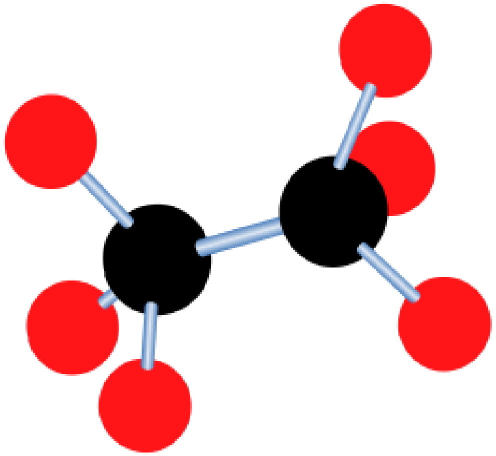


GURUKUL FOR JEE & NEET

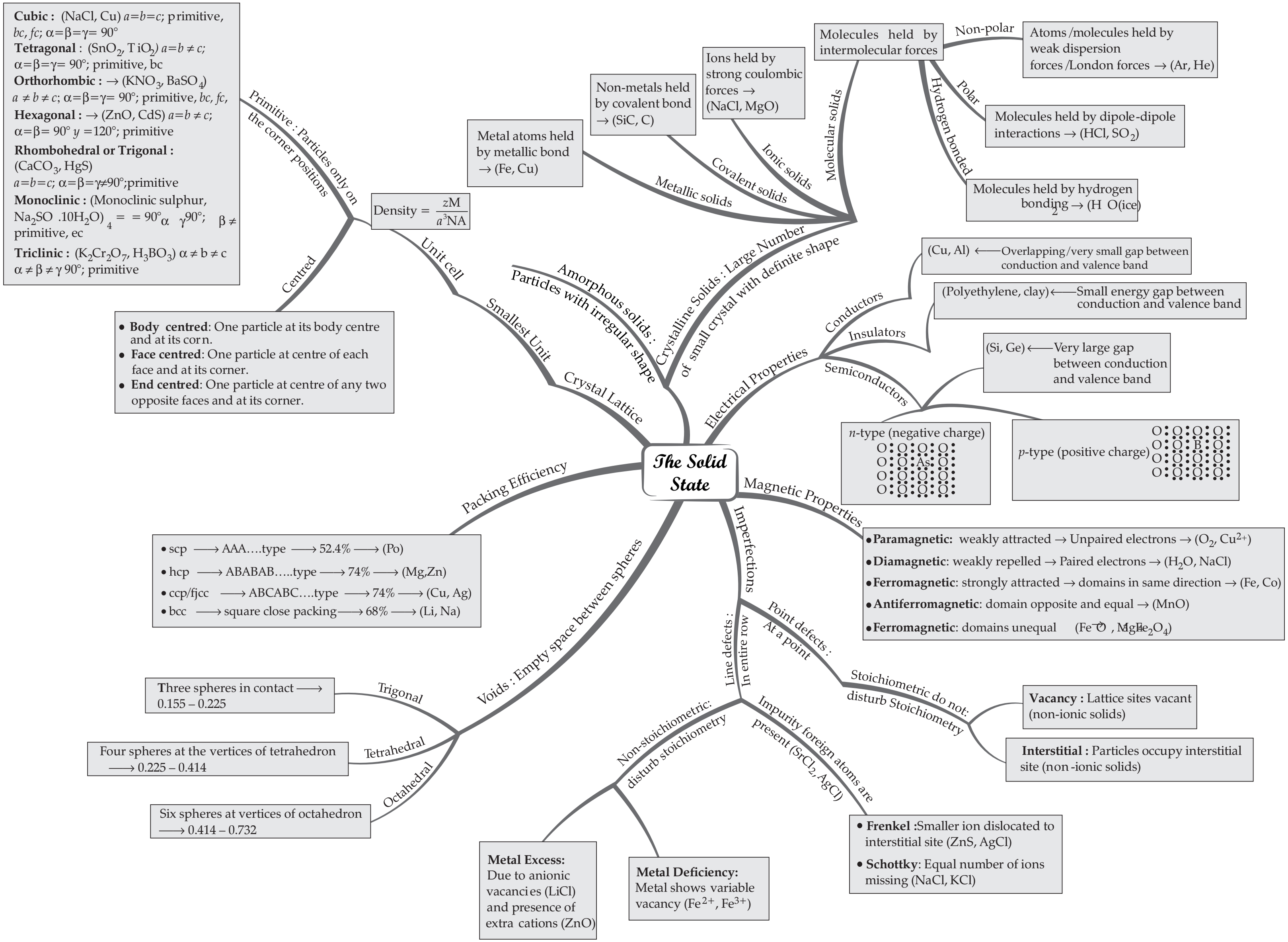
CONCEPT MAP

CHEMISTRY

CLASS 12

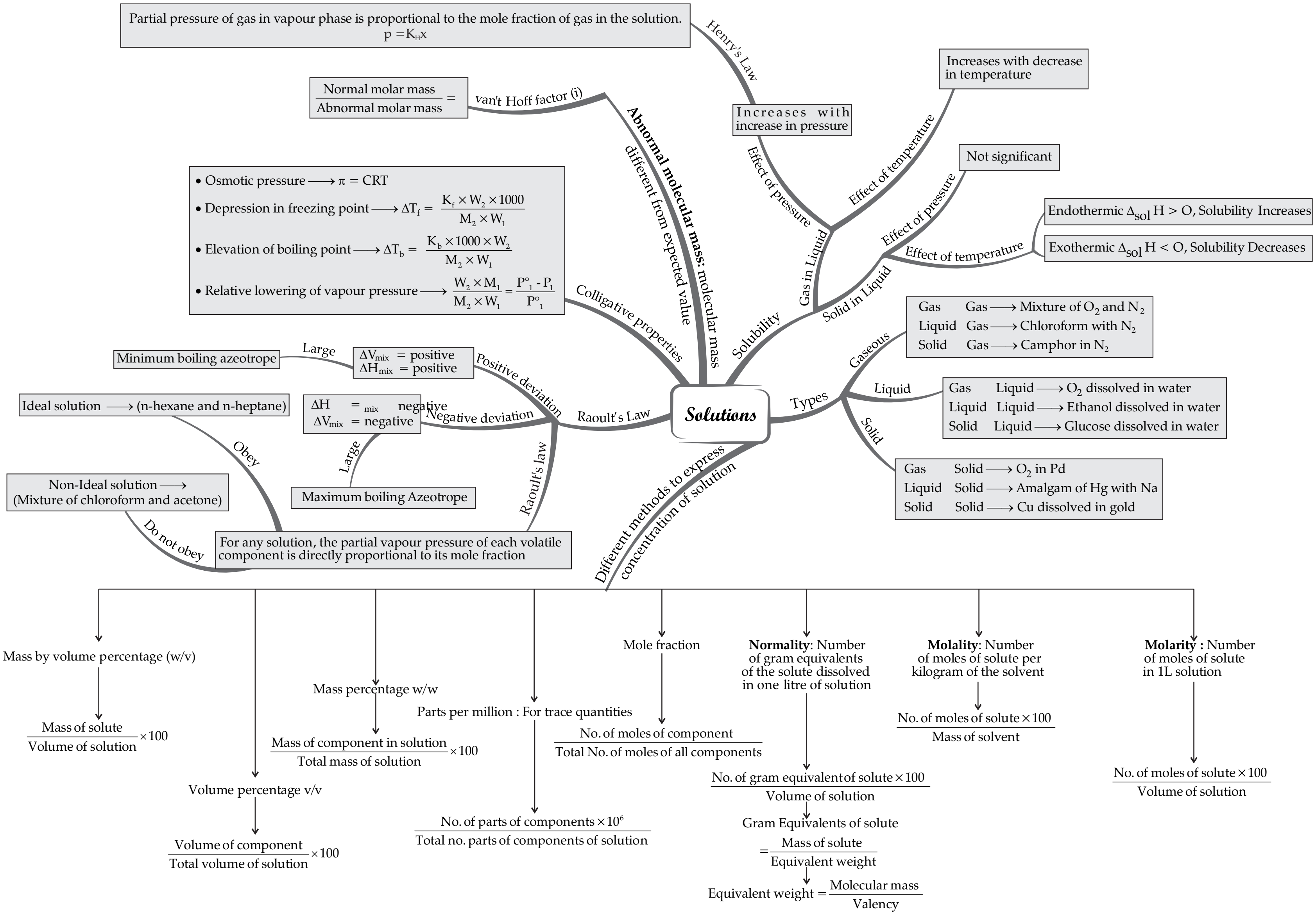
GURUKUL FOR JEE & NEET (GGN.) | WWW.PHYSICSGURUKUL.COM
CONTACT: 7065827902, 8595090558

Chapter 1



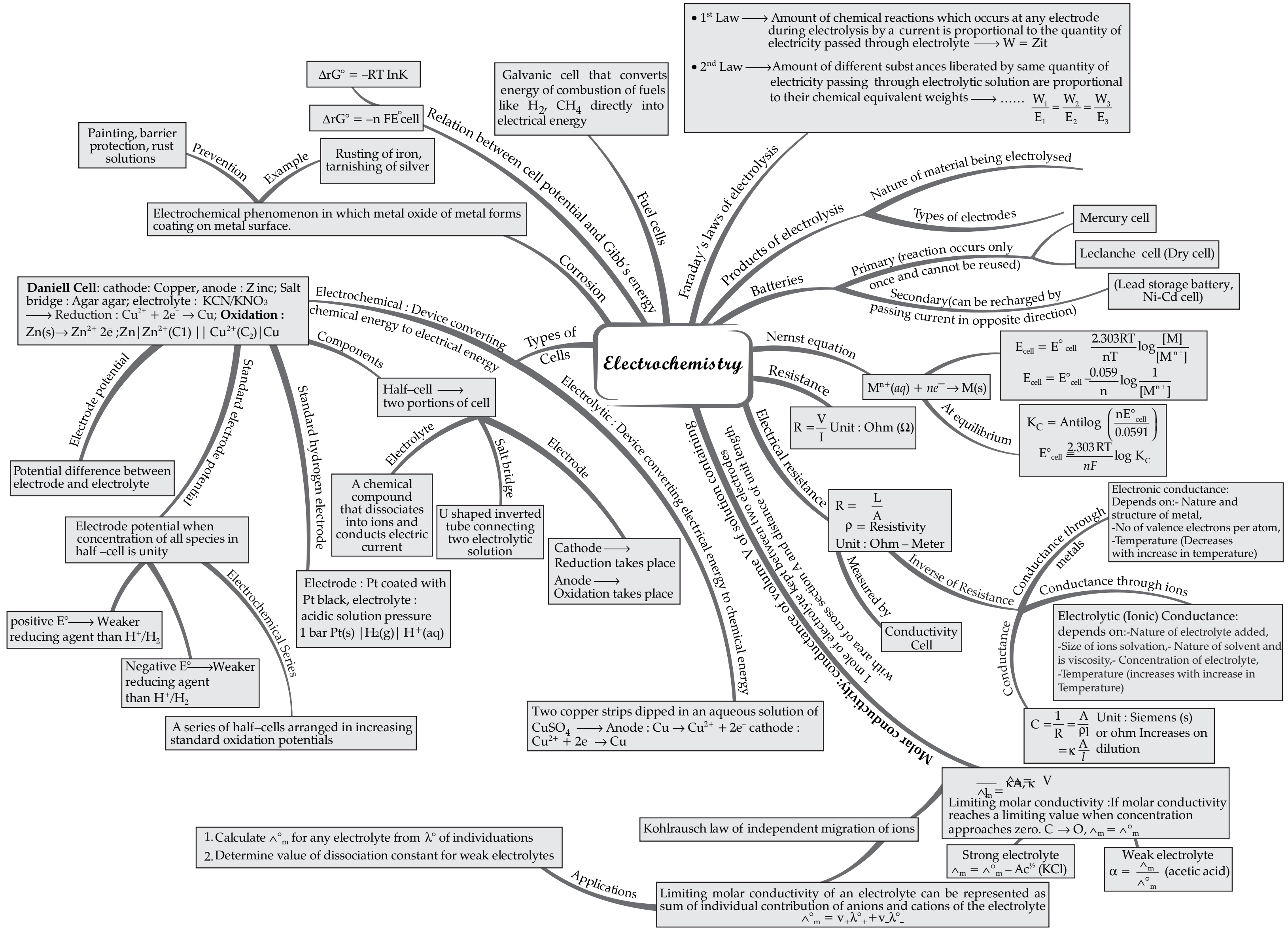
The Solid State
Cubic : (NaCl, Cu) a=b=c; primitive, bc, fc; α=β=γ= 90°
Tetragonal : (SnO2, TiO2) a=b ≠ c; α=β=γ= 90°; primitive, bc
Orthorhombic : → (KNO3, BaSO4) a ≠ b ≠ c; α=β=γ= 90°; primitive, bc, fc,
Hexagonal : → (ZnO, CdS) a=b ≠ c; α=β= 90° γ =120°; primitive
Rhombohedral or Trigonal : (CaCO3, HgS) a=b=c; α=β=γ≠90°;primitive
Monoclinic : (Monoclinic sulphur, Na2SO .10H2O) 4 = = 90° α γ90°; β ≠ primitive, ec
Triclinic : (K2Cr2O7, H3BO3) α ≠ b ≠ c α ≠ β ≠ γ 90°; primitive
Primitive : Particles only on the corner positions
Centred
Body centred: One particle at its body centre and at its corn.
Face centred: One particle at centre of each face and at its corner.
End centred: One particle at centre of any two opposite faces and at its corner.
Density = zM / a³NA
Unit cell
Smallest Unit
Crystal Lattice
Amorphous solids : Particles with irregular shape
Crystalline Solids : Large Number of small crystal with definite shape
Metal atoms held by metallic bond → (Fe, Cu)
Metallic solids
Non-metals held by covalent bond → (SiC, C)
Covalent solids
Ions held by strong coulombic forces → (NaCl, MgO)
Ionic solids
Molecules held by intermolecular forces
Molecular solids
Non-polar
Atoms /molecules held by weak dispersion forces /London forces → (Ar, He)
Polar
Molecules held by dipole-dipole interactions → (HCl, SO2)
Hydrogen bonded
Molecules held by hydrogen bonding → (H2O(ice))
Electrical Properties
Conductors
(Cu, Al) ⟵ Overlapping/very small gap between conduction and valence band
Insulators
(Polyethylene, clay) ⟵ Small energy gap between conduction and valence band
Semiconductors
(Si, Ge) ⟵ Very large gap between conduction and valence band
n-type (negative charge)
As
p-type (positive charge)
B
Magnetic Properties
Paramagnetic: weakly attracted → Unpaired electrons → (O2, Cu2+)
Diamagnetic: weakly repelled → Paired electrons → (H2O, NaCl)
Ferromagnetic: strongly attracted → domains in same direction → (Fe, Co)
Antiferromagnetic: domain opposite and equal → (MnO)
Ferromagnetic: domains unequal (Fe O , MgFe2O4)
Packing Efficiency
scp ⟶ AAA….type ⟶ 52.4% ⟶ (Po)
hcp ⟶ ABABAB…..type ⟶ 74% ⟶ (Mg,Zn)
ccp/fjcc ⟶ ABCABC….type ⟶ 74% ⟶ (Cu, Ag)
bcc ⟶ square close packing ⟶ 68% ⟶ (Li, Na)
Voids : Empty space between spheres
Trigonal
Three spheres in contact ⟶ 0.155 – 0.225
Tetrahedral
Four spheres at the vertices of tetrahedron ⟶ 0.225 – 0.414
Octahedral
Six spheres at vertices of octahedron ⟶ 0.414 – 0.732
Imperfections
Line defects : In entire row
Point defects : At a point
Stoichiometric do not: disturb Stoichiometry
Vacancy : Lattice sites vacant (non-ionic solids)
Interstitial : Particles occupy interstitial site (non -ionic solids)
Impurity foreign atoms are present (SrCl2, AgCl)
Frenkel :Smaller ion dislocated to interstitial site (ZnS, AgCl)
Schottky: Equal number of ions missing (NaCl, KCl)
Non-stoichiometric: disturb stoichiometry
Metal Excess: Due to anionic vacancies (LiCl) and presence of extra cations (ZnO)
Metal Deficiency: Metal shows variable vacancy (Fe2+, Fe3+)

Chapter 2



Solutions
Henry's Law
Partial pressure of gas in vapour phase is proportional to the mole fraction of gas in the solution.
$p = K_H x$
Abnormal molecular mass: molecular mass different from expected value
van't Hoff factor (i)
$\frac{\text{Normal molar mass}}{\text{Abnormal molar mass}} =$
Colligative properties
• Osmotic pressure ⟶ $\pi = CRT$
• Depression in freezing point ⟶ $\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$
• Elevation of boiling point ⟶ $\Delta T_b = \frac{K_b \times 1000 \times W_2}{M_2 \times W_1}$
• Relative lowering of vapour pressure ⟶ $\frac{W_2 \times M_1}{M_2 \times W_1} = \frac{P^\circ_1 - P_1}{P^\circ_1}$
Solubility
Gas in Liquid
Effect of pressure
Increases with increase in pressure
Effect of temperature
Increases with decrease in temperature
Solid in Liquid
Effect of pressure
Not significant
Effect of temperature
Endothermic $\Delta_{sol} H > O$, Solubility Increases
Exothermic $\Delta_{sol} H < O$, Solubility Decreases
Types
Gaseous
Gas Gas ⟶ Mixture of O_2 and N_2
Liquid Gas ⟶ Chloroform with N_2
Solid Gas ⟶ Camphor in N_2
Liquid
Gas Liquid ⟶ O_2 dissolved in water
Liquid Liquid ⟶ Ethanol dissolved in water
Solid Liquid ⟶ Glucose dissolved in water
Solid
Gas Solid ⟶ O_2 in Pd
Liquid Solid ⟶ Amalgam of Hg with Na
Solid Solid ⟶ Cu dissolved in gold
Raoult's Law
Positive deviation
ΔV_{mix} = positive
ΔH_{mix} = positive
Large
Minimum boiling azeotrope
Negative deviation
ΔH_{mix} = negative
ΔV_{mix} = negative
Large
Maximum boiling Azeotrope
Raoult's law
For any solution, the partial vapour pressure of each volatile component is directly proportional to its mole fraction
Obey
Ideal solution ⟶ (n-hexane and n-heptane)
Do not obey
Non-Ideal solution ⟶ (Mixture of chloroform and acetone)
Different methods to express concentration of solution
Mass by volume percentage (w/v)
$\frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$
Volume percentage v/v
$\frac{\text{Volume of component}}{\text{Total volume of solution}} \times 100$
Mass percentage w/w
$\frac{\text{Mass of component in solution}}{\text{Total mass of solution}} \times 100$
Parts per million : For trace quantities
$\frac{\text{No. of parts of components} \times 10^6}{\text{Total no. parts of components of solution}}$
Mole fraction
$\frac{\text{No. of moles of component}}{\text{Total No. of moles of all components}}$
Normality: Number of gram equivalents of the solute dissolved in one litre of solution
$\frac{\text{No. of gram equivalent of solute} \times 100}{\text{Volume of solution}}$
Gram Equivalents of solute
$= \frac{\text{Mass of solute}}{\text{Equivalent weight}}$
Equivalent weight $= \frac{\text{Molecular mass}}{\text{Valency}}$
Molality: Number of moles of solute per kilogram of the solvent
$\frac{\text{No. of moles of solute} \times 100}{\text{Mass of solvent}}$
Molarity : Number of moles of solute in 1L solution
$\frac{\text{No. of moles of solute} \times 100}{\text{Volume of solution}}$

Chapter 3



Electrochemistry
Relation between cell potential and Gibb's energy
$\Delta rG^\circ = -RT \ln K$
$\Delta rG^\circ = -nFE^\circ cell$
Fuel cells
Galvanic cell that converts energy of combustion of fuels like H_2, CH_4 directly into electrical energy
Faraday's laws of electrolysis
• 1st Law ⟶ Amount of chemical reactions which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through electrolyte ⟶ W = Zit
• 2nd Law ⟶ Amount of different substances liberated by same quantity of electricity passing through electrolytic solution are proportional to their chemical equivalent weights ⟶ …… $\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3}$
Products of electrolysis
Nature of material being electrolysed
Types of electrodes
Batteries
Primary (reaction occurs only once and cannot be reused)
Mercury cell
Leclanche cell (Dry cell)
Secondary(can be recharged by passing current in opposite direction)
(Lead storage battery, Ni-Cd cell)
Corrosion
Electrochemical phenomenon in which metal oxide of metal forms coating on metal surface.
Prevention
Painting, barrier protection, rust solutions
Example
Rusting of iron, tarnishing of silver
Types of Cells
Electrochemical : Device converting chemical energy to electrical energy
Daniell Cell: cathode: Copper, anode : Zinc; Salt bridge : Agar agar; electrolyte : KCN/KNO3 ⟶ Reduction : $Cu^{2+} + 2e^- \rightarrow Cu$; Oxidation : $Zn(s) \rightarrow Zn^{2+}\ 2\bar{e}$; $Zn|Zn^{2+}(C1)\ ||\ Cu^{2+}(C_2)|Cu$
Components
Half–cell ⟶ two portions of cell
Electrolyte
A chemical compound that dissociates into ions and conducts electric current
Salt bridge
U shaped inverted tube connecting two electrolytic solution
Electrode
Cathode ⟶ Reduction takes place
Anode ⟶ Oxidation takes place
Electrode potential
Potential difference between electrode and electrolyte
Standard electrode potential
Electrode potential when concentration of all species in half –cell is unity
positive E° ⟶ Weaker reducing agent than H^+/H_2
Negative E° ⟶ Weaker reducing agent than H^+/H_2
Electrochemical Series
A series of half–cells arranged in increasing standard oxidation potentials
Standard hydrogen electrode
Electrode : Pt coated with Pt black, electrolyte : acidic solution pressure 1 bar Pt(s) $|H_2(g)|\ H^+(aq)$
Electrolytic : Device converting electrical energy to chemical energy
Two copper strips dipped in an aqueous solution of $CuSO_4$ ⟶ Anode : $Cu \rightarrow Cu^{2+} + 2e^-$ cathode : $Cu^{2+} + 2e^- \rightarrow Cu$
Nernst equation
$M^{n+}(aq) + ne^- \rightarrow M(s)$
$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nT} \log \frac{[M]}{[M^{n+}]}$
$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$
At equilibrium
$K_C = \text{Antilog}\left(\frac{nE^\circ_{cell}}{0.0591}\right)$
$E^\circ_{cell} = \frac{2.303RT}{nF} \log K_C$
Resistance
$R = \frac{V}{I}$ Unit : Ohm (Ω)
Electrical resistance
$R = \rho\frac{L}{A}$
ρ = Resistivity
Unit : Ohm – Meter
Measured by
Conductivity Cell
Inverse of Resistance
Conductance
Conductance through metals
Electronic conductance: Depends on:- Nature and structure of metal, -No of valence electrons per atom, -Temperature (Decreases with increase in temperature)
Conductance through ions
Electrolytic (Ionic) Conductance: depends on:-Nature of electrolyte added, -Size of ions solvation,- Nature of solvent and is viscosity,- Concentration of electrolyte, -Temperature (increases with increase in Temperature)
$C = \frac{1}{R} = \frac{A}{\rho l} = \kappa\frac{A}{l}$ Unit : Siemens (s) or ohm Increases on dilution
Molar conductivity: conductance of volume V of solution containing 1 mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length
$\wedge_m = \kappa A, \kappa V$
Limiting molar conductivity :If molar conductivity reaches a limiting value when concentration approaches zero. $C \rightarrow O$, $\wedge_m = \wedge^\circ_m$
Strong electrolyte $\wedge_m = \wedge^\circ_m - Ac^{1/2}$ (KCl)
Weak electrolyte $\alpha = \frac{\wedge_m}{\wedge^\circ_m}$ (acetic acid)
Kohlrausch law of independent migration of ions
Limiting molar conductivity of an electrolyte can be represented as sum of individual contribution of anions and cations of the electrolyte $\wedge^\circ_m = v_+\lambda^\circ_+ + v_-\lambda^\circ_-$
Applications
1. Calculate $\wedge^\circ_m$ for any electrolyte from λ° of individuations
2. Determine value of dissociation constant for weak electrolytes

Chapter 4

Chemical Kinetics

Collision Theory: Rate of reaction depends on the collision frequency and effective collisions.

Effective Collision

Collision in which molecules collide with sufficient kinetic energy and proper orientation for breaking of bonds and formation of new bonds.

Rate = $PZ_{AB}e^{-Ea/RT}$
P is Steric or Probability factor

E_a and proper orientation of the molecules determine the criteria for an effective collision.

Collision Frequency

Number of collisions per unit volume of reaction mixture
Rate = $Z_{AB}\ e^{-Ea/RT}$

Arrhenius Equation

Activation Energy, E_a
: Energy required to form an intermediate called activated complex (c)
E_a = Threshold energy - Average Kinetic energy of reacting molecules

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

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

$\log \frac{k2}{k1} = \frac{E_a}{2.303RT}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

Integrated Rate Equation

Integration of differential rate equation to give a relation between concentrations at different times and rate constant.

Order	Integrated Rate Law	Straight Plot	Units (K)
0	$kt = [R]_0 - [R]$	[R] vs t	mol $L^{-1}s^{-1}$
1	$kt = \ln \{[R]_0/[R]\}$	In[R] vs t	s^{-1}

Pseudo First Order Reaction

- Are not truly of first order but under certain conditions behave as first order reaction
- Acid hydrolysis of ethyl acetate
- Inversion of sugar

Half-life Of A Reaction

Time in which the concentration of a reactant is reduced to one half of its initial concentration

1st Order: $t_{1/2} = \frac{0.693}{K}$

0 Order: $t_{1/2} = \frac{[R]_0}{2K}$

Molecularity Of A Reaction

Number of reacting species taking part in an elementary reaction colliding to bring out a reaction.

Order Of A Reaction

Sum of powers of concentration of the reactants in the rate law.

Rate Of Chemical Reaction

Change in concentration of reactants or products in unit time; Unit : mol $L^{-1}s^{-1}$ or atm s^{-1}

Average Rate:

Appearance of products or disappearance of reactants over a long time interval.

$r_{av} = \frac{d[P]}{dt}$ = slope

$r_{av} = \frac{-d[R]}{dt}$ = –slope

Instantaneous Rate

Rate of change in concentration of reactant/product at a particular time

$r_{inst} = \frac{-d[R]}{dt} = \frac{+d[P]}{dt}$

$R \rightarrow P$

Rate of disappearance of R $= \frac{\text{Decease in concentration of R}}{\text{Time taken}} = \frac{-\triangle[R]}{\triangle t}$

Rate of appearance of P $= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = \frac{+\triangle[P]}{\triangle t}$

Factors Influencing

Concentration : Higher the concentration of reactants, faster is the rate of reaction
Temperature : Increases with increase in temperature. becomes almost double with 10°C rise.
Presence of Catalyst : Increases with a catalyst.
Surface Area : Greater is the surface area, faster is the rate of reaction.
Activation Energy : Lower the activation energy, faster is the reaction.

Rate Law

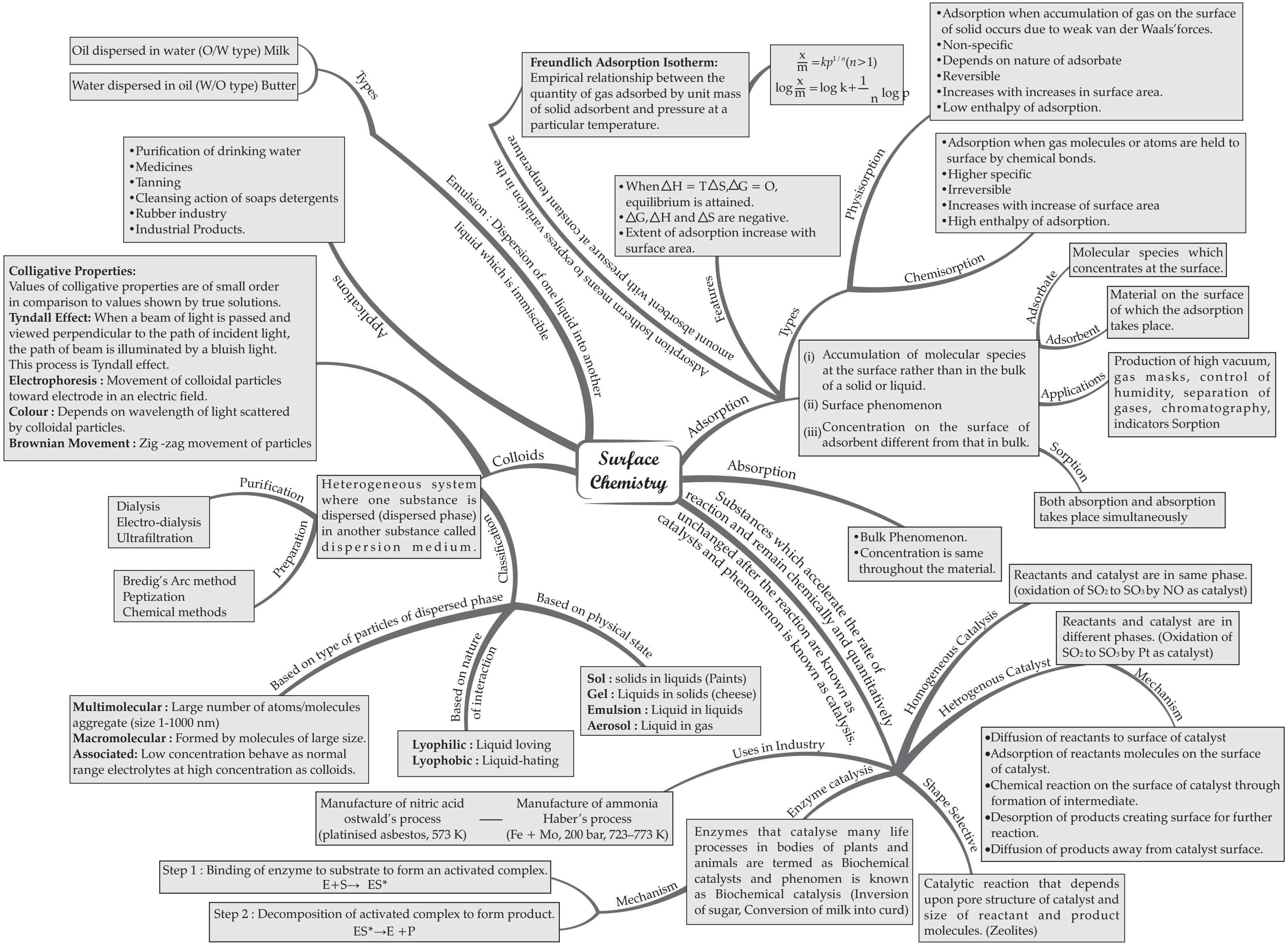
Expression in which reaction rate in given in terms of molar concentration of reactants with each term raised to power which may or may not be same as stoichiometric coefficient of reactants in a balanced chemical equation. $aA + bB — cC + dD$

Rate = $K[A]^x[B]^y = \frac{d[R]}{dt}$

Rate Constant: Rate of a reaction when concentration of each of the reactant in unity.

Order	Unit
0	$molL^{-1}s^{-1}$
1	s^{-1}
2	$mol^{-1}Ls^{-1}$

Chapter 5



Surface Chemistry
Adsorption
(i) Accumulation of molecular species at the surface rather than in the bulk of a solid or liquid.
(ii) Surface phenomenon
(iii) Concentration on the surface of adsorbent different from that in bulk.
Types
Physisorption
•Adsorption when accumulation of gas on the surface of solid occurs due to weak van der Waals' forces.
•Non-specific
•Depends on nature of adsorbate
•Reversible
•Increases with increases in surface area.
•Low enthalpy of adsorption.
Chemisorption
•Adsorption when gas molecules or atoms are held to surface by chemical bonds.
•Higher specific
•Irreversible
•Increases with increase of surface area
•High enthalpy of adsorption.
Adsorbate
Molecular species which concentrates at the surface.
Adsorbent
Material on the surface of which the adsorption takes place.
Applications
Production of high vacuum, gas masks, control of humidity, separation of gases, chromatography, indicators Sorption
Sorption
Both absorption and absorption takes place simultaneously
Features
•When $\Delta H = T\Delta S, \Delta G = O$, equilibrium is attained.
•$\Delta G, \Delta H$ and ΔS are negative.
•Extent of adsorption increase with surface area.
Adsorption Isotherm means to express variation in the amount absorbent with pressure at constant temperature
Freundlich Adsorption Isotherm:
Empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.
$\frac{x}{m} = kp^{1/n} (n>1)$
$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$
Absorption
•Bulk Phenomenon.
•Concentration is same throughout the material.
Colloids
Heterogeneous system where one substance is dispersed (dispersed phase) in another substance called dispersion medium.
Emulsion : Dispersion of one liquid into another liquid which is immiscible
Types
Oil dispersed in water (O/W type) Milk
Water dispersed in oil (W/O type) Butter
Applications
•Purification of drinking water
•Medicines
•Tanning
•Cleansing action of soaps detergents
•Rubber industry
•Industrial Products.
Colligative Properties:
Values of colligative properties are of small order in comparison to values shown by true solutions.
Tyndall Effect: When a beam of light is passed and viewed perpendicular to the path of incident light, the path of beam is illuminated by a bluish light. This process is Tyndall effect.
Electrophoresis : Movement of colloidal particles toward electrode in an electric field.
Colour : Depends on wavelength of light scattered by colloidal particles.
Brownian Movement : Zig -zag movement of particles
Purification
Dialysis
Electro-dialysis
Ultrafiltration
Preparation
Bredig's Arc method
Peptization
Chemical methods
Classification
Based on type of particles of dispersed phase
Multimolecular : Large number of atoms/molecules aggregate (size 1-1000 nm)
Macromolecular : Formed by molecules of large size.
Associated: Low concentration behave as normal range electrolytes at high concentration as colloids.
Based on nature of interaction
Lyophilic : Liquid loving
Lyophobic : Liquid-hating
Based on physical state
Sol : solids in liquids (Paints)
Gel : Liquids in solids (cheese)
Emulsion : Liquid in liquids
Aerosol : Liquid in gas
Substances which accelerate the rate of reaction and remain chemically and quantitatively unchanged after the reaction are known as catalysts and phenomenon is known as catalysis.
Homogeneous Catalysis
Reactants and catalyst are in same phase. (oxidation of SO_2 to SO_3 by NO as catalyst)
Hetrogenous Catalyst
Reactants and catalyst are in different phases. (Oxidation of SO_2 to SO_3 by Pt as catalyst)
Mechanism
•Diffusion of reactants to surface of catalyst
•Adsorption of reactants molecules on the surface of catalyst.
•Chemical reaction on the surface of catalyst through formation of intermediate.
•Desorption of products creating surface for further reaction.
•Diffusion of products away from catalyst surface.
Shape Selective
Catalytic reaction that depends upon pore structure of catalyst and size of reactant and product molecules. (Zeolites)
Enzyme catalysis
Enzymes that catalyse many life processes in bodies of plants and animals are termed as Biochemical catalysts and phenomen is known as Biochemical catalysis (Inversion of sugar, Conversion of milk into curd)
Mechanism
Step 1 : Binding of enzyme to substrate to form an activated complex. $E+S \rightarrow ES^*$
Step 2 : Decomposition of activated complex to form product. $ES^* \rightarrow E + P$
Uses in Industry
Manufacture of nitric acid ostwald's process (platinised asbestos, 573 K)
Manufacture of ammonia Haber's process (Fe + Mo, 200 bar, 723–773 K)

Chapter 6

General Principles and Processes of Isolation of Elements

Extraction of copper from cuprous oxide

Roasting/smelting

$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

$Cu_2O + C \longrightarrow 2Cu + CO$

$FeO + SiO_2 \longrightarrow FeSiO_3$

$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$

$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$ (Blister copper)

Extraction of iron from oxides

$\longrightarrow$ In blast furnace

$FeO_{(s)} + C_{(s)} \longrightarrow Fe_{(s/l)} + CO_{(g)}$

$\longrightarrow$ Reduction

(a) At 500 – 883 K

$2Fe_2O_3 + 3CO \xrightarrow{573-673K} 2Fe_3O_4 + CO_2\uparrow$

$Fe_3O_4 + 4CO \xrightarrow{773-883K} 3Fe + 4CO_2\uparrow$

$Fe_2O_3 + CO \xrightarrow{773-873K} 2FeO + CO_2\uparrow$

(b) At 900 – 1500K

$CO_2 + C \rightarrow 2CO(g)$; $FeO + CO \rightarrow Fe + CO_2$

$CaCO_3 + CaO \rightarrow CO_2$; $CaO + SiO_2 \rightarrow CaSiO_3$

(c) At 1500 – 2100 K

$C + O_2 \rightarrow CO_2$

$FeO + C \rightarrow Fe + CO$

Thermodynamic principles of metallurgy

$\Delta G = \Delta H - T\Delta S$

- If ΔG is negative, reaction proceeds.
- If reactions and products of two reactions are put together in a system and net ΔG of the two possible reactions is –ve, the overall reaction will occur.

$\Delta G^\circ = -RT \ln K$

Ellingham diagram

- Plots of $\Delta_f G^\circ$ vs T for reaction.
- Straight line except with some change in phase
- Point in a curve below which ΔG is –ve.

Minerals naturally occurring chemical substances in the earth's crust obtainable by mining.

Ores : Minerals from which metal can be extracted chiefly, profitably and easily

- Bauxite $AlO_x(OH)_{3-2x}$ where $0 < x < 1$
- Kaolinite $[Al_2(OH)_4 Si_2O_5]$
- Haematite Fe_2O_3
- Magnetite Fe_3O_4
- Siderite $FeCO_3$
- Copper pyrites $CuFeS_2$
- Malachite $CuCO_3.Cu(OH)_2$
- Cuprite Cu_2O
- Copper glance Cu_2S
- Zinc blende ZnS
- Calamine $ZnCO_3$
- Zincite ZnO

Metallurgy: Entire scientific and technological process used for isolation of the metal from its ores.

- Concentration of ore
- Isolation of metal
- Purification of metal

Concentration of Ores

Hydraulic washing : Based on difference in gravities of the ore and gangue particles

Upward stream of running water is used to wash the powdered ore. Lighter gangue particles are washed away and heavier are left behind.

Magnetic Separation : Based on differences in magnetic properties of ore components

Finely ground ore is carried on conveyor belt which passes over a magnetic roller. Magnetic particles fall nearer to roller and vice versa.

Froth floatation process : Based on the difference in wetting properties of gangue and ore particles

Powdered ore is mixed with pine oil and water and agitated with air froth formed carries minerals is skimmed off and dried.

Leaching : Based on the solubility of ore in suitable solvent

Bayer's process :

$Al_2O_3.2H_2O + 2NaOH + H_2O \longrightarrow 2Na[AL(OH)_4] + CO_2 \longrightarrow Al_2O_3.xH_2O + 2NaHCO_3 \xrightarrow{1470K} Al_2O_3 + xH_2O$

Extraction of zinc from zinc oxide

$ZnO + C \xrightarrow[1673K]{Coke} Zn + CO$

Electrochemical principles of metallurgy

Electrolysis :Difference of two E° values equals + ve E° and –ve ΔG°, less reactive metal will come out of solution and more reactive to the solution.

Metallurgy of aluminum

Purified Al_2O_3 mixed with Na_3AlF_6 / CaF_2

Fused matrix is electrolysed

Electrolysis (Hall–Heroult process)

$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$

Cathode : $Al^{3+}(melt) + 3e^- \longrightarrow Al_{(l)}$

Anode : $C_{(s)} + O^{2-}(melt) \longrightarrow CO(g) + 2e^-$

$C_{(s)} + 2O^{2-}(melt) \longrightarrow CO_2(g) + 4e^-$

Oxidation reduction (extraction of Cl from brine)

Uses

- Al
  - As wrappers for chocolates
  - Fine dust in paints and lacquers
  - Extraction of Cr and Mn
  - Wires
- Cu
  - Wires
  - Water and steam pipes
  - Alloys
- Zn
  - Galvanising iron
  - In batteries
  - Dust is used as reducing agent
- Fe
  - Cast iron for casting stoves, railway slippers, gutter pipes, toys etc.
  - Manufacture of wrought iron and steel.

Extraction of crude metal from concentrated ore

Reduction of oxide to metal:

Heating metal oxide with substances acting as a reducing agent which combines with the oxygen to get reduced easily.

Conversion to oxide

- Calcination: Heating when the volatile matter escapes leaving behind the metal oxide.
- Roasting: Ore is heated in a limited supply of air in a furnace at a temperature below the melting point of the metal.

Refining

Distillation : Impure metal is evaporated to obtain pure metal as distillate.
Liquation : Low melting metals made to flow on a sloping surface.
Electrolytic refining : Impure metal anode, strip of same metal in pur form–cathode dipped in soluble salt of same metal.
Zone refining : Based on principle that impurities are more soluble in melt than in solid state of metal.
Vapour phase refining : Metal is converted into its volatile compound and collected elsewhere.
Chromatography : Based on principle that different components of a mixture are differentially adsorbed on an adsorbent.

Chapter 7

The p- Block Elements

Group 18 Elements

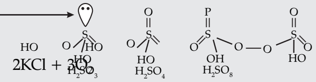
- **Occurrence :** All except radon occur in atmosphere
- **Electronic configuration :** $ns^2 np^6$ except He
- **IE :** High
- **Atomic radii :** Increases down group
- **Electron gain enthalpy :** Largely positive

Physical properties : Monoatmic, colourless, odorless and tasteless. Sparingly soluble in water.

- **M.P. and B.P. :** Low
- **Chemical properties :** Least reactive xenonefluorine compound : XeF_2, XeF_4 and XeF_6.
- **Xenone oxygen compounds :** XeO_3, $XeOF_2$, $XeOF_4$

Group 16 Elements

- Electronic configuration : ns^2np^4
- Atomic and ionic radii : Increase down the group
- IE : Decreases down the group
- Electron Gain enthalpy : O hass less–ve than S.
- Electro-negativity : Decreases with increase in atomic number
- Physical properties : O and S are non metals, Se and Te metalloids whereas Po is a metal. All exhibit allotropy
- M.P. and B.P. : Increases down the group
- Chemical properties : variable
  - ✓ Reactivity with hydrogen : stable hydrides
  - ✓ Reactivity with halogens : $F^- > Cl^- > Br^- > I^-$
- Oxoacids of S :



- Dioxygen (O_2) :

Preparation : $2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$

Properties : Colourless and odourless gas

$2Ca + O_2 \longrightarrow 2CaO;\ 4Al + 3O_2 \longrightarrow 2AlO_3$

$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$ $\quad 4HCl + O_2 \xrightarrow{CuCl_2} 2Cl + 2H_2O$

Group 17 Elements

- Occurrence : F and Cl are fairly abundant while Br and I less so
- Electronic configuration : ns^2np^5
- Atomic Ionic radii : Smallest in periods but increases from F to I
- IE : Decreases down the group
- Electron gain enthalpy : Less –ve down the group
- Electro-negativity : High, decreases down the group
- Physical properties : F and Cl are gases, Br is liquid and I solid
- M.P. and B.P. : Increases with atomic number
- Chemical properties :

All exhibit – 1 oxidation state Cl, Br and I exhibit + 1, + 3, + 5 and + 7.O.N
Reactivity towards hydrogen : H – F > H – Cl > H – Br > H – I
Reactivity towards oxygen : F form OF_2 (stable) and O_2F_2
Reactivity towards metals : MF > MCl > MBr > MI
Reactivity towards other halogens : Forms XX′, XX_3^1, XX_5^1 and XX'_7.

- Chlorine :

Preparation : $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$
Deacon's process : $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$
Properties : Greenish yellow gas with pungent and suffocating odour. Heavier than air

$2Al + 3Cl_2 \longrightarrow 2AlCl_3$
$H_2 + Cl_2 \longrightarrow 2HCl$
$H_2S + Cl_2 \longrightarrow 2HCl + S$
$8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$
$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$
(cold and dilute)
$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$
$CH_4 + Cl_2 \xrightarrow{uv} CH_3Cl + HCl$
$C_2H_4 + Cl_2 \xrightarrow{RT} C_2H_4Cl_2$
$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$
$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$
$Cl_2 + H_2O \longrightarrow 2HCl + 0$

Inter-halogen compounds: XX′– sp^3(linear), $XX'_3 sp^3d$ (T–shaped), $XX_5^1\ sp^3d^2$ (square pyramidal), $XX_7^1\ sp^3d^3$ (Pentagonal bipyramidal)

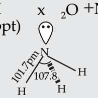
Group 15 Elements

- Electronic configuration : ns^2np^3
- Elements : $_7N$, $_{15}P$, $_{33}As$, $_{51}Sb$, $_{83}Bi$
- Atomic and Ionic radii : Increase in size down the group.
- Ionization enthalpy : Decreases down the group due to gradual increase in atomic size.
- Electro-negativity : Decreases down the group with increasing atomic size.
- Physical properties : Polyatomic, metallic character increases down the group. N and P are non-metals, As and Sb metalloids and Bi metal. B.P increases top to bottom and M.P. increases upto As and then decreases upto Bi. Except Ni all show allotropy
- Chemical properties : Common O.N : –3, +3 and +5. Nitrogen shows anomalous behaviour.
- Dinitrogen preparation :

•In laboratory :
$NH_4Cl + NaNO_2 \longrightarrow N_2 + 2H_2O + NaCl$
•Thermal decomposition :
$(NH_4)_2Cr_2O_7 \xrightarrow{Heat} N_2 + 4H_2O + Cr_2O_3$
$Ba(N_3)_2 \longrightarrow Ba + 3N_2$
•Properties :
Colourless, odourless, tasteless and non-toxic gas
$6Li + N_2 \xrightarrow{\Delta} 2Li_3N$
$3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$
$N_2 + 3H_2 \xrightarrow{773\,K} 2NH_3\ \Delta_fH^\circ = 46.1\ KJ\ mol^{-1}$
$N_2 + O_2 \xrightarrow{\Delta} 2NO$

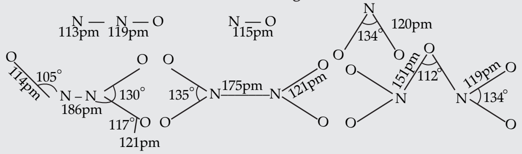
- Ammonia Preparation :

$NH_4CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$
$N_2 + 3H_2 \rightleftharpoons 2NH_3\ \ \Delta_fH^\circ = -46.1\ KJ\ mol^{-1}$
Properties :
Colourless with pungent odour, soluble in water
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 + (NH_4)SO_4$
(white ppt)
$FeCl_3 + NH_4OH \longrightarrow Fe_2O_3.\ H\ x\ _2O + NH_4Cl$
(Brown ppt)



- Oxides of nitrogen :

Oxides of nitrogen



Chapter 8

The d– And F– Block Elements

d– Block transition elements groups 3–12

- Position : Between s–and p–blocks
- Electronic configuration : $(n-1)d^{1-10}ns^{1-2}$
- Physical properties : Show typical metallic properties, melting and boiling point are high; High enthalpies of atomization
- Decrease in radius with increasing atomic number. Lanthanoid contraction is due to imperfect shielding of one e^- by another in same set of orbitals.
- Ionisation enthalpies : Increases from left to right
- Oxidation states : Variable ;higher ON stable
- Trends in M^{2+}/M E° : E° for Mn, Ni and Zn are more negative than expected.
- Trends in M^{3+}/M^{2+} E° : variable
- Chemical reactivity and E° values : Variable Ti, V and Cr^{2+} are strong reducing agents.
- Magnetic properties : Diamagnetism and paramagnetism. Magnetic moment increases with increasing atomic number.
- Formation of coloured ions : Form coloured compounds due to d – d transitions
- Formation of complex compounds : Form a large number of complex compounds
- Catalytic properties : Due to variable oxidation states and ability to form complexes.
- Forms interstitial compounds : Non - stoichiometric and are neither ionic nor covalent.
- Alloy formation : Due to similar atomic sizes.

Uses

- Helps in production of iron and steels.
- TiO in pigment industry
  - MnO_2 in dry battery cells.
- As catalysts in industry.
- Ni complexes useful in the polymerization of alkynes and other organic compounds such as benzene.
- Ag Br in photographic industry.

Lanthanoid contraction is progressive decrease in atomic/ionic radii from La^{3+} to Lu^{3+}

f– Block Transition Elements

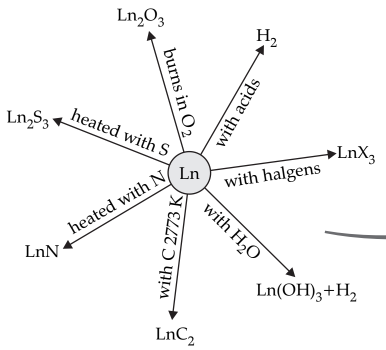
Actinoids

- Electronic : configuration $[Rn]5f^{1-14}6d^{0-2}7s^2$
- Ionic sizes : Gradual decrease along the series
- Oxidation states : Most common is +3. They show ON of +4, +5, +6 and +7.
- **General characteristics :**
  - –Silvery in appearance
  - –Display variety of structures
  - –Highly reactive metals
  - –Irregularities in metallic radii, greater than in Lanthanoids.
  - –Magnetic properties more complex than lanthanoids.

Lanthanoids

- Electronic configuration
  $4f^{1-14}\ 5d^{0-1}\ 6s^2$
- Atomic and ionic sizes
  Decreases from La to Lu
- Oxidation states
  Most common is +3. Some elements exhibit +2 and +4.
- General characteristics
  - Silvery while soft metals and tarnish rapidly in air.
  - Hardness increases with increasing atomic number.
  - Metallic structure and good conductors of heat and electricity.
  - Variable density
  - Trivalent Lanthanoid ions are coloured.
- Ionisation Enthalpies : Low third ionisation enthalpies
- Good reducing agents.

Chemical Properties



Oxides and oxoanions of metals

- Potassium dichromate $K_2Cr_2O_7$

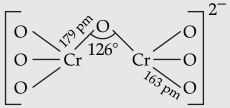
  Preparation : $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

  $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

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

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

  Oxidises iodides to iodine, H_2S to S, SO_3^{2-} to SO_4^{2-}, NO_2^- to NO_3^-



- Potassium permanganate $KMnO_4$

  Preparation : $2MnO_2 + 4KOH + O_2 \rightarrow 2KMnO_4 + 2H_2O$

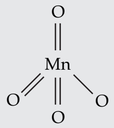
  $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

  $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$

  Properties : Intense colour, weak temperature dependent paramagnetism

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

  Oxidizes I^- to I_2, Fe^{2+} to Fe^{3+}, $C_2O_4^{2-}$ to CO_2, S^{2-} to S, SO_3^{2-} to SO_4^{2-}, NO_2^- to NO_3^-



Chapter 9

Coordination Compounds

Formulas of mononuclear
- Central atom is listed first
- Ligands in alphabetical order.
- Formula is enclosed in square bracket.
- Polyatomic ligands in parenthesis.
- No space between ligand and metal.
- Charge is indicated outside brackets.
- Charge of cation(s) balanced by charge of anion(s)

Naming of mononuclear
- Cation is named first.
- Naming of ligands in alphabetical order.
- Anionic ligands end in–o, neutral and cationic are same
- Prefixes mono, di, tri etc. are used.
- Followed by roman numeral in parentheses.

Complex compound
Complex compound : Do not dissociate into simple ions when dissolved in water. ($K_4[Fe(Cn)_6]$)

Double salt
Double salt : Dissociate completely into simple ions when dissolved in water. (Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O$)

Compounds in which a central metal atom or ion is linked to a fixed number of ions or molecules through coordinate bonds.

Stability : expressed by equilibrium constant $B_r = k_1 \times k_2 \times k_3 \ldots\ldots k_n$

Terms
- **Coordination entity :** A central metal atom/ion bonded to fixed number of ions or molecules. $[Ni(CO)_4]$
- **Central atom/ion :** Atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement.
- **Ligands :** Ions or molecules bound to central atom/ion types : Unidentate – single donor, Didentate –two donors Polydentate – several donors, Chelating – Di-or polydentate which forms more than one coordinate bonds. Ambidentate : Can ligate through two different atoms.
- **Coordination number :** No. of ligand donor atoms to which metal is directly bonded
- **Coordination sphere :** Central atom/ion and the ligands attached to it and enclosed in square bracket.
- **Coordination polyhedron :** spatial arrangement of ligand atoms with central atom/ion.
- **Oxidation number :** Charge of central atom if all ligands are removed along with e– pairs shared with central atom.
- **Homoleptic complex :** Metal is bound to one type of donor groups. $[Co(NH_3)_6]^{3+}$
- **Heteroleptic complex :** Metal is bound to more than one type of donor groups

Bonding
Valance bond theory: Metal atom/ion under the influence of ligands can use its (n–1)d, ns, np or ns, np, nd orbitals for hybridisation; sp^3(Tetrahedral), dsp^2(square) planar, sp^3d (Trigonal pyramidal), sp^3d^2 and d^2sp^3 (Octahedral); Magnetic moment $= \sqrt{n(n+2)}$ BM

In metal carbonyls: Metal–carbon bond possess both σ and π character

Crystal field theory: Ligands are point charges and there is electrostatic force of attraction between ligands and metal atom/ion. Degeneracy of d orbitals is lighted causing splitting of d orbitals. Δ_0 depends upon the field produced by the ligand and charge on metal ion.

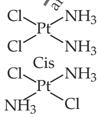
Werner's Theory: Postulates
- In coordination compounds metals show primary and secondary linkages (valances)
- Primary valences are ionisable and are satisfied by negative ions.
- Secondary valences are non-ionisable and are satisfied by neutral molecules or negative ions.
- Ions/groups bound by secondary linkages to metal have characteristic spatial arrangements corresponding to different coordination numbers.

Colour
Caused by d-d transition; the colour is complementary to wavelength absorbed

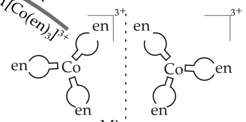
Uses
- In qualitative and quantitative chemical analysis.
- Estimation of hardness of water.
- In extraction metals.
- In purification of metals.
- In biological systems.
- As catalysts for industrial processes.
- In black and white photography.
- In medicinal chemistry.

Isomerism
Structural: different bonds
- Linkage occurs in ambidentate ligand: $[CO(NO_2)(NH_3)_5]Cl$, $[CO(ONO)(NH_3)_5]Cl$
- Coordination interchange of ligands between catonic and anionic entities of different metal ions: $[CO(NH_3)_6][Cr(CN)_6]$, $[Cr(NH_3)_6][CO(CN)_6]$
- Ionisation counter ion is a potential ligand and can displace a ligand: $[Co(NH_3)_5SO_4]Br$, $[CO(NH_3)_5Br]SO_4$
- Solvate differ in number of water molecules attached to metal atom/ion.: $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2.H_2O$

Stereoisomerism : different spatial arrangements
- Geometrical : Different arrangement Ligand



- Optical: images which cannot be superimposed $[Co(en)_3]^{3+}$



Chapter 10

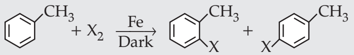
Haloalkanes and Haloarenes

Polyhalogen compounds
- Chloroform
  - Solvent for fats, alkaloids, I_2 etc.
  - Production of Freon
- Iodoform – Antiseptic
- Carbon tetrachloride
  - Manufacture of refrigerants and propellants.
  - Cleaning fluid
- Freons – For aerosol propellants, refrigeration and air conditioning purposes
- D.D.T. – As insecticide
- Dichloromethane
  - Paint remover
  - Propellant in aerosols
  - Metal cleaning and finishing solvent.

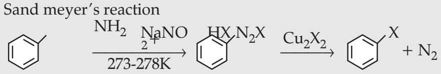
Racemisation S_N1
- Chiral : Objects which are non-superimposable
- Achiral : objects which are superimposable

S_N2 Stereochemical inversion
- (a) Dextro (+/d)
- (b) laevo (–/l)

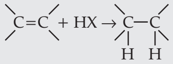
Haloalkanes
- Preparation
  - From alcohol :
    - $R\text{–}OH + HCl \xrightarrow{ZnCl_2} R\text{–}Cl + H_2O$
    - $3R\text{–}OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3$
    - $ROH + PCl_5 \longrightarrow R\text{–}Cl + POCl_3 + HCl$
  - From hydrocarbons :
    - (a) By free radical halogenations
      $CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UV} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$
    - (b) By electrophilic substitution



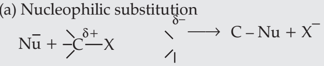
    - (c) Sand meyer's reaction



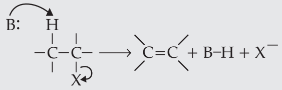
    - (d) From alkenes



      $H_2C{=}CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2\text{–}CH_2Br$
  - Halogen exchange :
    $R\text{–}X + NaI \rightarrow R\text{–}I + NaX$
- Properties
  - Physical : Colourless, volatile, sweet smell.
    Lower members are gases at room temperature while higher are solids.
    B.P : RI > R Br > RCl > RF.
    M.P : Para isomers have high m.p. than ortho and meta – isomers.
    Density : Increases with increase in number of C/X atoms and atomic masses of the X atoms.
    Solubility : Very slightly soluble in water.
  - Chemical :
    - (a) Nucleophilic substitution

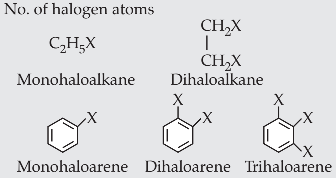


      For S_N2 reaction →
      Tertiary, Secondary, Primary
      ← For S_N1 reaction
    - (b) Elimination reaction

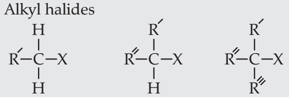


      B = Base; X = Leaving group
    - (c) Reaction with metals
      $CH_3CH_2Br + M \longrightarrow CH_3CH_2MgBr$
      Wurtz reaction :
      $2RX + 2Na \xrightarrow{\text{Dry ether}} RR + 2NaX$

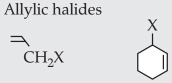
Classification
- No. of halogen atoms



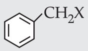
- Compounds containing sp^3 C–X bond
  - (a) Alkyl halides



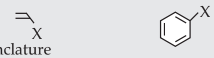
  - (b) Allylic halides



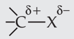
  - (c) Benzylic halides



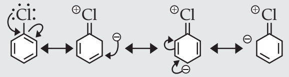
- Compounds containing sp^2 C–X bond
  - (a) Vinylic halides
  - (b) Aryl halides



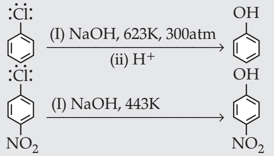
- Nomenclature
  Common name : alkyl group followed by halides. Dihalogen derivatives, prefixes o–, m–, p– are used.
  IUPAC name : numerals are used
- Nature of C –X bond
  : Carbon –halogen bond is polarized



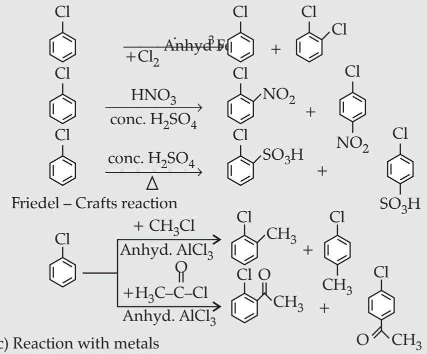
Haloarenes
- Reactions :
  - (a) Nucleophilic substitution
    - (i) Resonance effect



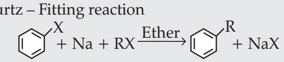
    - (ii) Hybridization of C – X bond in :
      Haloalkane –sp^3; Haloarence –sp^2
    - (iii) Phenyl cation unstabilised by resonance



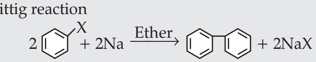
  - (b) Electrophilic substitution



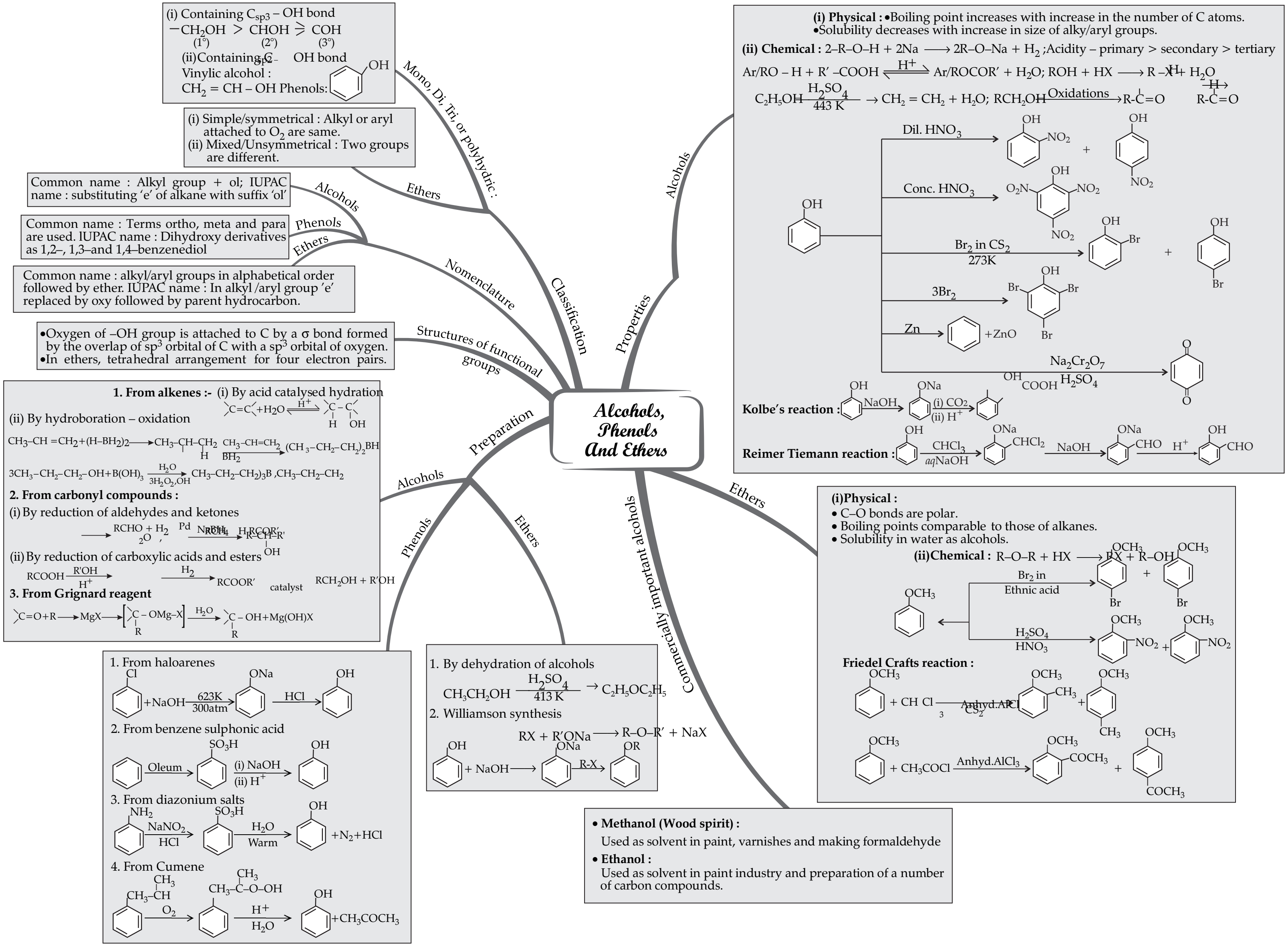
  - (c) Reaction with metals
    Wurtz – Fitting reaction



    Fittig reaction



Chapter 11



Alcohols, Phenols And Ethers
Classification
Mono, Di, Tri, or polyhydric :
(i) Containing Csp3 – OH bond
–CH2OH > CHOH > COH
(1°) (2°) (3°)
(ii) Containing Csp2 – OH bond
Vinylic alcohol :
CH2 = CH – OH Phenols:
OH
Ethers
(i) Simple/symmetrical : Alkyl or aryl attached to O2 are same.
(ii) Mixed/Unsymmetrical : Two groups are different.
Nomenclature
Alcohols
Common name : Alkyl group + ol; IUPAC name : substituting 'e' of alkane with suffix 'ol'
Phenols
Common name : Terms ortho, meta and para are used. IUPAC name : Dihydroxy derivatives as 1,2–, 1,3–and 1,4–benzenediol
Ethers
Common name : alkyl/aryl groups in alphabetical order followed by ether. IUPAC name : In alkyl /aryl group 'e' replaced by oxy followed by parent hydrocarbon.
Structures of functional groups
•Oxygen of –OH group is attached to C by a σ bond formed by the overlap of sp3 orbital of C with a sp3 orbital of oxygen.
•In ethers, tetrahedral arrangement for four electron pairs.
Preparation
Alcohols
1. From alkenes :- (i) By acid catalysed hydration
(ii) By hydroboration – oxidation
2. From carbonyl compounds :
(i) By reduction of aldehydes and ketones
(ii) By reduction of carboxylic acids and esters
3. From Grignard reagent
Phenols
1. From haloarenes
+NaOH 623K 300atm HCl
2. From benzene sulphonic acid
Oleum (i) NaOH (ii) H+
3. From diazonium salts
NaNO2 HCl H2O Warm +N2+HCl
4. From Cumene
O2 H+ H2O +CH3COCH3
Ethers
1. By dehydration of alcohols
CH3CH2OH H2SO4 413 K → C2H5OC2H5
2. Williamson synthesis
RX + R′ONa → R–O–R′ + NaX
+ NaOH R-X
Properties
Alcohols
(i) Physical : •Boiling point increases with increase in the number of C atoms.
•Solubility decreases with increase in size of alky/aryl groups.
(ii) Chemical : 2–R–O–H + 2Na → 2R–O–Na + H2 ;Acidity – primary > secondary > tertiary
Ar/RO – H + R′ –COOH ⇌ (H+) Ar/ROCOR′ + H2O; ROH + HX → R –X + H2O
C2H5OH (H2SO4, 443 K) → CH2 = CH2 + H2O; RCH2OH (Oxidations) → R-C=O
Dil. HNO3
Conc. HNO3
Br2 in CS2 273K
3Br2
Zn +ZnO
Na2Cr2O7 H2SO4
Kolbe's reaction : NaOH (i) CO2 (ii) H+
Reimer Tiemann reaction : CHCl3 aqNaOH NaOH H+
Ethers
(i)Physical :
• C–O bonds are polar.
• Boiling points comparable to those of alkanes.
• Solubility in water as alcohols.
(ii)Chemical : R–O–R + HX → RX + R–OH
Br2 in Ethnic acid
H2SO4 HNO3
Friedel Crafts reaction :
+ CH3Cl Anhyd.AlCl3 CS2
+ CH3COCl Anhyd.AlCl3
Commercially important alcohols
• Methanol (Wood spirit) :
Used as solvent in paint, varnishes and making formaldehyde
• Ethanol :
Used as solvent in paint industry and preparation of a number of carbon compounds.

Chapter 12

Aldehydes, Ketones and Carboxylic Acids

Properties

ALDEHYDES AND KETONES:

(i) Physical:
Boiling points are higher than hydrocarbons and ethers of comparable molecular masses.

(ii)Chemical :Nucleophilic addition reactions :
Aldehydes are more reactive than ketones due to steric and electronic reasons.

$HCN + OH^- \rightleftharpoons :CN^- + H_2O$; $\overset{\delta+}{C}=\overset{\delta-}{O} \rightleftharpoons [C(O^-)(CN)] \rightleftharpoons C(OH)(CN)$

$R_2C=O + CH_2OH\text{–}CH_2OH \underset{\text{Dil. HCl}}{\overset{\text{HCl gas}}{\rightleftharpoons}} R_2C(O\text{-}CH_2)_2 + H_2O$

Reduction : (a) To alcohols – aldehydes and ketones reduce to primary and. secondary alcohols respectively by $NaBH_4$ or $LiAlH_4$.
(b) To hydrocarbons –

$>C=O \xrightarrow[\text{HCl}]{\text{Zn-Hg}} >CH_2 + H_2O$ (Clemmensen Reduction)

$>C=O \xrightarrow[-H_2O]{NH_2NH_2} >C=NNH_2 \xrightarrow[\text{Heat}]{\text{KOH/Ethylene glycol}} >CH_2 + N_2$ (Wolf-Kishner)

Oxidation: $RCHO \xrightarrow{[O]} R\text{–}COOH$

Tollen's test : $RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCOO^- + 2Ag + 2H_2O + 4NH_3$

Fehling's test : $RCHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + Cu_2O + 3H_2O$
Red brown ppt

Haloform reaction:
$R\text{–}CO\text{–}CH_3 \longrightarrow R\text{–}CO\text{–}ONa + CHX_3$

Reactions due to α- hydrogen:

$2CH_3CHO \underset{}{\overset{\text{dil NaOH}}{\rightleftharpoons}} CH_3\text{–}CH(OH)\text{–}CH_2\text{–}CHO \xrightarrow[-H_2O]{\Delta} CH_3\text{–}CH=CH\text{–}CHO$

$2CH_3COCH_3 \overset{Ba(OH)_2}{\rightleftharpoons} (CH_3)_2C(OH)\text{–}CH_2COCH_3 \xrightarrow{-H_2O} CH_3\text{–}C(CH_3)=CH\text{–}CO\text{–}CH_3$

$CH_3CHO \xrightarrow[\Delta]{NaOH} CH_3\text{–}CH=CH\text{–}CHO + CH_3\text{–}CH_2\text{–}CH=C(CH_3)\text{–}CHO$

Cannizzaro reaction : $2HCHO + \text{conc KOH} \xrightarrow{\Delta} CH_3OH + HCOOK$

Electrophilic substitution reaction:

$C_6H_5CHO \xrightarrow[\text{273-283 K}]{HNO_3/H_2SO_4} m\text{-}O_2N\text{–}C_6H_4\text{–}CHO$

Carboxylic acids:

(i) Physical: Higher boiling points than aldehydes, ketones or alcohols. Solubility decreases with increasing number of C atoms

(ii)Chemical : $2RCOOH + 2Na \longrightarrow 2RCOONa + H_2$
Forms corresponding anhydride on heating with mineral acids

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

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

$CH_3COOH + NH_3 \rightleftharpoons CH_3COONH_4 \xrightarrow[-H_2O]{\Delta} CH_3CONH_2$

$RCOOH \xrightarrow[H_3O^+]{B_2H_6} RCH_2OH$

$RCOONa \xrightarrow[\text{NaOH \& CaO}]{\text{Heat}} R\text{–}H + Na_2CO_3$

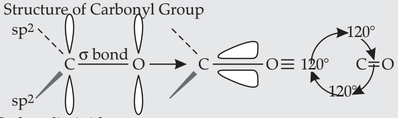
$RCH_2COOH \xrightarrow[H_2O]{X_2/\text{Red P}} R\text{–}CH(X)\text{–}COOH$ (HVZ reaction)

$C_6H_5CHO \xrightarrow[\text{Conc.}H_2SO_4]{\text{Conc.}HNO_3} m\text{-}NO_2\text{–}C_6H_4\text{–}CHO$

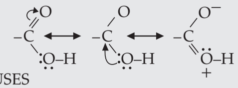
Nomenclature

1. Aldehydes and Ketones
   Common names :
   - Replace corresponding carboxylic acids with aldehyde
   - Alkyl phenyl ketones by adding acyl group as prefix to phenone.

   IUPAC names :
   - Replacing –e with –al and –one as required.
   - Structure of Carbonyl Group



2. Carboxylic Acids
   - Common names : end with –ic
   - IUPAC names : replace –e in the corresponding alkane with –oic acid.
   - Structure of Carboxyl Group



3. USES
   (a) Carboxylic acids
   - Methanoic acid in rubber, textile, dyeing, leather industries.
   - Ethanoic acid as solvent
   - Higher tatty acids in manufacture of soaps and detergents.

   (b) Aldehydes of ketones
   - As solvents.
   - Starting materials and reagents for synthesis of products.

Preparation

ALDEHYDES:

1. From acyl chloride
$C_6H_5COCl \xrightarrow[\text{Pd-BaSO}_4]{H_2} C_6H_5CHO$

2. From nitriles and esters : Stephen reaction
$RCN + SnCl_2 + HCl \longrightarrow RCH=NH \xrightarrow{H_3O^+} RCHO$

3. From hydrocarbons : Etard reaction
$C_6H_5CH_3 + CrO_2Cl_2 \xrightarrow{CS_2} C_6H_5CH(OCrOHCl_2)_2 \xrightarrow{H_3O^+} C_6H_5CHO$

$C_6H_5CH_3 \xrightarrow{Cl_2/h\nu} C_6H_5CHCl_2 \xrightarrow[373K]{H_2O} C_6H_5CHO$

Gratterman – Koch reaction $C_6H_6 \xrightarrow[\text{Anhyd.AlCl}_3]{\text{CO.HCl}} C_6H_5CHO$

KETONES:

1.From acyl chloride
$2R\text{–}Mg\text{–}X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$
$R_2Cd + 2R'\text{-}CO\text{-}Cl \longrightarrow 2R'\text{-}CO\text{-}R' + CdCl_2$

2.From nitriles
$CH_3CH_2CN + C_6H_5MgBr \xrightarrow{\text{Ether}} CH_3CH_2\text{-}C(=NMgBr)\text{-}C_6H_5 \xrightarrow{H_3O^+} C_2H_5\text{-}CO\text{-}C_6H_5$

3.From benzene or substituted benzenes
$C_6H_6 + Ar/R\text{-}CO\text{-}Cl \xrightarrow{\text{Anhyd.AlCl}_3} C_6H_5\text{-}CO\text{-}Ar/R$

Carboxylic Acids:

1.From primary alcohols and aldehydes $RCH_2OH \xrightarrow[H_3O^+]{\text{alk. KMnO}_4} RCOOH$

2.From alkylbenzine $C_6H_5CH_3 \xrightarrow{\text{KMnO}_4\text{-KOH}} C_6H_5COOK \xrightarrow{H_3O^+} C_6H_5COOH$

3.From nitriles and amides $R\text{–}CN \xrightarrow[H_2O]{H^+ \text{or } OH^-} R\text{-}CO\text{-}NH_2 \xrightarrow[\Delta]{H^+ \text{or } OH^-} RCOOH$

4.From Grignard reagents $R\text{–}Mg\text{–}X + CO_2 \longrightarrow R\text{-}CO\text{-}OMgX \xrightarrow{H_3O^+} RCOOH$

5.From acyl halides and anhydrides
$RCOCl \xrightarrow{OH^-/H_2O} RCOO^- + Cl^- \xrightarrow{H_3O^+} RCOOH$
$C_6H_5COOCOCH_3 \xrightarrow{H_2O} C_6H_5COOH + CH_3COOH$

6.From esters
$C_6H_5COOC_2H_5 \overset{H_3O^+}{\rightleftharpoons} C_6H_5COOH + C_2H_5OH$
$CH_3CH_2CH_2COOC_2H_5 \overset{NaOH}{\rightleftharpoons} CH_3CH_2CH_2COONa + C_2H_5OH$
$\downarrow H_3O^+$
$CH_3CH_2CH_2COOH$

Chapter 13

Amines

Chemical reactions

(i) Basic character of amines

- Reacts with acids to form salts $R-NH_2 + HX \rightleftharpoons R-NH_3X$ (salt)
- Reacts with base to regenerate parent amines $RNH_3X + OH \longrightarrow RNH_2 + H_2O + X$
- Order of stability of ions : 1° > 2° > 3°

(ii) $C_2H_5NH_2 + CH_3COCl \xrightarrow{Base} C_2H_5NHCOCH_3 + HCl$

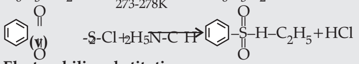
(iii) Carbylamines reaction : $R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$

(iv) With nitrous acid

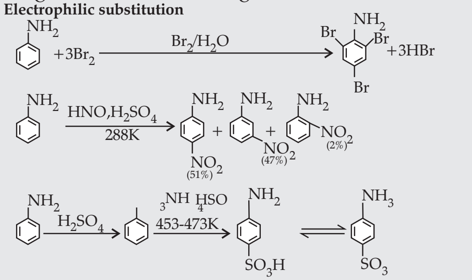
$RNH_2 + HNO_2 \xrightarrow{NaNO_2+HCl} [R-N_2Cl] \xrightarrow{H_2O} ROH + N_2 + HCl$

$C_6H_5NH_2 \xrightarrow[273-278K]{NaNO_2+HCl} C_6H_5N_2Cl + NaCl + 2H_2O$

(v)

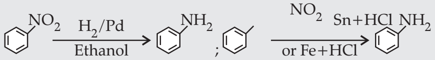


(vi) Electrophilic substitution

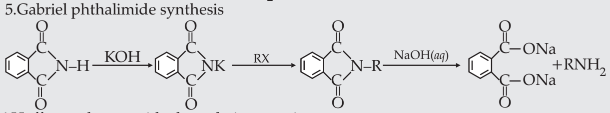


Preparation :

1. Reduction of nitro compounds



2. Ammonolysis of alkyl halides: $NH_3 + R-X \longrightarrow R-\overset{+}{N}H_3\overset{-}{X}$
3. Reduction of nitriles: $R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5]{H_2/Ni} R-CH_2NH_2$
4. Reduction of amides: $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[H_2O]{LiAlH_4} R-CH_2-NH_2$
5. Gabriel phthalimide synthesis



6. Hoffmann bromamide degradation reaction

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

Physical properties

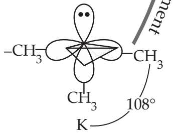
- Lower aliphatic amines are gases. Primary amines with three or more C atoms are liquid and higher ones are solid.
- Arylamines are colourless but get coloured on storage.
- Lower aliphatic amines are soluble in water, while higher are insoluble.
- Primary and secondary amines form intermolecular association
- Boiling point : primary > secondary > tertiary

Importance of diazonium salts in synthesis of aromatic compounds :

In preparation of substituted aromatic compounds which cannot be prepared by direct substitution in benzene/ substituted benzene.

Derivatives of ammonia, obtained by replacement of one, two or all the three Hatoms by alkyl and/or aryl groups

Structure



Classification

$NH_3 \longrightarrow RNH_2 \longrightarrow R(R')N-H \longrightarrow R(R')N-R''$

Nomenclature:

Common name : Aliphatic amine is named by prefixing alkyl group to amine. In secondary and tertiary amines prefix di or tri is put before name of alkyl group. IUPAC name : replacement of 'e' of alkane by the word amine. Suffix 'e' of arene is replaced by amine.

Diazonium Salts (RN_2X)

Preparation :

$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278K} C_6H_5N_2Cl + NaCl + 2H_2O$

Physical properties : Colourless crystalline solid, soluble in water, stable in cold but reacts with water on warming.

Chemical properties :

(i) Sandmeyer reaction:

- $ArN_2X \xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2$
- $ArN_2X \xrightarrow{Cu_2Br_2/HBr} ArBr + N_2$
- $ArN_2X \xrightarrow{CuCN/KCN} ArCN + N_2$

Gattermann reaction :

- $ArN_2X \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$
- $ArN_2X \xrightarrow{Cu/HBr} ArBr + N_2 + CuX$

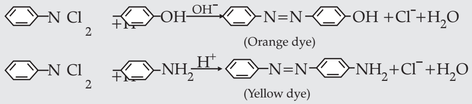
(ii) $ArN_2Cl + KI \longrightarrow ArI + KCl + N_2$

(iii) $ArN_2Cl + HBF_4 \longrightarrow ArN_2BF_4 \xrightarrow{\Delta} ArF + BF_3 + N_2$

(iv) $ArN_2Cl + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$

(v) $ArN_2Cl + H_2O \longrightarrow ArOH + N_2 + HCl$

(iv) **Coupling reaction :**



Chapter 14

Biomolecules

Proteins

(Polymers of α–amino acids)
Amino acids contain $-NH_2$ and $-COOH$ group.

Classification:

- On the basis of relative number of $-NH_2$ and $-COOH$ group
  - (I) Neutral–equal number of $-NH_2$ and $-COOH$ group.
  - (ii) Basic – more number of $-NH_2$ than $-COOH$ group.
  - (iii) Acidic – more number of $-COOH$ than $-NH_2$ group.
- On the basis of place of synthesis
  - (i) Essential – cannot be synthesized in the body.
  - (ii) Non-essential – synthesized in the body.
- On the basis of shape
  - (I) Fibrous – fibre –linke structure
  - (ii) Globular – spherical

Structure : $H_2N-CH_2-CO-NH-CH(CH_3)-COOH$ (CO–NH: Peptide linkage)

Denaturation of proteins :
When a protein in its native form is subjected to physical change, globules unfold, helix get uncoiled and protein loses its biological activity.

Carbohydrates

Optically active polyhydroxy aldehydes or ketones or compounds which produce such units on hydrolysis.

- **Classification:**

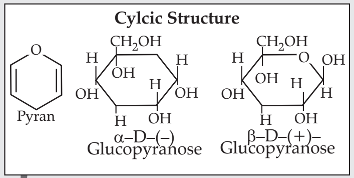
(I) Monosaccharides : (Aldehyde group – aldose, keto group –ketose)
Glucose : Preparation :

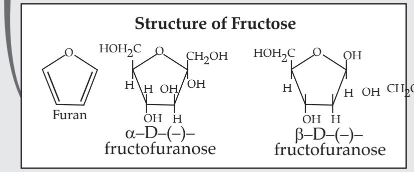
(a) From sucrose : $\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$

(b) From starch : $(C_6H_{10}O_5)n + nH_2O \xrightarrow[393K;\ 2\text{-}3\ atm]{H^+} nC_6H_{12}O_6$

- **Structure:**

CHO–$(CHOH)_4$–CH_2OH





Reactions of CHO–$(CHOH)_4$–CH_2OH:

- $\xrightarrow{HI,\ \Delta}$ $CH_3CH_2CH_2CH_2CH_3$
- $\xrightarrow{NH_2OH}$ CH=N–OH–$(CHOH)_4$–CH_2OH
- $\xrightarrow{HCN}$ CH(CN)(OH)–$(CHOH)_4$–CH_2OH
- $\xrightarrow{Br_2\ Water}$ COOH–$(CHOH)_4$–(CH_2OH)
- $\xrightarrow{\text{Acetic Anhydride}}$ CHO–$(CH-O-CO-CH_3)_4$–$CH_2-O-CO-CH_3$
- $\xrightarrow{\text{Oxidation}}$ COOH–$(CHOH)_4$–COOH

(ii) Disaccharides : Linkage between 2 monosaccharides– Glycosidic linkage (Sucrose, maltose)
(iii) Polysaccharides : Large number of monosaccharides units joined by glycosidic linkages.
(a) Starch : Polymer of –glucose with two components amylase and amylopectin
(b) Cellulose
(c) Glycogen

Importance:

- Form a major portion of food.
  As storage molecules.
  Cellulose forms cell wall of bacteria and plants.
  Raw materials for industries like textiles, paper, lacquers and breweries.

Vitamins

Organic compounds required in diet in small amounts to perform specific biological functions for maintenance and growth.

Classification:
(i) Fat soluble : Soluble in fats and oils but insoluble in water. (vitamins A,D,E and K)
(ii) Water soluble : B group and vitamin C are soluble in water.

Nucleic Acids

Chromosomes : Particles in nucleus responsible for heredity. Chromosomes are made up of proteins and nucleic acid.
Two types : Deoxyribonucleic acid (DNA), ribonucleic acid (RNA)
Composition : In DNA, sugar is β–D–2–deoxyribose whereas in RNA is β–D–ribose. DNA contains A,G,C,T whereas RNA has A,G,C,U.
Structure : –
Nucleoside : Formed by attachment of a base to 1′ of sugar′
Nucleotide : Formed by link to phosphoric acid at 5′ of sugar.

–Sugar(Base)–Phosphate–[Sugar(Base)–Phosphate]–Sugar(Base)–

Types of RNA : m–RNA, r–RNA, t–RNA

Biological Functions :

- Chemical basis of heredity.
  Responsible for identity of different species of organisms.
  Nucleic acids are responsible for protein synthesis in cell.

DNA Fingerprinting

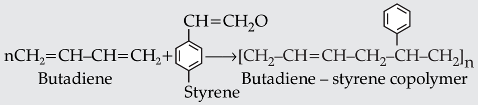
DNA Fingerprinting:Unique sequence of bases on DNA.

Enzymes

Globular proteins specific for particular reaction and for particular substrate. Mechanism : Reduces the magnitude of activation energy

Chapter 15

Polymers



Copolymerization : A mixture of more than one monomeric species undergoes polymerization

Rubber

Types :
(i) **Natural rubber :** natural and manufactured from rubber latex. It is a liner polymer of isoprene.
(ii) **Synthetic rubber :** Any vulcanisable rubber. These are homopolymers of 1,3 butadiene derivatives.

N–CH$_2$=C(Cl)–CH=CH$_2$ $\xrightarrow{\text{Polymerisation}}$ [CH$_2$–C(Cl)=CH–CH$_2$]$_n$

Molecular mass of polymers

- Expressed as an average.
- Determined by chemical and physical methods.

Biodegradable polymers

Contain functional groups similar to biopolymers (PHBV, Nylon 2– nylon 6)

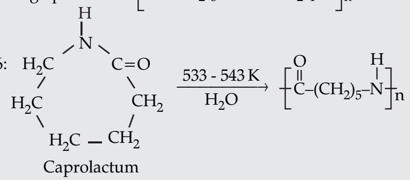
Very large molecules having high molecular mass

Classification

- **Based on source**:
  - (i) **Natural polymers :** Found in plants and animals. (Proteins, rubber)
  - (ii) **Semi–synthetic polymers :** (Cellulose derivatives)
  - (iii) **Synthetic polymers :** Man-made. (Polythene, Buna –S)
- **Based on structure of polymers high density**:
  - (i) **Linear polymers :** Long and straight. (Polythene, PVC)
  - (ii) **Branched chain polymers :** Linear chains with branches (low density polythene)
  - (iii) **Cross linked or network polymers :** Strong covalent bond between various linear polymer chains. (Bakelite, Melamine)
- **Based on mode of polymerization**:
  - (i) **Addition polymers :** Repeated addition of monomers containing double or triple bonds. (Polythene from ethene)
    Homopolymer : Single monomeric species (Polythene)
    Copolymer : Two different monomers (Buna–S, Buna–N)
  - (ii) **Condensation polymers :** Repeated condensation between two different bi–functional or tri–functional monomeric units. (Terylene, Nylon 6)
- **Based on Molecular Forces:**
  - (I) **Elastomers :** Rubber–like solids with elastic properties (Buna–S, Buna–N)
  - (ii) **Fibres :** Thread forming solids. (Nylon 6,6, Terylene)
  - (iii) **Thermoplastic polymers :** Linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. (polythene, polystyrene)
  - (iv) **Thermosetting polymers :** Cross linked or heavily branched molecules which on heating undergo extensive cross linking in moulds and become infusible. (Bakelite)

Preparation

- Polythene
  Low density : Polymerization of ethene under 1000–2000 atm at 350–570 K + catalyst
  Higher density : addition polymerization of ethene in a hydrocarbon solvent at 333–343 K and 6–7 atm + catalyst
- Teflon $nCF_2=CF_2 \xrightarrow[\text{High pressure}]{\text{Catalyst}} -[CF_2-CF_2]_n$
- Polyacrylonitrile: $nCH_2=CHCN \xrightarrow[\text{Peroxide}]{\text{Polymerisation}} -[CH_2-CH(CN)]_n$
- Nylon 6,6: $nHOOC(CH_2)_4COOH + nH_2(CH_2)_6NH_2 \xrightarrow[\text{High pressure}]{533K} -[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO]_n$
- Nylon 6:



Types of Polymerization Reactions

- (i) Addition/Chain Growth : Molecules of the same/different monomers add together on a large scale.
  Free radical mechanism :
  (a) Chain initiation step:
  $C_6H_5-CO-O-O-CO-C_6H_5 \longrightarrow 2C_6H_5-CO-\dot{O} \longrightarrow 2\dot{C}_6H_5$
  $\dot{C}_6H_5 + CH_2=CH_2 \longrightarrow C_6H_5-CH_2-\dot{C}H_2$
  (b) Chain propagating step:
  $C_6H_5-CH_2-\dot{C}H_2 + CH_2=CH_2 \longrightarrow C_6H_5-CH_2-CH_2-CH_2-\dot{C}H_2 \longrightarrow C_6H_5-(CH_2-CH_2)_n-\dot{C}H-CH_2$
  (c) Chain terminating step:
  $2[C_6H_5-(CH_2-CH_2)_n-\dot{C}H-CH_2] \longrightarrow C_6H_5-(CH_2-CH_2)_n-CH_2-CH_2-CH_2-(CH_2-CH_2)_n-C_6H_5$
- (ii) Condensation/Step Growth : Repetitive condensation reaction between two bi–functional monomers. (Formation of terylene)

Chapter 16

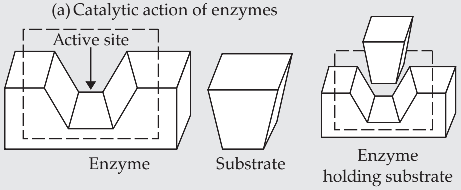
Chemistry in Everyday Life

Therapeutic Action of Different Classes of Drugs

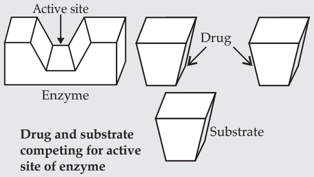
- **Antacids :** Substances that neutralize the excess HCl and raise pH in stomach (Ranitidine, Cimetidine)
- **Antihistamines :** Interfere with natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect
- **Neurologically Active Drugs**
  - (a) **Tranquilizers :** Class of chemical compounds used for the treatment of stress and mild or even severe mental diseases. (Iproniazid, Phenelzine)
  - (b) **Analgesics :** Reduce/abolish pain without causing impairment of consciousness, mental confusion, incoordination or paralysis or other disturbances of nervous system. These are classified as
    - (i) Non-narcotic (non-addictive) : (Aspirin, Paracetamol)
    - (ii) Narcotic : (Morphine)
- **Antimicrobials**
  - (a) Antibiotics : Drugs to treat infections because of their low toxicity for humans and animals. (Prontosil)
  - (b) Antiseptics and Disinfectants : Chemicals which either kill or prevent the growth of microorganisms. Antiseptics are applied to living tissues whereas disinfectants are applied to inanimate objects.
- **Antifertility Drugs :** Birth control pills (Norethindrone, ethynylestradiol)

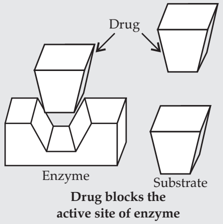
Medicines: Chemicals which generate therapeutic and useful biological response

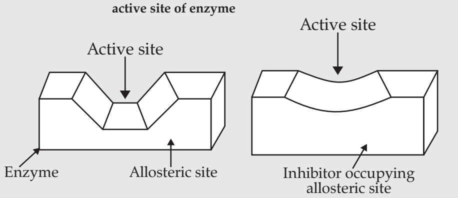
- Drugs are chemicals of low molecular masses. Interact with macromolecular targets to produce a biological response.
- **Classification of drugs:**
  - (a) On the basis of pharmalogical effect : Provides range of drugs available for a particular type of problem. (Analgesics, Antiseptics).
  - (b) On the basis of drugs action : (Antihistamines inhibit action of histamine responsible for causing inflammation in the body.
  - (c) On the basis of chemical structure : Common structural features. (Sulphonamides)
  - (d) On the basis of molecular targets : Most useful.
- **Drugs Target Interaction:**
  - (i) Enzymes as Drug Targets
    - (a) Catalytic action of enzymes



    - (b) Drug–enzyme interaction







  - (ii) **Receptors as Drug Targets**: Receptors are proteins crucial for body's communication and are embedded in cell membrane.

Chemicals In Food

Purpose:

- For their preservation.
- Enhancing their appeal.
- Adding nutritive value.
  - (a) Artificial Sweetening Agents : Natural sweeteners (sucrose), artificial sweeteners (Aspartame, Saccharin)
  - (b) Food Preservatives : Prevent spoilage of food due to microbial growth. (Table salt, sugar)

Cleansing Agents — Detergents — Types

(i) **Soap (Saponification)**

Glyceryl ester of stearic acid (fat) + Sodium hydroxide ⟶ Sodium stearate + Glycerol

(ii) **Synthetic Detergents :**

- Anionic detergents : Sodium salts of sulphonated long chain alcohols or hydrocarbons. (sodium salts of alkyl benzene sulphonates)
- Cationic detergents : Quaternary ammonium salts of amines with acetates, chlorides or bromides as anions. (Cetyltrimethylammonium bromide)
- Non-ionic Detergents : Non-ionic type.