO \xrightarrow[\Delta]{OH^-} C_6H_5CH_2OH + HCOONa$

Properties of aldehydes and ketones:

- **Physical state**: Formaldehyde (methanal) is a gas. All other aldehydes and ketones upto C_{11} are colourless volatile liquids. Higher members are solids at room temperature.
- **Odour**: Lower aldehydes have an unpleasant odour. Higher aldehydes and ketones have a pleasant odour.
- **Solubility**: Lower carbonyl compounds are soluble in water due to the formation of hydrogen bonds between the solute and water molecules but solubility decreases with increase in molecular weight due to the hydrophobic nature of the bigger alkyl groups in the higher members.
- **Boiling point**: Boiling point and Melting point $\propto$ Molecular weight $\propto 1/\text{Branching}$
  Boiling points of carbonyl compounds are less than the corresponding alcohols of comparable molecular weight but are higher than corresponding alkanes. The relative boiling points of the carbonyl compounds with the same number of carbon atoms follow the order,
  Amides > Carboxylic acids >> Esters ≈ Acyl chlorides ≈ Ketones ≈ Aldehydes
- **Reactivity**: Reactivity depends on the nature of alkyl group attached to it. Smaller the alkyl group, the more reactive is the compound.
  Reactivity ∝ Magnitude of (+)ve charge on carbon atom of the carbonyl group.
- 40% aqueous solution of HCHO is called formalin. It is used as a disinfectant and antiseptic. It is also used for preserving biological specimen.
- HCHO + Lactose = Formamint used for throat infection.
- **Chemical Reaction**:
  Aldehydes are more reactive than ketones in nucleophilic addition reactions **due to electric and electronic resonance**. These reactions are following:



$\text{Aldehydes} + \text{alcohols} \xrightarrow{dry\ HCl} \text{Acetal}$

$\text{Ketones} + \text{alcohols} \xrightarrow{dry\ HCl} \text{Ketal}$

$\rangle C = O + H_2N - Z \longrightarrow \rangle C = N - Z + H_2O$

(Z = Alkyl, aryl, $-NH_2$, –OH
$-NH-C_6H_5$, $-NHCONH_2$ etc.)

MIND MAP-13

AMINES

Tests for amines (Hinsberg's test)

1° amine + $C_6H_5SO_2Cl \rightarrow$ ppt. soluble in NaOH

2° amine + $C_6H_5SO_2Cl \rightarrow$ ppt soluble in NaOH

3° amine + $C_6H_5SO_2Cl \rightarrow$ No reaction

Classification of amines: Primary, secondary and tertiary on the basis of hydrogen atom (s) replaced by alkyl or aryl group of NH_3
When alkyl groups are similar they are called simple amines and when alkyl groups different they are called mixed.

Preparations:

- Reduction of nitro compounds:

$$RNO_2 \xrightarrow[\text{or } H_2/\text{Pd or LiAlH}_4/\text{ether}]{\text{Sn/HCl or Fe/HCl}} RNH_2$$

- Ammonolysis of alkyl halides:

$$R-X \xrightarrow{NH_3} R-\overset{+}{N}H_3X^- \xrightarrow{NaOH} R-NH_2 + H_2O + N\overset{+}{a}X^-$$

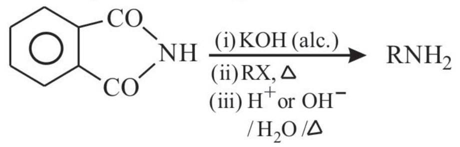
- Reduction of nitriles:

$$R-C\equiv N \xrightarrow[\text{or Na(Hg)}/C_2H_5OH]{H_2/\text{Ni or LiAlH}_4} RCH_2NH_2$$

- Reduction of amides

$$RCONH_2 \xrightarrow[\text{(ii)}H_2O]{\text{(i)}LiAlH_4} R-CH_2NH_2$$

- Gabriel phthalimide synthesis:



* Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

- Hoffmann bromamide degradation reaction:

$$R-CONH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

* The amine formed by this reaction contains

Diazonium Salts

Preparations:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5\overset{+}{N_2}Cl^- + NaCl + 2H_2O$$

Physical Properties: colourless, soluble in water, decompose in dry state, benzene chloride aqueous solution is a good conductor of electricity.

Chemical Properties:

$C_6H_5\overset{+}{N_2}X^-$

- $\xrightarrow{CuX/HX} C_6H_5X$ (Sandmeyer reaction)
- $\xrightarrow{CuCN/KCN} C_6H_5CN$
- $\xrightarrow{Cu+HX} C_6H_5X$ (Gatterman reaction)
- $\xrightarrow{KI} C_6H_5I$
- $\xrightarrow{HBF_4,\Delta} C_6H_5F$ (Balz-Schiemann)
- $\xrightarrow[Cu^+]{H_3PO_2+H_2O} C_6H_6$
- $\xrightarrow{H_2O,\Delta} C_6H_5OH$
- $\xrightarrow{C_6H_5OH,OH^-} C_6H_5-N=N-C_6H_4-OH$
- $\xrightarrow{C_6H_5NH_2,H^+} C_6H_5-N=N-C_6H_4-NH_2$

Physical Properties:

- **Physical state**: Lower aliphatic amines are gases, intermediate members are liquids (Fishy odour), while higher members are solids.
- **Solubility**: Lower aliphatic amines (up to C_6) are soluble in water because of H-bonding, while higher amines (>C_6) are insoluble in water. In general,

$$\text{Solubility} \propto \xrightarrow[\text{Molecular weight}]{1}$$

- **Boiling point**: (a) b.p. of alcohols and carboxylic acids > b.p. of amines > b.p. of alkanes
  (b) b.p. of 1° amine > 2° amine >3° amine

* Primary and secondary amines form intermolecular H-bonds, while tertiary amines do not form inter-molecular H-bonds. As a result, 1° & 2° amines show high b.p. than 3°amines.

* H-bonding in amines is through nitrogen atoms while in alcohols and carboxylic acids, it is through oxygen atoms and nitrogen is less electronegative than oxygen. So H-bonding in amines is weaker than that in carboxylic acids and alcohols.

Chemical Properties:

Basic character: All aliphatic amines are strong bases than NH_3 while aromatic amines are weaker bases than NH_3.

- Factors affect the basicity are: (i) Inductive effect (ii) Solvation effect (iii) Steric hindrance

Thus, the order of basicity of amines is

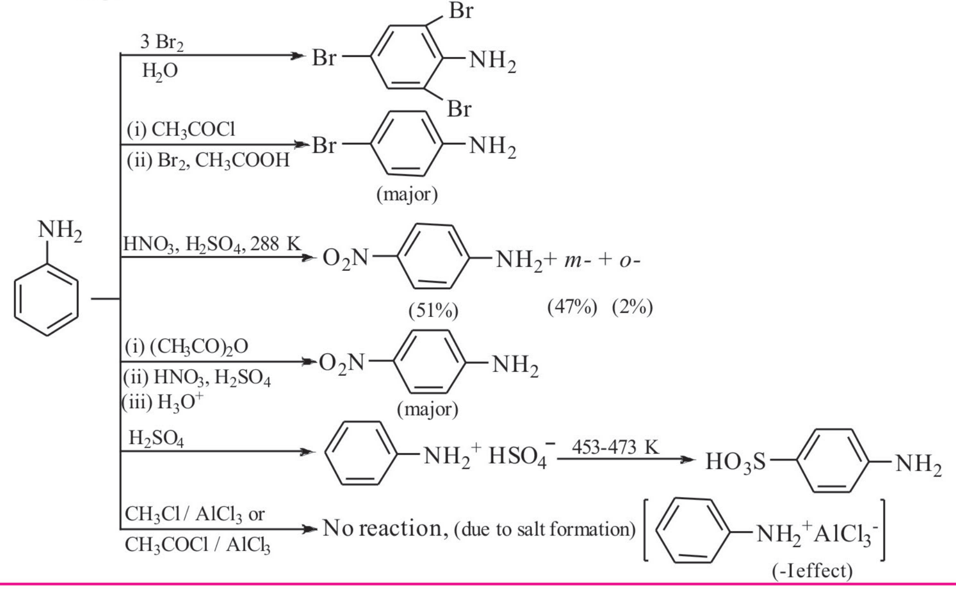
3° amine > 2° amine > 1° amine > NH_3 (In gaseous phase)

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ (In aqueous phase)

$(C_2H_5)_2NH > (C_2H_5)_2N > C_2H_5NH_2 > NH_3$ (In aqueous phase)

R–NH_2

- $\xrightarrow{R'-X} R-NH-R'$
- $\xrightarrow[\text{Carbylamine reaction}]{CHCl_3+KOH} R-NC$ (used as a test of 1° amine)
- $\xrightarrow{HNO_2} R-OH$
- $\xrightarrow{R^1-COCl} R-NH-CO-R^1$
- $\xrightarrow[-HCl]{C_6H_5SO_2Cl} RNHSO_2C_6H_5$ (soluble in NaOH)



MIND MAP-14

BIOMOLECULES

Carbohydrates

Classification

- **Monosaccharides :** cannot be hydrolysed further.
- **Oligosaccharides :** yield two to ten monosaccharides
- **Polysaccharides :** yield a large number of monosaccharide units

Maltose:
- It is prepared by hydrolysis of starch with the enzyme diastase.
- It is **reducing sugar**.
- It hydrolyses into two α-D-glucose molecules in the presence of enzyme maltase.

Lactose:
- It is found in the milk.
- It is a **reducing sugar**.
- Lactose on hydrolysis gives equimolar quantities of β-D-glucose and β-D-glactose.

Sucrose:
- It is obtained commercially from sugarcane or sugar beets.
- It is **non-reducing sugar**.
- Sucrose on hydrolysis gives equimolar mixture of α-D-glucose or β-D-fructose.

Glucose

- Preparation : Sucrose $\xrightarrow{H^+}$ Glucose + Fructose

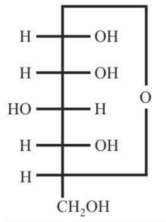
  Starch + $nH_2O \xrightarrow{H^+}$ Glucose
- Chemical Properties

$$\text{Glucose} \xrightarrow{\Delta,\ HI} \text{n-Hexane}$$
$$\text{Glucose} \xrightarrow{NH_2OH} \text{Oxime}$$
$$\text{Glucose} \xrightarrow{Br_2\ /\ Water} \text{Gluconic acid}$$
$$\text{Glucose} \xrightarrow{\text{Acetic anhydride}} \text{Glucosepenta-acetate}$$

Limitations of the Open Chain Structure:

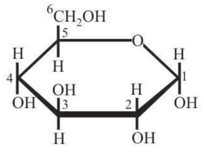
Glucose penta-acetate does not react with hydroxyl amine thus indicating the absence of free –CHO group.

Cyclic Structure of Glucose:



α -D-(+) - Glucose

(Fischer formula)



α -D- Glucopyranose

(Haworth structure)

Starch:
- It is found exclusively in plants as stored as food.
- It is a polymer of α-D-glucose and consists of two components, amylose and amylopectin.
- Amylose–water soluble, constitutes about 15–20% of starch.
  - * It is a long unbranched chain with 200–1000 glucose units.
  - * 1,4–α-glycosidic linkage is present.
- Amylopectin-water insoluble, constitutes about 80-85% of starch.
  - * It is a branched chain polymer of glucose units in which main chain is formed by C1–C4 linkage where branching occurs by C1–C6 glycosidic linkage.

Cellulose:
- It is the chief constituents of the cell walls of plant.
- It contains 1-4 glycosidic linkages.
- Cellulose on hydrolysis gives β-D-glucose.

Glycogen:
- It is commonly known as animal starch.
- Its structure is similar to amylopectin.
- It is present in liver, muscles and brain.

Proteins

Amino acids Classification

- Essential aminoacids: cannot be synthesised in the body.
- Non Essential aminoacids : can be synthesised in the body.

(i) **Essential amino acids :** These are as follows

(a) Leucine (b) Isoleucine (c) Lysine (d) Methionine
(e) Phenylalanine (f) Threonine (g) Tryptophan (h) Valine (i) Histidine

Arginine and histidine are **semi-essential** amino acids i.e. they are partly synthesized in tissues.

(ii) **Non - essential amino acids :** These are as follows

(a) Alanine (b) Aspargine (c) Aspartic acid (d) Cysteine
(e) Glutamic acid (f) Glutamine (g) Hydroxyproline (h) Glycine
(i) Proline (j) Serine (k) Tyrosine (l) Arginine (m) Cystine

Properties

- They are **fairly soluble in water,** but insoluble in non-polar solvents like petroleum ether, benzene, or ether.
- Amino acids have much **larger dipole moments** than simple amines and simple acids.

$H_3N^+-CH_2-COO^-$
Glycine, μ=14D

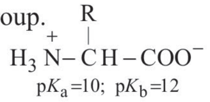
$CH_3CH_2CH_2NH_2$
Propylamine, μ=1.4D

CH_3CH_2COOH
Propanoic acid, μ=1.7D

- Amino acids are **less acidic than most carboxylic acids and less basic than most amines.** In fact, the acidic part of the amino acid molecule is the $-\overset{+}{N}H_3$ group, not a –COOH group, while the basic part of the amino acid is the $-COO^-$ group, and not a free $-NH_2$ group.

$R-COOH$
$pK_a = 5$

$R-NH_2$
$pK_b = 4$



$$H_3\overset{+}{N}-\overset{R}{\overset{|}{C}}H-COO^-$$
pK_a=10; pK_b=12

The above properties point out toward the salt like character (dipolar ion structure) to amino acids. Actually, in the dry state, amino acids exist as **dipolar ions** (also known as **zwitterions** or **inner salts**), a form in which the carboxyl group is present as a carboxylate ion, $—COO^-$, and the amino group as an aminium ion, $—NH_3^+$.

Proteins
- Polymero of α-amino acids
- connected by peptide bond.

Classification
- **Fibrous Protein :** Polypeptide chains run parallel and held together by hydrogen and disulphide bonds e.g kertin, myosin
- **Globular Proteins :** Polypeptide chain is folded, looped and twisted e.g., albumin, haemoglobin.

Structure
- **1° structure :** It is the unique sequence of amino acids in each kind or protein.
- **2° structure :** Exist in two different type α– helix and β- pleated.
- **3° structure :** Overall folding of polypeptide chains
- **4° structure :** Spatial arrangement of subunits (two or more polypetide chain) with respect to each other.

The main forces which stabilise the 2° and 3°structures of proteins are hydrogen bonds, disulphide linkages, vander waals and electrostatic force of attraction.

Denaturation of proteins :

Native protein $\xrightarrow{\text{change in temp, pH}}$ Hydrogen bonds are disturbed

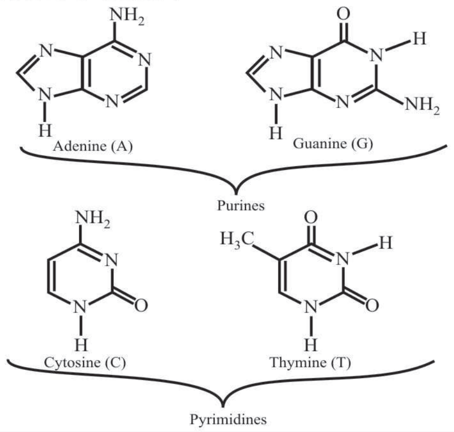
(Protein looses its biological activity)

The denaturation causes change in 2° or 3° structures but 1° structure remains intact.

Nucleic Acids Properties

- Play important role in replication and protein synthesis polymer of nucleotides
- Nucleotide consist of a sugar unit, nitrogeneous base and a phosphate group.
- During formation of dinucleotide or polynucleotide, nucleotide units are joined by.3' – 5' phosphodiester linkages
- Nucleoside : Sugar + base

Structure of bases :



Types of nucleic acid

DNA
- Carries genetic information
- Sugar unit is 2- deoxyribose
- Bases are : adenine, thymine, cytosin and guanine
- It has double stranded structure

In both chains, in between A and T, 2 hydrogen bonds are present while in C and G, 3 H-bonds are present. (A = T) (C°G)

RNA
- Control protein synthesis
- Sugar unit is robose
- Bases are adenine, uracil, cytosin and guanine
- It has single stranded structure

On the basis of their function RNAs mainly are of three types.
Messenger RNA (m-RNA),
Transfer RNA (t-RNA),
Ribosomal RNA (r-RNA)

Vitamins

It has been observed that certain organic compounds are required in small amounts in our diet but their deficiency causes specific diseases. These compounds are called vitamins.

Classification of Vitamins

Vitamins are classified into two groups depending upon their solubility in water or fat.

(i) **Fat Soluble Vitamins :** Vitamins which are soluble in fat and oils but insoluble in water are kept in this group. These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.

(ii) **Water Soluble Vitamins :** B-complex and vitamin C are soluble in water so they are grouped together. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and can not be stored (except vitamin B_{12}) in our body.

Enzymes:

Proteins which are used as catalysts in biochemical reactions are known as biocatalysts (enzymes). Enzymes have following two specific characteristics :

(i) **Specificity of Enzymes:**
(a) Generally one enzyme can catalyze only one biochemical reaction. (b) It can increase rate of reaction upto 10^{20} times.
(ii) **Efficiency of Enzymes:**
(a) One molecule of enzyme can convert millions of substrate molecules into product(s) per second.
eg. Carbonic anhydrase enzyme present in red blood cells has a highest turn over number.
(b) Enzymes are denatured at higher temperature.
(c) Enzymes are very efficient and very specific in nature. The optimum temperature for enzyme activity lies between 40°C to 60°C.

MIND MAP-15

POLYMERS

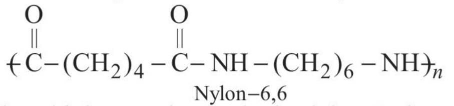
Important Condensation Polymers

i) **Nylons :** Synthetic polyamides are known as nylons

(a) **Nylon-6,6 :** Copolymer of adipic acid (6C) and hexamethylenediamine (6C).

$$n\,\mathrm{HOOC(CH_2)_4COOH} + n\,\mathrm{H_2N(CH_2)_6NH_2} \rightarrow$$

Adipic acid Hexamethylenediamine

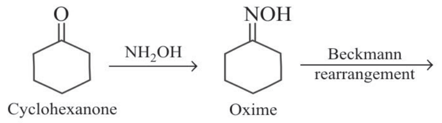


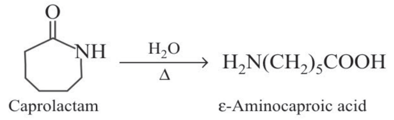
$$\left(\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-NH-(CH_2)_6-NH\right)_n$$

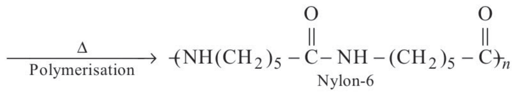
Nylon−6,6

It has high tenacity and elasticity. It is resistant to abrasion and not affected by sea water. It is used for reinforcement of rubber tyres, manufacture of parachute, safety belts, carpets and fabrics.

(b) **Nylon 6 :** Homopolymer of caprolactam (6C)







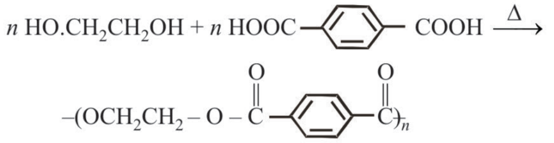
$$\xrightarrow[\text{Polymerisation}]{\Delta} \left(NH(CH_2)_5-\overset{\overset{\displaystyle O}{\|}}{C}-NH-(CH_2)_5-\overset{\overset{\displaystyle O}{\|}}{C}\right)_n$$

Nylon-6

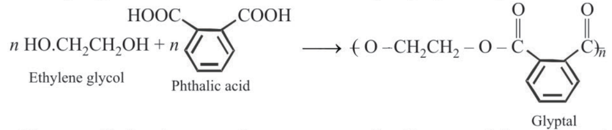
(ii) **Polyesters :** Condensation polymers of a dibasic acid and a diol

(a) **Terylene** (dacron) / Polyethylene terephthalate (PET)

It is resistant to mineral and organic acids. It is used for blending with wool to provide better crease, in safety helmets and aircraft battery boxes.



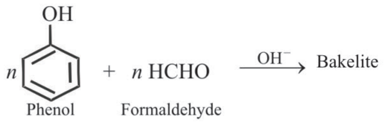
(b) **Glyptal or Alkyd resin** (general name) **:** Condensation polymers of dibasic acids and polyhydroxy alcohols



Cross linked copolymer; used for making good insulators, sheets, rods, switches, lacquers and adherant paints.

(iii) **Thermosetting Resins**

(a) **Bakelite :** Phenol formaldehyde resin



Rubber

Natural rubber (manufactured from rubber latex: It is linear polymer of isoprene (2-methyl-1,3-butadiene)

Vulcanisation of rubber :

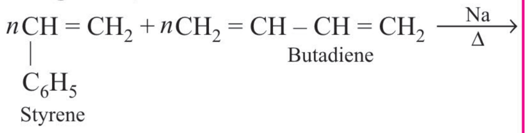
Raw rubber + Sulphur $\xrightarrow[373-415\,K]{\Delta}$

stiffened rubber (cross linked)

Synthetic rubber :

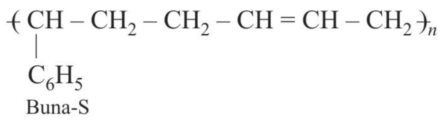
(i) **Buna-S or SBR:**

It is used for manufacture of tyres, floor tiles, gaskets, cable insulators etc.



$$n\underset{\underset{\displaystyle C_6H_5}{|}}{CH}=CH_2 + nCH_2=CH-CH=CH_2 \xrightarrow[\Delta]{Na}$$

Styrene Butadiene

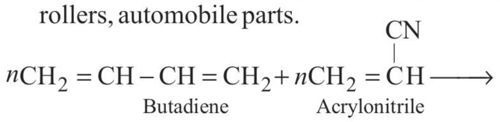


$$\left(\underset{\underset{\displaystyle C_6H_5}{|}}{CH}-CH_2-CH_2-CH=CH-CH_2\right)_n$$

Buna-S

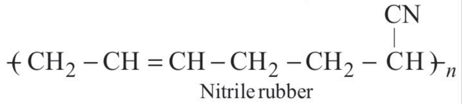
(ii) **Nitrile Rubber (Buna – N):**

Excellent resistant to heat and chemicals. It is used for making conveyer belts, printing rollers, automobile parts.



$$nCH_2=CH-CH=CH_2 + nCH_2=\overset{\overset{\displaystyle CN}{|}}{CH} \longrightarrow$$

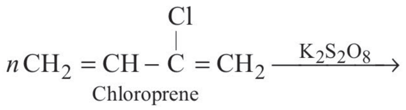
Butadiene Acrylonitrile



$$\left(CH_2-CH=CH-CH_2-CH_2-\overset{\overset{\displaystyle CN}{|}}{CH}\right)_n$$

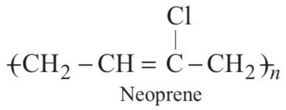
Nitrile rubber

(iii) **Neoprene:**



$$nCH_2=CH-\overset{\overset{\displaystyle Cl}{|}}{C}=CH_2 \xrightarrow{K_2S_2O_8}$$

Chloroprene



$$\left(CH_2-CH=\overset{\overset{\displaystyle Cl}{|}}{C}-CH_2\right)_n$$

Neoprene

Biodegradable polymers

Non-resistent to environmental degradation

(i) PHBV

(ii) Nylon-2-nylon-6

Polymerisation reaction:

•Addition Polymerisation:

Governed by free radical mechanism.

Steps involved:

(a) Chain initiation

(b) Chain Propagating

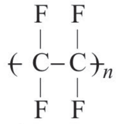
(c) Chain terminating

• Condensation Polymerisation: involves stepwise intermolecular condensation.

Teflon or •Polytetrafluoroethylene(PTFE):

$$n\,CF_2=CF_2 \xrightarrow[\text{Amm. peroxosulphate }(NH_4)_2S_2O_8]{\text{Benzoyl peroxide or}}$$

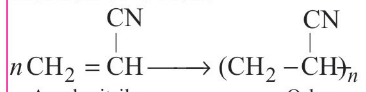
Tetrafluoroethene



$$\left(\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}}-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}}\right)_n$$

It is extremely tough, resistant to heat and chemicals. It is used for making gaskets, pump parts, coating utensils, high frequency insulators.

•Polyacrylonitrile (PAN), Acrilon or Orlon:



$$n\,CH_2=\overset{\overset{\displaystyle CN}{|}}{CH} \longrightarrow \left(CH_2-\overset{\overset{\displaystyle CN}{|}}{CH}\right)_n$$

Acrylonitrile Orlon

It is hard used in preparing clothes and carpets.

Classification

- **Based on Source :**

(a) Natural polymers: protein, cellulose (b) **Semi-synthetic:** cellulose nitrate

(c) Synthetic: PVC, nylon-6, 6

- **Based on structure :**

(a) Linear: Polymers containing the monomeric units linked together to form long straight chains stacked over one another to give packed structure. Such polymers have high tensile strength, high densities, high m.p. and b.p. Examples - fibres and plastics.

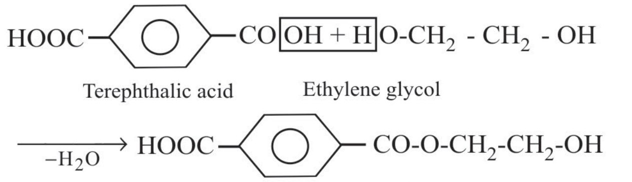
(b) Brached : Long chain of monomer units containing side chains of different lengths form branched polymers. The chains are loosely packed, hence polymers have low density, low m.p. and low tensile strength. Examples - amylopectin and glycogen.

(c) Cross linked: Such polymers have three dimensional network and are hard, brittle and rigid. Examples - bakelite, melamine.

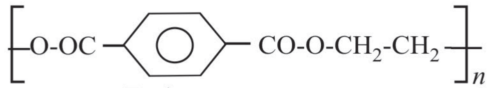
- **Based on Polymerisation :**

(a) Addition Polymers: In addition polymerisation, the unsaturated monomeric molecules undergo repeated addition reactions in the presence of catalysts like O_2, organic peroxides. Some examples of addition polymers are polythene from ethylene, polypropylene from propylene, polyisoprene from isoprene, etc.

(b) Condensation Polymers: Condensation polymerisation normally takes place by repeated condensation of monomeric molecules usually with the elimination of small molecules like water, alcohol, CO_2, HCl, etc. For example, terylene is formed by removal of water molecule from ethylene glycol and terephthalic acid molecules.



This condensation step goes on repeating to form terylene.



Terylene

Condensation is also known as *step growth polymerisation.*

- **Based on Molecular force :**

(a) Elastomers: Here, the intermolecular forces of attraction between the polymer chains are the weakest. They have high degree of elasticity and consist of randomly called molecular chains of irregular shape having a few cross-links. For ex : natural rubber, vulcanized rubber, etc.

(b) Fibres: These polymers have very least stretchability, because the polymeric chains in them are joined together by very strong intermolecular forces like innumerable hydrogen bonds and have sharp melting points. Nylon-6,6 is an important example of this class.

(c) Thermoplastics: Thermoplastic polymers readily become soft on heating and thus can be moulded into required shapes. Some important examples of this class of polymers are polyvinyl chloride, polythene, polypropylene, polystyrene etc.

(d) Thermosetting: They are semi-fluid substances with low molecular masses which when heated become hard and infusible, because of sufficiently large number of cross links. They acquire a shape of three-dimensional network. Important examples of this class of polymers are bakelite, urea formaldehyde resin, etc.

MIND MAP-16

CHEMISTRY IN EVERYDAY LIFE

Drug - Target Interaction:

•**Enzyme as drug targets :** Drugs inhibit the attachment of substrate for their attachment on the active sites of enzymes. Some drugs have the capability to bind allosteric site of the enzyme and changing the shape of active site so that substrate cannot recognise it.

•**Receptors as drug targets :** Drugs that bind to the receptor site and inhibit its natural function (antagonists). These are useful when blocking of message is required. Some drugs mimmic the natural messenger by switching on the receptor (agonists). These are useful when there is lack of natural chemical messenger.

Classification of Drugs:

- **Based on pharmacological effect :** This classification is based on pharmacological effect of the drugs. It is useful for doctors.
- **Based on drug action :** Drugs which act on a particular biochemical process are kept under one class.
- **Based on Chemical Structure :** Drugs having common structural features are grouped together in one class
- **Based on molecular target :** It is based on the interaction with biomolecules such as lipids, proteins, carbohydrates and nucleic acid.

Therapeutic Action of Drugs

- **Antacids :** Antacids are the drugs which neutralize excess acid in the gastric juices and give relief from acid indigestion. They remove the excess acid and raise the pH to appropriate level in stomach. There are mainly weak bases. Examples– $Mg(OH)_2$, $KHCO_3$ Omeprazole,Lansoprazole, Histamine, Cimetidine and Ranitidine.
- **Antihistamines :** Antihistamines are the drugs which diminish the main action of histamine(Chemical substance which cause allergic reactions in body) released in the body and thus prevent the allergic reactions. These are also anti-allergic drugs. Examples diphenhydramine hydrochloride (Banadryl) , Pheniramine maleate (Avil) etc.
- **Tranquilizers :** The chemical substances used to cure mental diseases are called **tranquilizers**.These are used to release mental tension and reduce anxiety.These are the constituents of sleeping pills. They act on higher centres of nervous system. e.g. equanil, serotonin, valium etc.
- **Analgesics :** For relieving pain.
- **Non-narcotic analgesics (non-addictive) :** Aspirin and paracetamol
- **Narcotic analgesics (addictive) :** Morphine, heroin, codeine etc.
- **Antibiotics :** (a) Bactericidal destroy microbes e.g. penicilin, ofloxacin etc.
  (b) Bacteriostatic : Inhibit growth of microbes e.g. Chloramphenicol, erythromycin etc.
- **Spectrum :** The complete range of microorganism that can be killed by a particular antibiotic is known as spectrum. These are of following types:
  (i) Narrow spectrum antibiotics : Streptomycin, Chloromycetin.
  (ii) Broad spectrum antibiotics : Chloramphenicol, Tetracycline.
- **Antiseptics :** May kill or stop growth of microbes e.g. dettol.
- **Antifertility :** Control menstrual cycle and ovulation of females e.g., norethindrone, novestrol etc.

Soaps and Detergents

Detergents:

- Sodium salts of alkylbenzene sulphonic acids.
- **Types of detergents :**

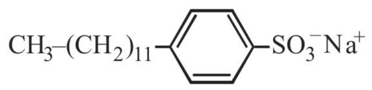
Detergents are of three types :
(i) Anionic detergents
(ii) Cationic detergents
(iii) Non-ionic detergents.

(i) Anionic detergents. These are so called because a large part of their molecules are anions. These are of two types.

(a) Sodium alkyl sulphates :
Example of this type of detergents is : sodium lauryl sulphate,

$C_{11}H_{23}CH_2OSO_3^-Na^+$

(b) Alkyl benzene sulphonates :
Example :
Sodium-4-(1-dodecyl) benzenesulphonate (SDS).

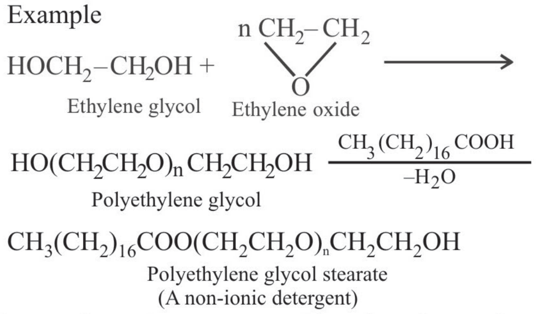


$CH_3-(CH_2)_{11}-C_6H_4-SO_3^-Na^+$

Sod. 4-(dodecyl)benzenesulphonate

(ii) Cationic detergents :
e.g., cetyltrimethylammonium bromide.

(iii) Non-ionic detergents :
Example



$$HOCH_2-CH_2OH + n\,CH_2-CH_2(O) \longrightarrow HO(CH_2CH_2O)_nCH_2CH_2OH \xrightarrow[-H_2O]{CH_3(CH_2)_{16}COOH} CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$$

Ethylene glycol Ethylene oxide

Polyethylene glycol

Polyethylene glycol stearate
(A non-ionic detergent)

•**Cleansing action of detergents:** The cleansing action of detergents are same as that of soaps. For example. A detergents, Sodium lauryl sulphate, $CH_3(CH_2)_{11}CH_2O$--SO_2Na, contains the polar group $-OSO_3^-$ alongwith the long hydrocarbon chains. It is an anionic detergent in which anions associate together to form an ionic micelle. Similarly, Cationic detergent also forms micelle.

Soaps:

- Sodium salts of long chain fatty acids like stearic acid, oleic acid, palmitic acid etc, are called hard soaps and the potassium salts of these fatty acids are called soft soaps
- **Types of Soaps:**
  (a) Toilet soaps
  (b) Floating soaps
  (c) Medicated soaps
  (d) Transparent soaps
  (e) Shaving soaps
  (f) Laundary soaps

Chemicals in Food:

- **Food Additives:** The chemicals, synthetic or natural substances added to food preparations for different purposes as given below are known as food additives.

(i) Nutrients : To increase the nutritive value of the food e.g., carbohydrates, proteins etc.

(ii) Preservatives : To retard spoilage from bacterial action. e.g., $NaNO_2$ and $NaNO_3$ (in meat), C_6H_5COONa (in tomato katchup, fruit juices), Sodium metabisulphite (in pickles), Citric acid (fruit drinks), Sodium propionate (in bread and chease) and SO_2 (in wine and juices).

(iii) Flavouring agents : To enhance the flavour or to develop flavour e.g., alkyl alkanoates (esters), mono-sodium glutamate (MSG), vanillin, cinnamaldehyde.

(iv) Antioxidants : To exclude oxygen to retard or prevent spoilage eg. BHT (Butylated hydroxy toluene) and BHA (Bulylated hydroxy anisole).

(v) Sweetners : To add sweet taste e.g., saccharin, aspartame, sucralose.

Artificial sweetener	Sweetness Value
Aspartame	100
Saccharin	550
Sucralose	600
Alitame	2000

(vi) Colourants : To give colour eg. Amaranth, Kesar etc.