CHAPTER 1

The Solid State

Crystal Lattice

A regular arrangement of the constituent particles of a crystal in the three dimensional space is called crystal lattice or space lattice.

Unit Cell

The smallest three dimensional portion of the space lattice which when repeated over and again in different directions producing the complete space lattice is called the unit cell.

Types of unit cells

(*i*) **Simple:** Here the particles are present only on the corners.

(*ii*) **Face centred:** Here in addition to the particles on the corners, there is one particle present on the centre of every face.

(*iii*) **End face centred:** Here in addition to the particles on the corners, there is one particle in the centre of two opposite faces.

(*iv*) **Body centred:** Here in addition to the particles on the corners, there is one particle present within the body of the unit cell.

Relation between the nearest neighbour distance (d), atomic radii (r) and the edge (a) of the unit cell

Co-ordination number: Of any particle is the number of its nearest neighbours.

Simple	Body-centred	Face centred
$d = a$	$d = \frac{\sqrt{3}}{2}a$	$d = \frac{a}{\sqrt{2}}$
	(It is half of the body diagonal)	(It is half of the face diagonal)
$r = \frac{a}{2}$	$r = \frac{\sqrt{3}}{4}a$	$r = \frac{a}{2\sqrt{2}}$

Expression of density for cubic lattice

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

where Z = Number of atoms present per unit cell; M = Atomic mass of the element

a = Edge of the cubic crystal in cm; N_A = Avogadro's number

Type of close packed structures

There are three ways in which atoms in a crystal are packed:

(*i*) **Hexagonal close packing (hcp)** i.e. ABAB... pattern e.g. in Be, Mg, Ca, Cr, Mo, V, Zn.

(*ii*) **Cubic close packing (ccp)** i.e. ABC ABC... pattern e.g. in Fe, Cu, Ag, Au, Pt, Al and Ni.

Space occupied = 74%, space unoccupied = 26%.

(*iii*) **Body centred cubic (bcc)** i.e. in alkali metals, space occupied = 68%, empty space = 32%. This is not a close packed arrangement.

Voids

Types of Voids

Tetrahedral void: It is a triangular void surrounded by four sphere arranged tetrahedrally around it.

Octahedral void: It is a combination of two triangular voids surrounded by six spheres.

Number of Voids

Number of octahedral voids = Number of atoms in the close packed arrangement.

Number of tetrahedral voids = 2 × Number of atoms in the close packed arrangement.

Location of Voids

In ccp or fcc, there are 4 atoms per unit cell, therefore, there are 4 octahedral & 8 tetrahedral voids.

Octahedral voids are 12 at the edge centres and 1 at the body centre. Distance of octahedral void from the corner is a/2 and at the body centre from the corner is $\frac{\sqrt{3} \times a}{2}$.

Tetrahedral voids are 8 at $\frac{1}{4}$ of Body diagonal from each corner as each spheres at the corner touches the three spheres present on the face centres of three adjoining faces, giving rise to a tetrahedral void. Distance of tetrahedral void from corner is $\frac{\sqrt{3} \times a}{4}$.

Relation between radius ratio, co-ordination number and structural arrangement:

Limiting ratio = r^+/r^-	Co-ordination Number of cation	Structural Arrangement (Geometry of voids)
0.155 –0.225	3	Plane Trigonal
0.225–0.414	4	Tetrahedral
0.414–0.732	4	Square planar
0.414–0.732	6	Octahedral
0.732–1	8	Body centred cubic

Main features of NaCl, CsCl, ZnS, AB_2 type structure

(*i*) **NaCl:** It has FCC arrangement of ions where Cl^- creates FCC unit and Na^+ ion is present in octahedral voids. Here, Na^+ and Cl^- ions have 6 : 6 co-ordination and each unit cell has 4 NaCl units.

Examples: Halides of alkali metals (except those of Cs) and those of NH_4^+, oxides and sulphides of alkaline earths (except BeS), halides of Ag (except Agl).

(*ii*) **CsCl:** It has BCC arrangement of ions where Cs^+ and Cl^- ions have 8 : 8 co-ordination number. Each unit cell has only one CsCl unit.

Examples: CsBr, CsCl, CsCN, TlCl, TlBr and TiCN.

(*iii*) **ZnS (sphalerite type):** It has FCC arrangement of ions, where S^{2-} creates FCC and Zn^{2+} ions are present at 1/4th of the distance along each body diagonal.

Zn^{2+} and S^{2-} ions have 4 : 4 co-ordination.

Examples: CuCl, CuBr, CuI, AgI, BeS

(*iv*) **AB_2:** Calcium fluorite (CaF_2) type, it has CCP/FCC arrangement of Ca^{2+} ions Ca^{2+} and F^- ions have 8 : 4 co-ordination.

Defects in Solids

Schottky defect: Is that in which cations and anions are missing form their lattice sites in stoichiometric ratio. As a result, density decreases. Schottky defect arises where cation and anions are of nearly equal size (radius ratio high).

Frenkel defect: Is that in which cations are missing from their lattice sites and occupy interstitial sites. As a result density remains unchanged, where size of cation is small as compared to size of anion.

F-centres: Are the sites where anions are missing leaving behind electrons. These are responsible for colour (F = Farbe [Colour]).

Doping

It means incorporating small amount of foreign impurity. Doping of group 14 elements with group 15 elements gives rise to excess electrons whereas with group 13 elements give rise to holes. Both make group 14 elements semi-conductors. The former are called n-type (as negative charge flows) and the latter are called p-type (as holes move like positive charge i.e. in a direction opposite to the flow of electrons).

CHAPTER

2

Solutions

Concentration Term

$$\text{Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Weight of solvent (kg)}}$$

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (L)}}$$

$$\text{Normality (N)} = \frac{\text{Number of gram-equivalents of solute}}{\text{Volume of solution (L)}}$$

$$\text{Formality (F)} = \frac{\text{Number of gram-formula mass of solute}}{\text{Volume of solution (L)}}$$

PPM = mass fraction × 10^6

Henry's Law

The dissolution of a gas in a liquid is governed by Henry's law, according to which, at a given temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas.

$$p = K_H.X \begin{cases} p = \text{partial pressure of gas in vapour phase} \\ K_H = \text{Henry's law constant} \\ X = \text{Mole fraction of gas} \end{cases}$$

Clausius - Clapeyron Equation

$$\log\frac{P_2}{P_1} = \frac{\Delta H_{\text{vapour}}}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where, P_1, P_2 are vapour pressure of liquid at T_1 and T_2 respectively.

Roult's Law

$P_T = P^o_A\,\chi_A + P^o_B\,\chi_B$ (Solution)

$$Y_A = \frac{P_A}{P_T} = \frac{P^o_A\,\chi_A}{P^o_A\,\chi_A + P^o_B\,\chi_B}$$

{Y_A; Y_B = mole fraction of A and B in vapour phase

$P_T = P_A + P_B$

Colligative Properties

These are the properties of solutions which depends on the number of solute particles and independent of their chemical identity. These are relative lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure.

Relative Lowering of Vapour Pressure

The vapour pressure of the solvent is lowered by the presence of a non-volatile solute in the solution and this lowering is governed by Raoult's law, according to which relative lowering of vapour pressure of solvent is equal to the mole fraction of non-volatile solute present in solution.

Relative lowering of vapour pressure = χ_B

$$\frac{P^o_A - P_S}{P^o_A} = \chi_B \qquad \{\chi_B = \text{mole fraction of solute}\}$$

Elevation of boiling point

$\Delta T_b = K_b \times m$ {m = molality}

$$K_b = \frac{RT_b^2}{1000\,L_{\text{vapourisation}}} = \frac{M_A RT_b^2}{1000\Delta H_{\text{vapourisation}}}$$

where $L_{\text{vapourisation}}$ is latent heat of vapourisation in cal./g

$\Delta H_{\text{vapourisation}}$ is enthalpy of vapourisation in cal./mol

Depression in freezing point

$\Delta T_f = K_f \times m$

$$K_f = \frac{RT_f^2}{1000\,L_{\text{fusion}}} = \frac{M_A RT_f^2}{1000\Delta H_{\text{fusion}}}$$

where L_{fusion} is latent heat of fusion in cal./g

ΔH_{fusion} is enthalpy of fusion in cal./mol

Osmotic pressure

$\pi = CRT$

For isotonic solution, $\pi_1 = \pi_2$ thus, $C_1 = C_2$.

Van't Hoff Factor

Van't Hoff Factor 'i' is the extent to which a solute is dissociated or associated. This can be defined as ratio of observed colligative property to calculated colligative property.

$$i = \frac{\text{Experimental colligative property (observed)}}{\text{Calculated colligative property(Normal)}}$$

$$i = \frac{\text{Theoritical molar mass of solute}}{\text{Actual / observed molar mass of solute}}$$

Solutes which dissociate in solution exhibit the molar mass lower than the actual molar mass and those which associate show higher molar mass.

$$\frac{P_A^o - P_S}{P_A^o} = \frac{(i\,n_B)}{(i\,n_B + n_A)}$$

where n_B = moles of solute

n_A = moles of solvent

P_A° is vapour pressure of pure solvent A

P_S is vapour pressure of solution

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

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

$\pi = iCRT$

Association of solute

$nA \rightarrow (A)_n$

$$i = \frac{(1-\alpha) + \frac{\alpha}{n}}{1} \quad \{\alpha = \text{degree of association}\}$$

Dissociation of solute

$(A)_n \rightarrow nA$

$$i = \frac{1 + (n-1)\alpha}{1} \quad \{\alpha = \text{degree of dissociation}\}$$

Ideal and Non-Ideal Solutions

Solutions which obey Raoult’s law over the entire range of concentration are called ideal solutions. For non-ideal solutions, positive and negative deviations are observed from Raoult’s law. Azeotropes arise due to very large deviations from Raoult's law.

CHAPTER

3

Electrochemistry

Galvanic Cell

For a cell reaction in an electrochemical cell

$$Zn(s) + CuSO_4(aq) \rightleftharpoons Cu(s) + ZnSO_4(aq)$$

Cell representation $\Rightarrow$ $Zn \mid \underset{\text{Anode}(-)}{Zn^{2+}(aq.)} \mid\mid \underset{\text{Cathode}(+)}{Cu^{2+}(aq.)} \mid Cu$

For half cell reaction

$$M \rightarrow M^{n+}(aq.) + ne^-; E^o_{OX} = E^o_{M/M^{n+}}$$

$$M^{n+}(aq) + ne^- \rightarrow M; E^o_{red} = E^o_{M^{n+}/M}$$

Emf of cell, $E^0_{cell} = E^0_{right} - E^0_{left} = E^0_{\substack{cathode\\R.P.}} - E^0_{\substack{anode\\R.P}}$

(R.P. = Reduction potential)

- Oxidation potential for half cell reaction:

  $M \rightarrow M^{+n} + ne^-$

  $$E_{OX} = E^0_{OX} - \frac{2.303RT}{nF}\log[M^{n+}]$$

- Reduction potential for half-cell reaction:

  $$M^{n+} + ne^- \rightarrow M,\ E_{red} = E^0_{red} + \frac{2.303\,RT}{nF}\log[M^{n+}]$$

Nernst's Equation

- $\Delta G = -nFE_{cell} = -W$

  $\Delta G = \Delta G^\circ + 2.303\,RT\log Q$

  $\Delta G^\circ = -nFE^o_{cell}$

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

  ΔG = Change in free energy

  W = Useful work done

  n = Number of electrons exchanged

  F = Faraday constant (96500 coulomb)

  Q = Reaction quotient

  At room temperature (25°C)

  $\Rightarrow$ Nernst's equation

  $$\Rightarrow\ E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log Q$$

Concentration Cell

For concentration cells, $E^0_{cell} = 0$

- **For Electrode Concentration Cell**

  $Pt \mid H_2(P_1) \mid H^+(c\,M) \parallel H^+(c\,M) \mid H_2(P_2) \mid Pt$

  $E_{cell} = \frac{0.0591}{2}\log\frac{P_1}{P_2}$; (P = Pressure)

- **For Electrolyte Concentration Cell**

  $Cu \mid \underset{\text{anode}(-)}{Cu^{2+}(C_1)} \parallel \underset{\text{Cathode}(+)}{Cu^{2+}\ (C_2)} \mid Cu$

  $$E_{cell} = \frac{0.0591}{2}\log\frac{C_2}{C_1}$$

- **At Equilibrium**

  $E_{cell} = 0$ (as $\Delta G = 0$)

Thermodynamics for the Cell

- **Temperature Coefficient (T.C.)**

  $$(T.C.) = \left(\frac{\partial E_{cell}}{\partial T}\right)_\rho$$

- **Change in Entropy**

  $$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_p$$

- **Relation Between E_{Cell} & (T.C.)**

  $$E_{cell} = \left(\frac{-\Delta H}{nF}\right) + T\left(\frac{\partial E}{\partial T}\right)_p$$

  $\{\Delta H = \text{Heat of cell reaction}\}$

  $\left(\frac{\partial E}{\partial T}\right)_p > 0 \Rightarrow$ Cell reaction is endothermic and vice versa.

Quantitative Analysis

- **Faraday's 1st Law of Electrolysis**

  m = ZIt

  m = mass of substance deposited

  Z = electrochemical equivalent

  I = current

  t = time

  $$Z = \frac{\text{Atomic mass}}{n \times F}$$

- Faraday's 2nd Law of Electrolysis (Q = constant)

$$\frac{m_1}{m_2} = \frac{E_1}{E_2}$$ (E = equivalent weight)

Conductance

- **Ohm's Law**

  $V = RI$

  $$R = \rho\frac{\ell}{a}$$

  V = Potential difference

  R = Resistance

  I = Current

  ρ = Specific resistance (resistivity)

  ℓ = length of conductor

  a = cross-section area of conductor

- **Conductance**

  $$G = \frac{1}{R}$$

- **Specific Conductance (Conductivity)**

  $$\kappa = \frac{1}{\rho}$$

- **Cell Constant**

  $$G^* = \frac{\ell}{a}$$

  $$\kappa = G \times G^*$$

- **Molar Conductance**

  $$\Lambda_m = \frac{1000 \times \kappa}{C(\text{or } M)}$$

  {C = concentration of electrolyte in terms of molarity}

- **Equivalent Conductance**

  $$\Lambda_{eq} = \frac{1000 \times \kappa}{N}$$

  {N = Normality}

  $$\Lambda_{eq} = \frac{\Lambda_M}{(n - \text{factor})}$$

  $$\Lambda_0 = \lim_{C \to 0} \Lambda_C$$

  {Λ_0 = equivalent conductance at infinite dilution (or zero concentration)}

- **For Weak Electrolyte**

  $$\Lambda_C \propto \frac{1}{\sqrt{C}}$$

  For strong electrolyte, $\Lambda_C = \Lambda_0 - B(C)^{1/2}$ (B = constant)

- **At Infinite Dilution, for an Electrolyte A_xB_y**

  $$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

  $$\Lambda^0_{A_xB_y} = x\lambda^0_{A^{y+}} + y\lambda^0_{B^{x-}}$$

  {$\lambda^0_{A^{y+}}, \lambda^0_{B^{x-}}$ = equivalent conductance at infinite dilution of cation and anion}

- **Ionic Mobility**

  $$\mu = \frac{\text{Ionic Velocity}}{\text{Potential gradient}}$$

Degree of Dissociation

- **For a Weak Electrolyte**

  $(CH_3COOH \rightleftharpoons CH_3COO^- + H^+)$

  $$\alpha = \frac{\Lambda_m}{\Lambda_0}, \; K_a = \frac{C(\Lambda_m / \Lambda_0)^2}{1 - (\Lambda_m / \Lambda_0)}$$

Solubility Product

For solubility of salt $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$$K_{sp} = \left(\frac{1000\kappa}{\Lambda_0}\right)^2$$

CHAPTER

4

Chemical Kinetics

Chemical Kinetics

Chemical Kinetics is the study of chemical reactions with respect to reaction rates and effect of various variables.

The rate of a reaction

The rate of a reaction is concerned with decrease in concentration of reactants or increase in concentration of products per unit time. It can be expressed as an instantaneous rate at a particular instant of time and average rate over a large period of time.

Factors affecting rate of reaction

A number of factors such as nature of reactants and products, exposure to radiations, temperature, concentration of reactants, catalyst and surface area of solid reactants affect the rate of a reaction.

Rate Law

Rate law is the mathematical representation for rate of reaction, it can be determined experimentally and cannot be predicted.

Order of a reaction

Order of a reaction with respect to a reactant is the power of its concentration term which appears in the rate law, it is an experimentally determined quantity.

Molecularity

Molecularity of a reaction is the number of reacting species taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction. Molecularity of a reactant greater than 3 are rare. Order and molecularity of elementary reactions are same.

Rate Constant

Rate constant is the proportionality constant in rate law.

Integrated Rate

Integrated rate equations can be determined by integrating the differential rate equations.

Half Life

Half life is the time, in which half of the initial amount of reactants is converted into products. (Time taken for 50% completion of reactions)

Collision Theory

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

Nuclear Chemistry

Nuclear chemistry is the study of chemical reactions involving changes in nuclei of atoms. It provides information about kinetic of radioactive decay and time period (unaffected by temperature, pressure catalyst).

Formulae Chart

(*i*) For a general chemical transformation

$nA + mB \rightarrow pC + qD$

$$\text{Rate} = \frac{-1}{n}\frac{d[A]}{dt} = \frac{-1}{m}\frac{d[B]}{dt} = +\frac{1}{p}\frac{d[C]}{dt} = +\frac{1}{q}\frac{d[D]}{dt}$$

(*ii*) For general chemical changes

$mA + nB \rightarrow \text{Products}$

$$\text{Theoretical rate} = \frac{dx}{dt} = k[A]^m \times [B]^n$$

(*iii*) For a general reaction:

$aA + bB \rightarrow \text{Products}$

$$\text{Rate} = \frac{dx}{dt} = k[A]^m \times [B]^n$$

Order of reaction w.r.t. A = m

Order of reaction w.r.t. B = n

(*iv*) Unit of rate constant $= (\text{mole litre}^{-1})^{1-n}\,(\text{time})^{-1}$

where, n = order of reaction

(*v*) For a zero order reaction: $A \rightarrow B$

$$\text{Rate} = \frac{-d[A]}{dt} = k[A]^0 = k(\text{constant})$$

(*vi*) For a first order reaction $A \rightarrow B$

$$\text{Rate} = \frac{-d[A]}{dt} = k[A]$$

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t} = \frac{2.303}{t}\log_{10}\left(\frac{a}{a-x}\right)$$

(*vii*) For a first order reaction, $A \rightarrow B$

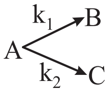
$$\log_{10}[A]_t = \frac{-k}{2.303}t + \log_{10}[A]_0$$

(*viii*) For a zero order reaction $t_{1/2} = \frac{[A]_0}{2k}$

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

For an nth order reaction, $t_{1/2} = \frac{1}{[A]_0^{n-1}}$ (for $n \geq 2$)

(*ix*) For a parallel reaction



$$\frac{-d[A]}{dt} = (k_1 + k_2)[A]$$

(*x*) For hydrolysis of sucrose, $S \xrightarrow{H^+} G + F$

$$k = \frac{2.303}{t}\log_{10}\left(\frac{r_0 - r_\infty}{r_t - r_\infty}\right).$$

(r = rotation due to all S, G and F)

(*xi*) Temperature coefficient $= \frac{k_{T+10}}{k_T} = 2 \text{ to } 3$

Arrhenius equation, $k = Ae^{-E_a/RT}$

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{[2.303R]}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

(A = Arrhenius's constant E_a = Activation energy)

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$$

(*xii*) In a radioactive decay, $N_t = N_0e^{-\lambda t}$

Amount of radioactive substance after 'n' half life periods

$$N_t = \left(\frac{1}{2}\right)^n N_0$$

CHAPTER

5

Surface Chemistry

Surface Chemistry

It deals with phenomenon occuring at the surface or interface.

Adsorption

Accumulation of particles at surface is known as adsorption. It is classified as physisorption & chemisorption.

Physisorption & Chemisorption

In physisorption, adsorbate is held to adsorbent by weak van der Waal's forces and in chemisorption, adsorbate is held to the adsorbent by strong chemical bond.

Sorption

When both the phenomenon of adsorption & absorption occur simultaneously, then it is termed as sorption.

Factors affecting Adsorption:

1. Nature of gas (adsorbate)
2. Nature of solid (adsorbent)
3. Specific area of solid (adsorbent)
4. Pressure of gas
5. Temperature
6. Activation energy of solid.

Adsorption Isotherms

1. Freundlich Adsorption Isotherm:

$$\boxed{\frac{x}{m} = kp^{\frac{1}{n}}}\ ; n > 1$$

2. Langmuir Adsorption Isotherm

$$\boxed{\frac{x}{m} = \frac{k_1P}{1 + k_1p}}$$

Catalysis

Catalysis is the phenomenon, by which the rate of a reaction is altered (accelerated or retarded) by the presence of a substance, which itself remains unchanged, chemically in the process. The substance altering the rate of the reaction is called a catalyst.

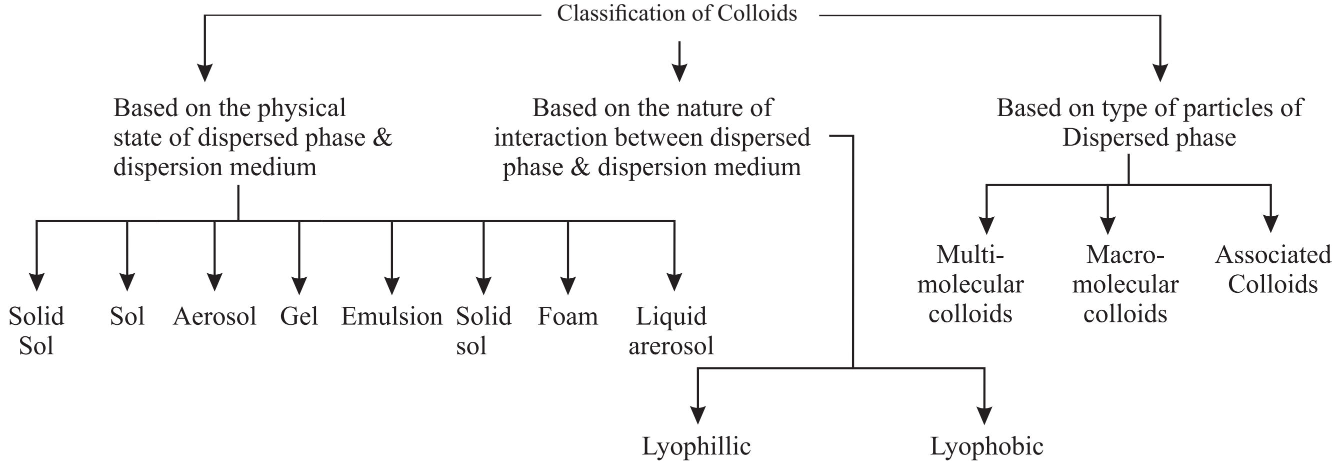
Types of Catalysis

1. Positive catalysis
2. Negative catalysis
3. Auto catalysis
4. Homogeneous catalysis
5. Heterogeneous catalysis
6. Induced catalysis

Colloidal System

Colloidal system is a two phase system, consisting of a dispersion medium, in which extremely minute particles are lying within colloidal range (1-1000) nm and second substance is termed as dispersed phase.

Classification of Colloids

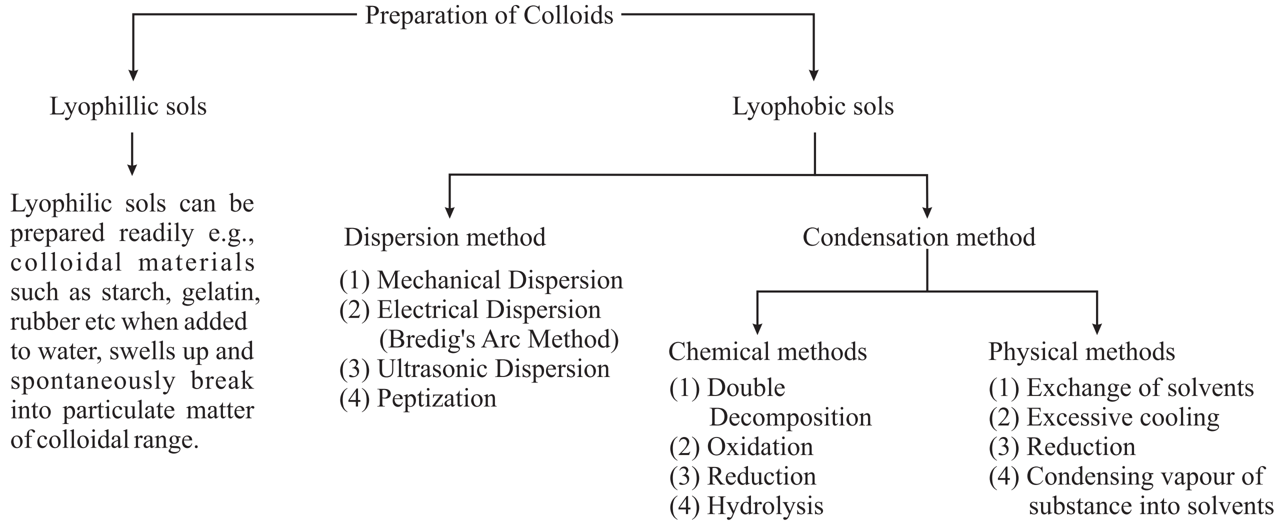


Micelles

Micelles are aggregated spherical structures of many smaller entities (amphiphilic molecules) giving rise to a colloidal system.

1. **Kraft temperature:** The formation of micelles takes place only at a particular temperature, that temperature is known as kraft temperature.
2. **CMC (Critical Micelle Concentration):** The concentration above which micelle formation becomes appreciable is termed as the critical micelle concentration. Its value depends on the nature of dispersed phase and the dispersion medium.

Preparation of Colloids



Purification of Colloidal System

The colloidal sols obtained by various methods are impure and contain impurities of electrolytes and other soluble substances, these impurities may destabilise the sol. Hence, they have to be removed.

1. **Dialysis:** It is a process of removing dissolved substance from colloidal solution by means of diffusion through a suitable membrane.
2. **Ultrafiltration:** Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially prepared filters, which are permeable to all substances except the colloidal particles.

Properties of Colloidal Sols

1. **Optical property:**

   Tyndall effect: If a strong beam of light is passed through a colloidal sol placed in a dark place, the path of the beam gets illuminated. This phenomenon is called Tyndall Effect, Which is due to the scattering of light by the colloidal particles.
2. **Electrical property:**

   Electrophoresis: The movement of colloidal particles under an applied electric potential is called electrophoresis. Depending upon the direction of movement of particle towards cathode or anode, electrophoresis can be termed as cataphoresis or anaphoresis
3. **Mechanical property:**
   - **Brownian motion:** The phenomenon of random movement of colloidal particles in zig-zag directions is known as Brownian motion.
   - **Sedimentation potential or Dorn potential:** When the charged colloidal particles are made to settle down under centrifugal field, there occurs a charge separation and a potential difference is developed. This effect is called **Dorn effect** and the potential difference thus developed is called Dorn potential or sedimentation potential. This process is **reverse of electrophoresis.**
4. **Eletro-osmosis:**

   When movement of colloidal particles is prevented by some suitable means (porous diaphragm or semi-permeable membrane), it is observed that the dispersion medium begins to move in an electric field. This phenomenon is termed electro-osmosis.
5. **Isoelectric point:**

   The H^+ concentration, at which the colloidal particles have no charge is known as the isoelectric point. At this point, stability of colloidal particles becomes very less & particles do not move under influence of electric field.
6. **Streaming potential:**

   A potential difference is developed across a porous partition when the dispersion medium of a charged colloid is forced through it. This is called Streaming potential. This process is reverse of electro-osmosis.

Coagulation/Flocculation

The process of aggregation of colloidal particles into an insoluble precipitate by the addition of some suitable electrolyte is known as coagulation.

$$\boxed{\text{Coagulation value} = \frac{\text{Millimoles of an electrolyte added}}{\text{Volume of sol in Litre}}}$$

1. **Factors affecting Coagulation:**
   - (*a*) Nature of Sols
   - (*b*) Nature of electrolytes
2. **Hardy-Schulze rule:**

   According to this rule, greater is the valency of coagulating ion, greater is its power to cause precipitation.
3. **Gold Number:**

   "The minimum amount of the protective colloid in milligrams which when added to 10 ml of a standard gold sol is just sufficient to prevent a colour change from red to blue on the addition of 1 ml of 10% sodium chloride solution. Smaller is the gold number, greater will be protecting power of the protective colloid.

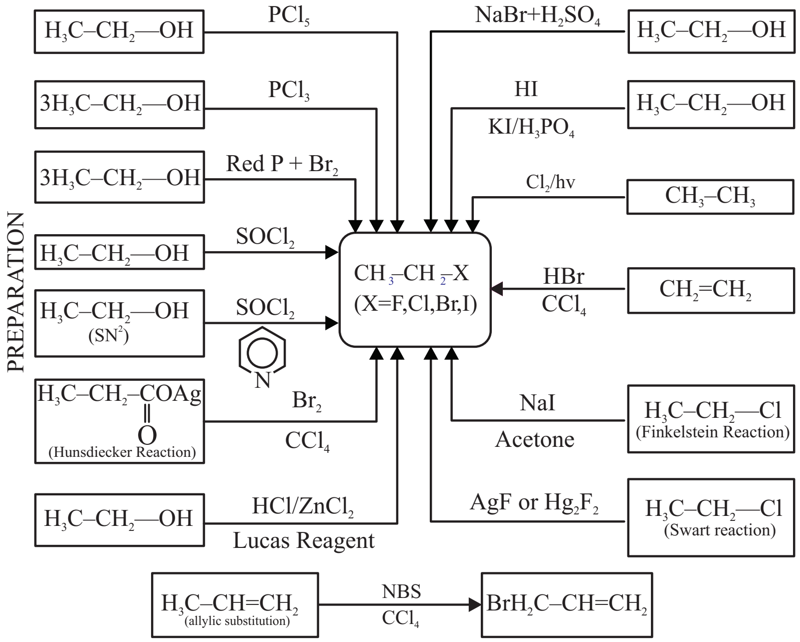
$$\boxed{\text{Protective power} \propto \frac{1}{\text{gold number}}}$$

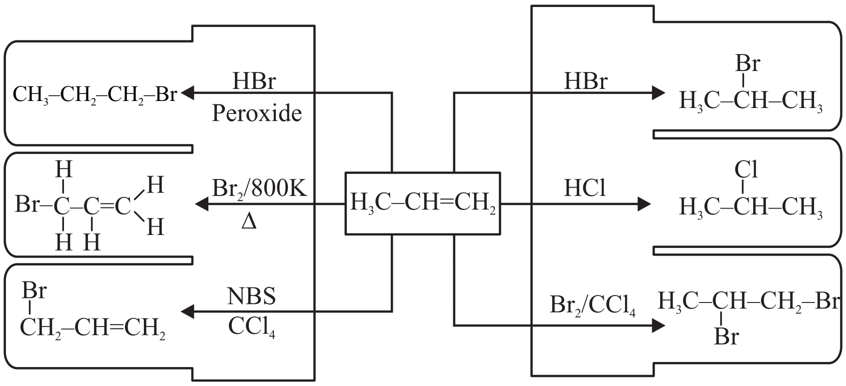
$$\boxed{\text{Gold Number} = \frac{\text{Weight of lyophilic sol in mg} \times 10}{\text{Volume of gold sol in mL}}}$$

CHAPTER

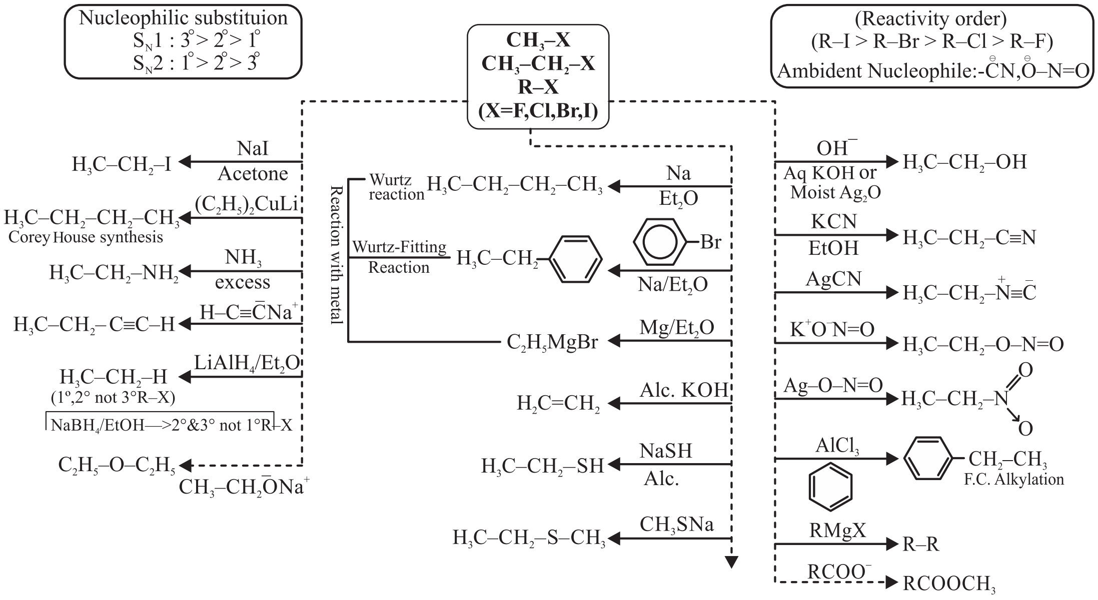
6

Haloalkanes and Haloarenes





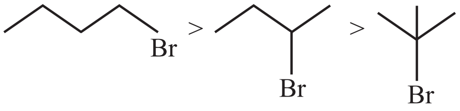
REACTIONS



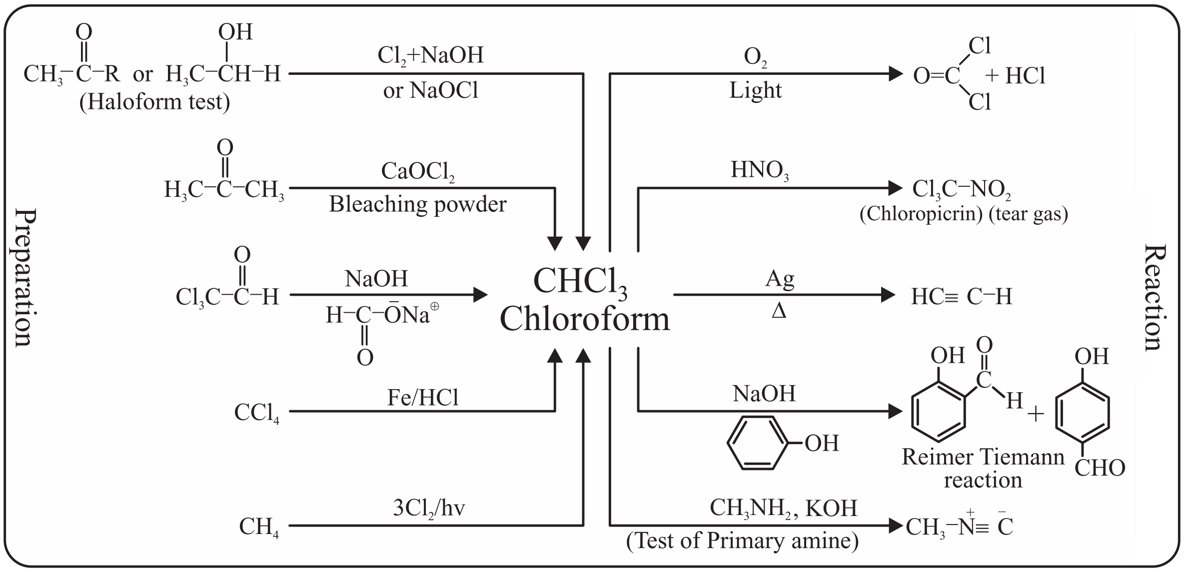
PHYSICAL PROPERTIES

(1) Dipole moment: $CH_3–Cl > CH_3–F > CH_3–Br > CH_3–I$

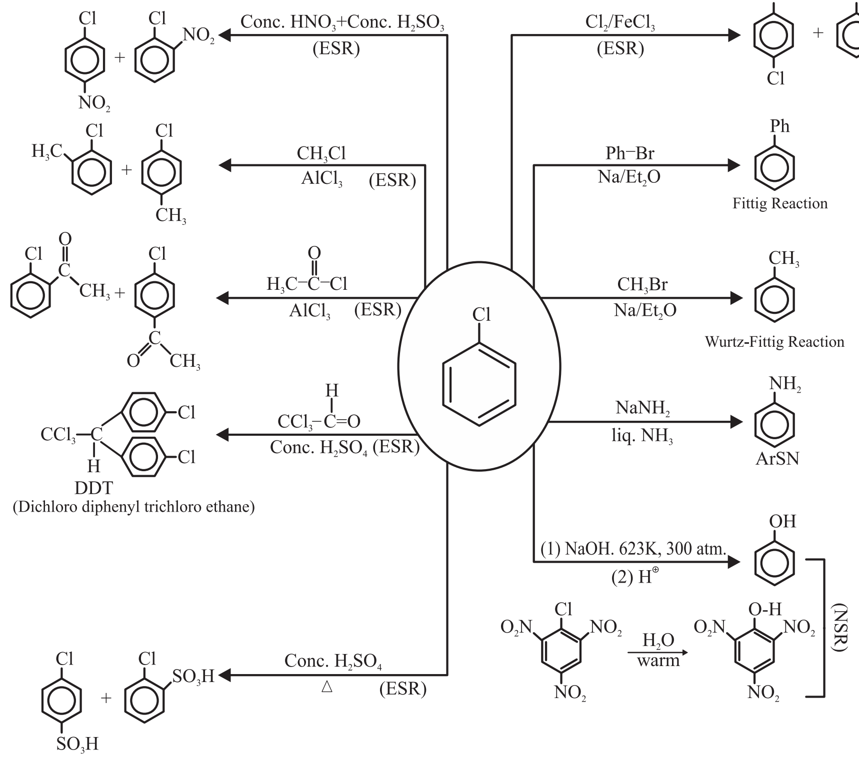
(2) Boiling point: R–I > R–Br > R–Cl > R–F



TRI-HALO ALKANE

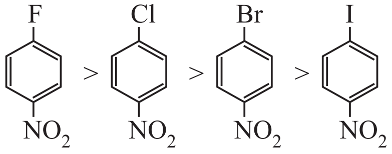


HALO-ARENE

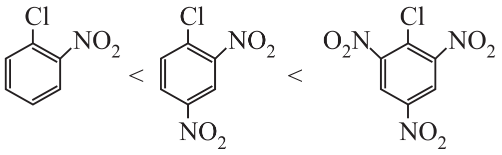


- **Reactivity Order towards Nucleophile**

(i)

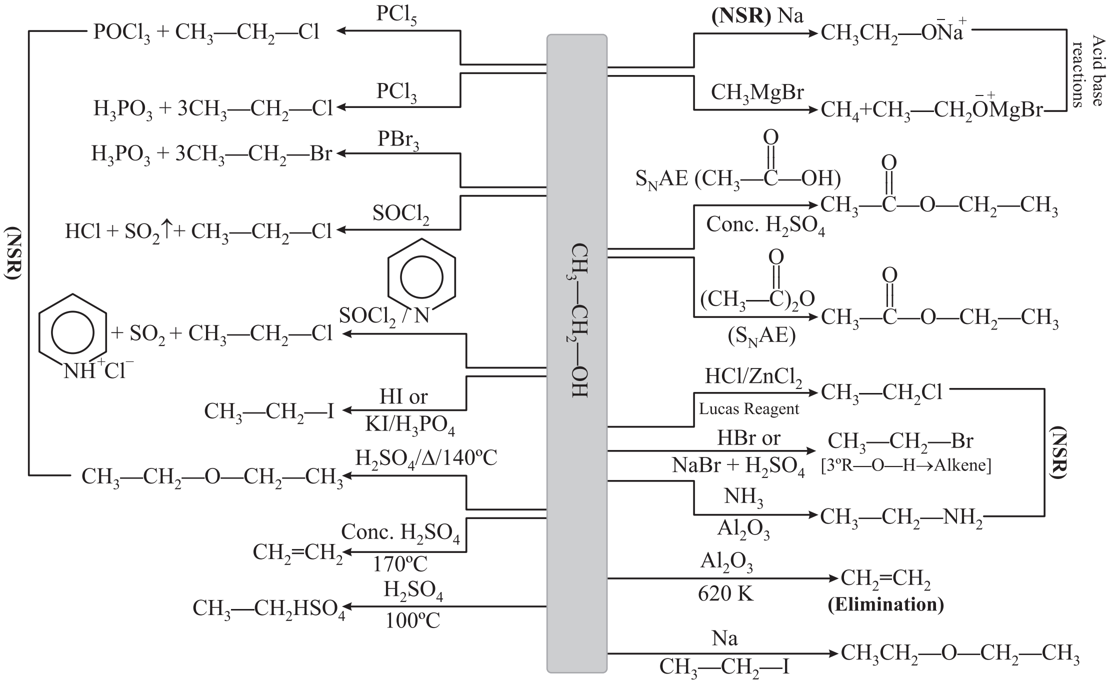


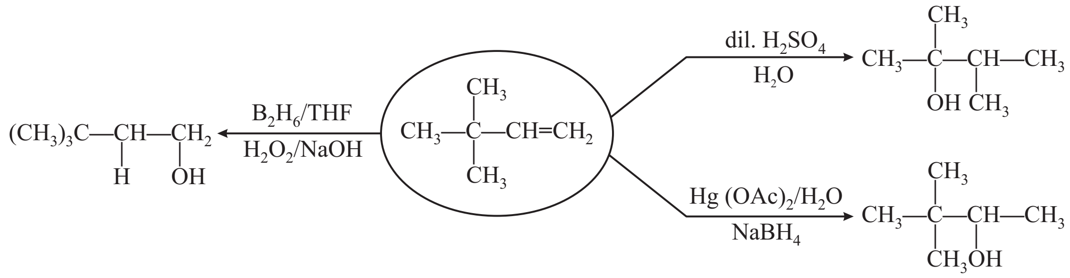
(ii)

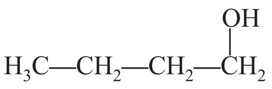
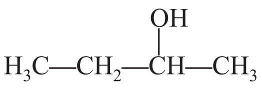
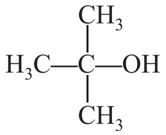
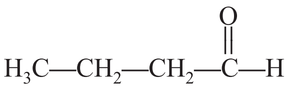
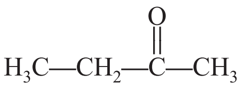
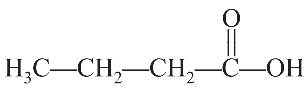
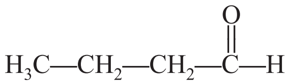
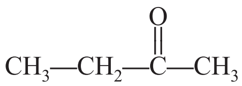
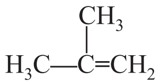


CHAPTER 7

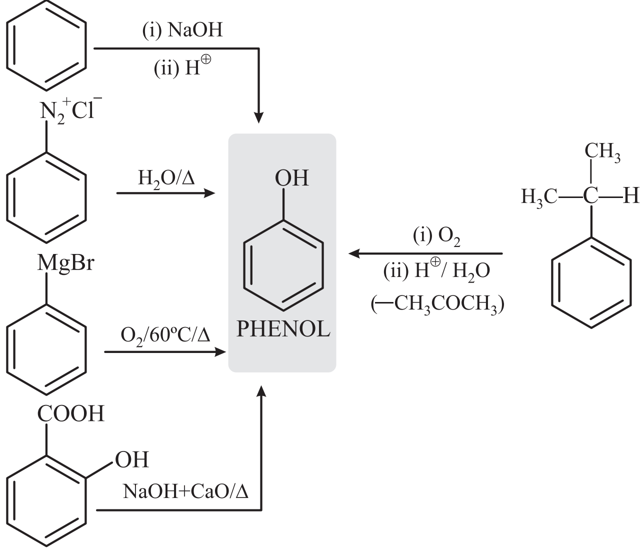
Alcohols, Phenols and Ether



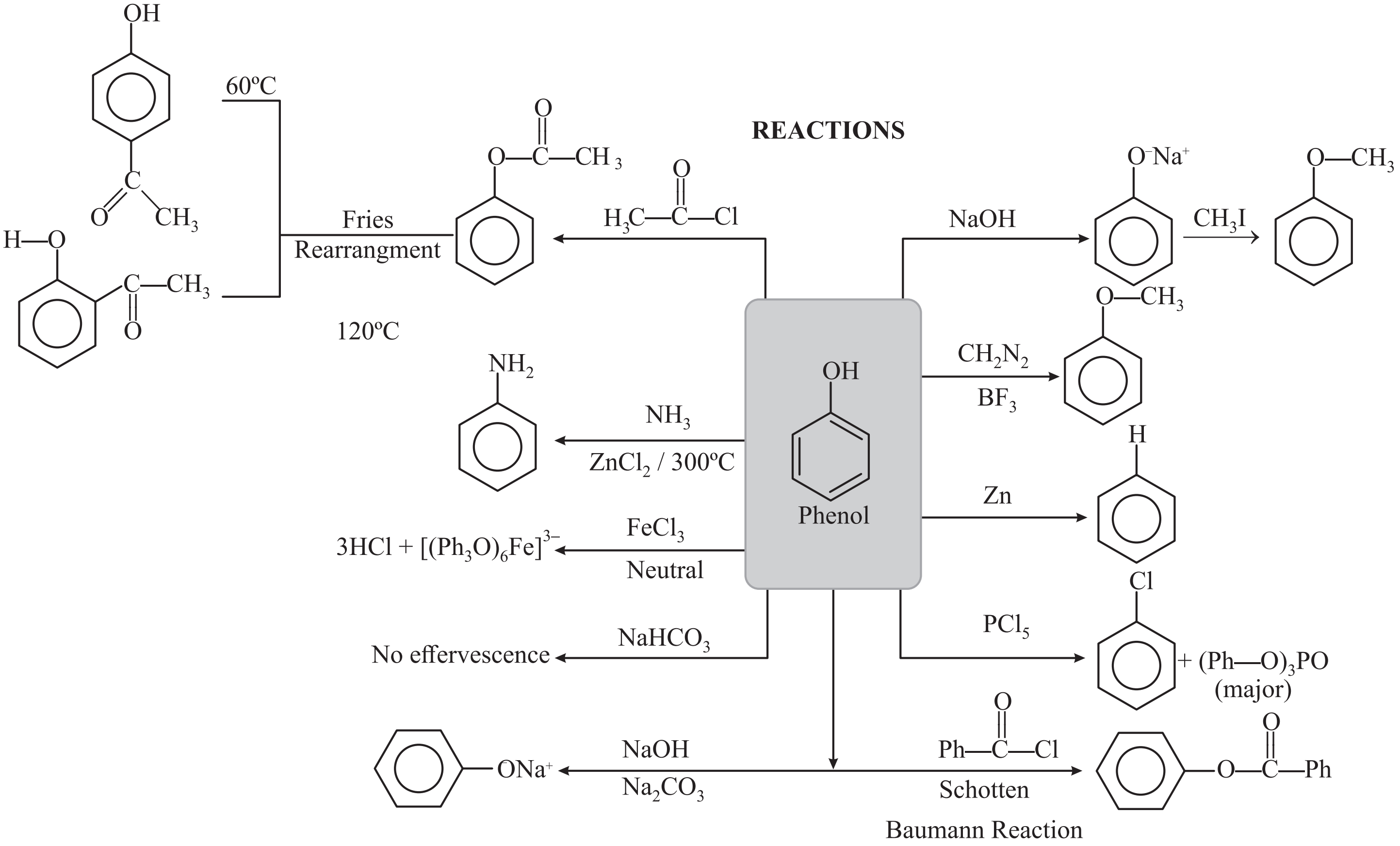


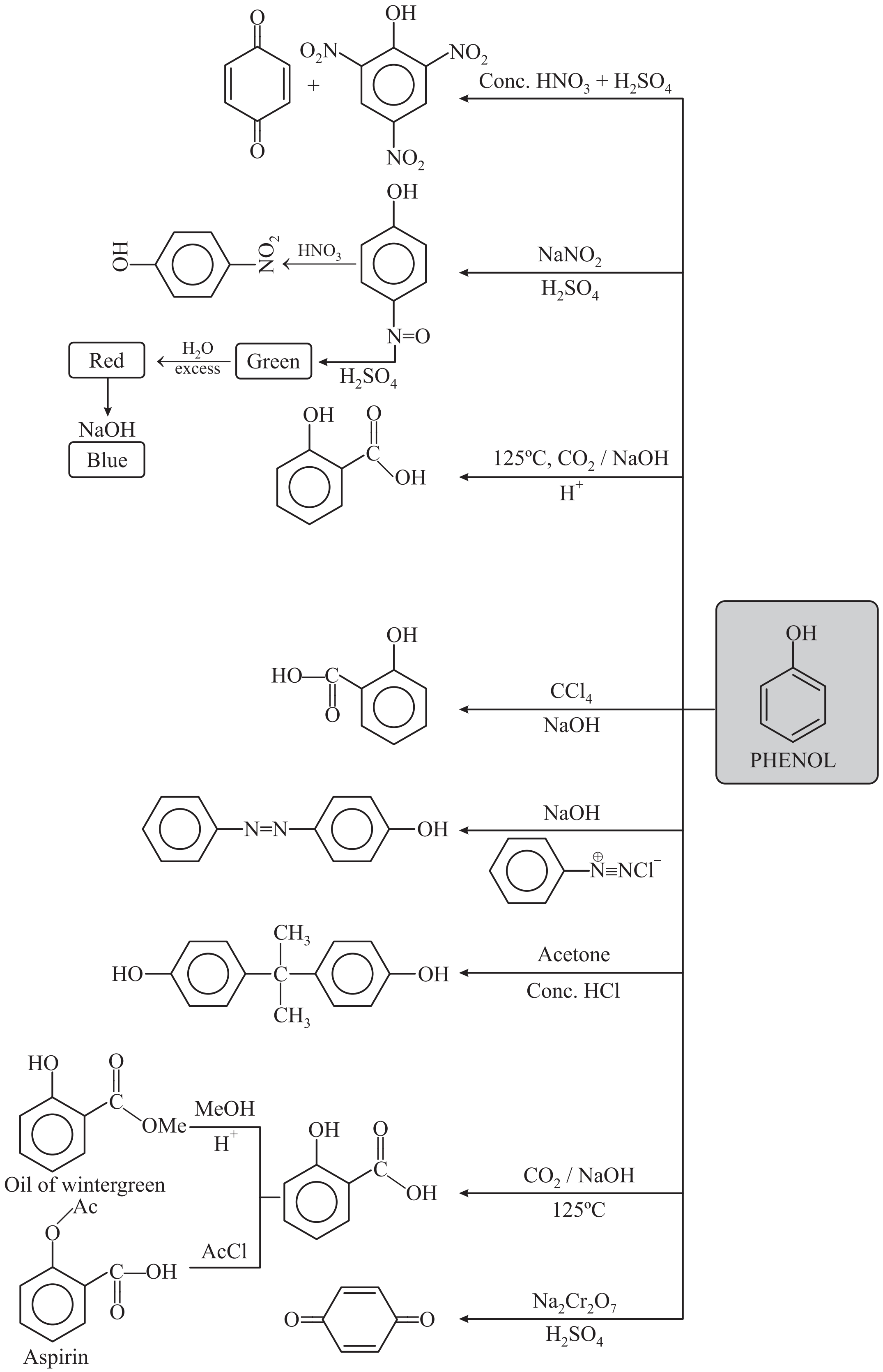
Distinction between 1°, 2° and 3° alcohols			
Reagent	 $H_3C-CH_2-CH_2-\overset{\overset{OH}{\vert}}{CH_2}$ 1ºAlcohol	 $H_3C-CH_2-\overset{\overset{OH}{\vert}}{CH}-CH_3$ 2ºAlcohol	 $H_3C-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-OH$ 3ºAlcohol
PCC / PDC Anhy. CrO_3	 $H_3C-CH_2-CH_2-\overset{\overset{O}{\Vert}}{C}-H$	 $H_3C-CH_2-\overset{\overset{O}{\Vert}}{C}-CH_3$	No reaction
$K_2Cr_2O_7/H^{\oplus}$ $KMnO_4/H^+/^-OH/\Delta$ Jones Reagent	 $H_3C-CH_2-CH_2-\overset{\overset{O}{\Vert}}{C}-OH$	 $H_3C-\overset{\overset{O}{\Vert}}{C}-OH + CH_3-\overset{\overset{O}{\Vert}}{C}-OH$	No reaction
Cu/500ºC	 $H_3C-CH_2-CH_2-\overset{\overset{O}{\Vert}}{C}-H$	 $CH_3-CH_2-\overset{\overset{O}{\Vert}}{C}-CH_3$	 $H_3C-\overset{\overset{CH_3}{\vert}}{C}=CH_2$
Lucas Reagent $HCl/ZnCl_2$	Cloudiness appear upon heating after 30 mins.	Within five min.	Immediately

PHENOL
GMP

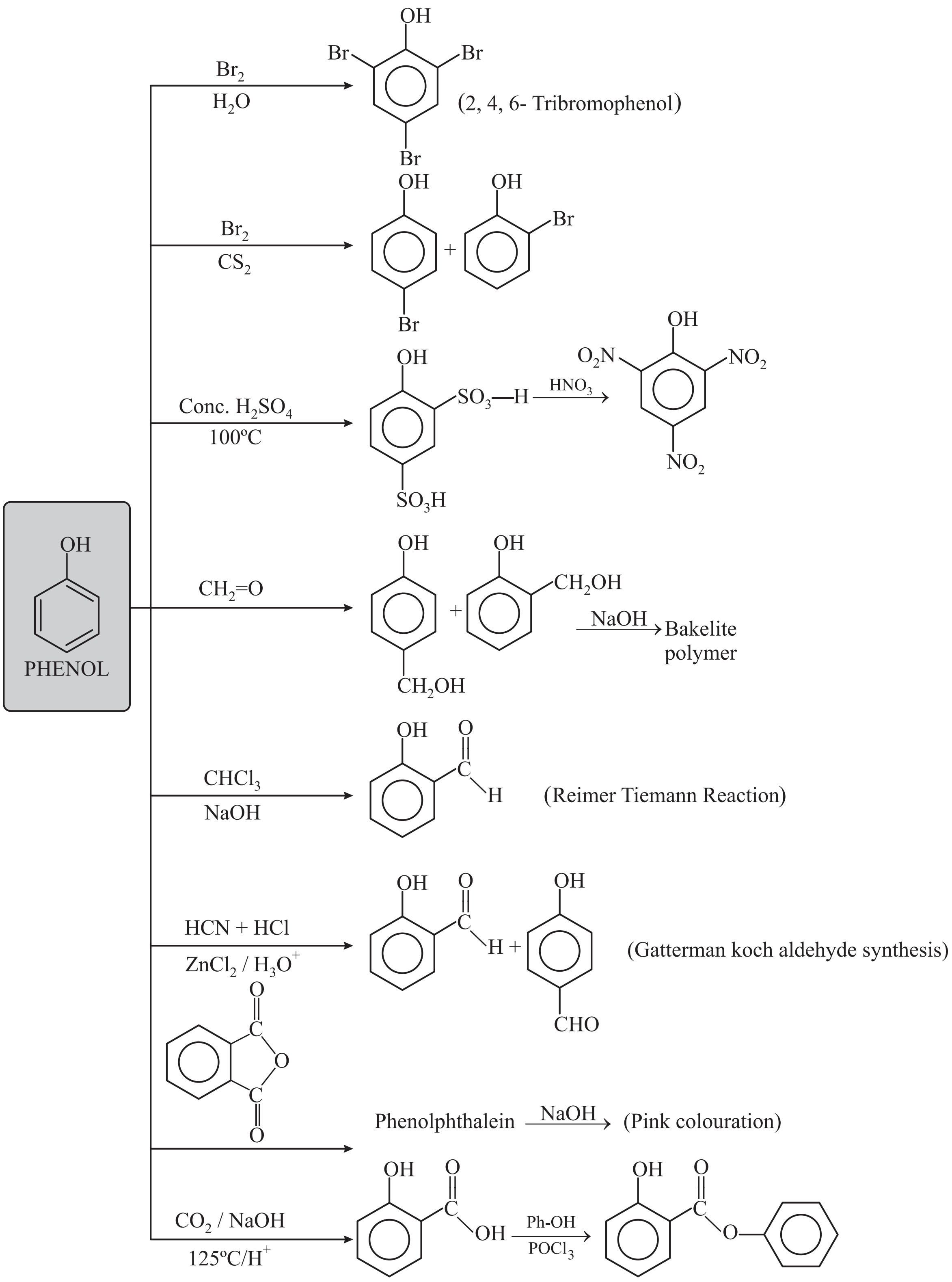


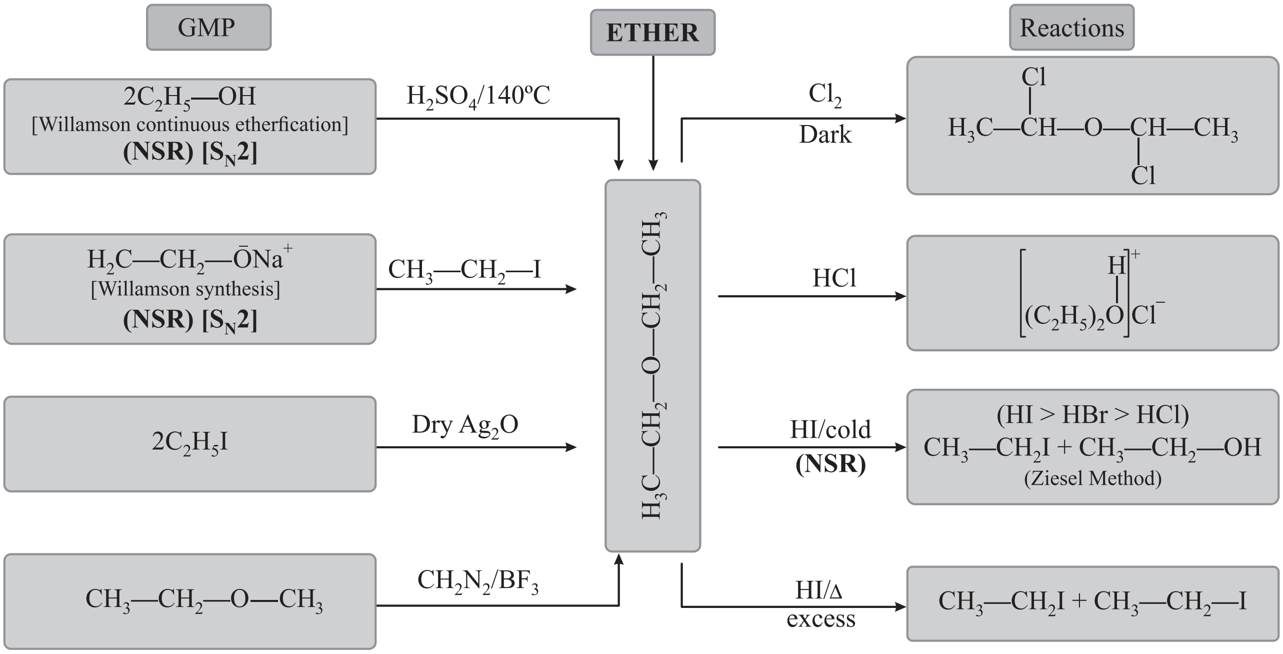
REACTIONS


OH
60ºC
O
O—C—CH 3
H—O
C
O
CH3
C—CH3
O
Fries
Rearrangment
120ºC
H3C—C—Cl
O
NaOH
O⁻Na⁺
CH3I
O—CH3
CH2N2
BF3
O—CH3
NH2
NH3
ZnCl2 / 300ºC
OH
Phenol
H
Zn
FeCl3
Neutral
3HCl + [(Ph3O)6Fe]3–
No effervescence
NaHCO3
PCl5
Cl
+ (Ph—O)3PO
(major)
ONa⁺
NaOH
Na2CO3
Ph—C—Cl
O
Schotten
Baumann Reaction
O—C—Ph
O



O
O
+
OH
O2N
NO2
NO2
Conc. HNO3 + H2SO4
OH
HO
NO2
HNO3
N=O
NaNO2
H2SO4
Red
H2O excess
Green
H2SO4
NaOH
Blue
OH
O
C
OH
125ºC, CO2 / NaOH
H+
OH
HO—C
O
CCl4
NaOH
PHENOL
N=N
OH
NaOH
N≡NCl−
CH3
HO
C
OH
CH3
Acetone
Conc. HCl
HO
O
C
OMe
MeOH
H+
Oil of wintergreen
OH
O
C
OH
CO2 / NaOH
125ºC
Ac
O
C—OH
O
AcCl
Aspirin
O
O
Na2Cr2O7
H2SO4

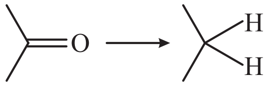
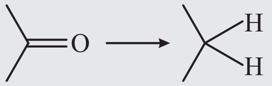
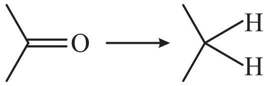
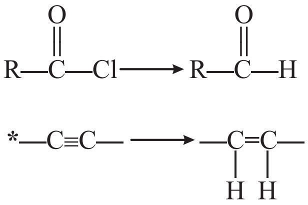
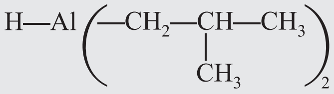
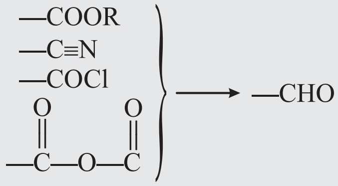
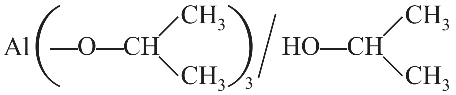
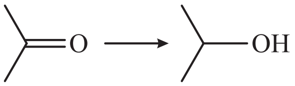
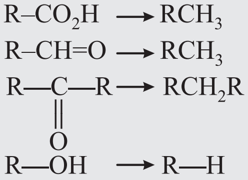

PHENOL
OH
Br2 / H2O
(2, 4, 6- Tribromophenol)
Br2 / CS2
Conc. H2SO4 / 100ºC
SO3—H
SO3H
HNO3
O2N
NO2
CH2=O
CH2OH
NaOH
Bakelite polymer
CHCl3 / NaOH
(Reimer Tiemann Reaction)
HCN + HCl / ZnCl2 / H3O+
CHO
(Gatterman koch aldehyde synthesis)
Phenolphthalein
NaOH
(Pink colouration)
CO2 / NaOH / 125ºC/H+
Ph-OH / POCl3

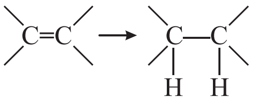
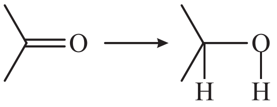
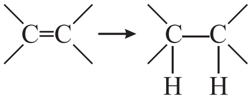

GMP
ETHER
Reactions
$2C_2H_5$—OH
[Willamson continuous etherfication]
(NSR) [S_N2]
H_2SO_4/140ºC
H_2C—CH_2—$\bar{O}Na^+$
[Willamson synthesis]
(NSR) [S_N2]
CH_3—CH_2—I
$2C_2H_5I$
Dry Ag_2O
CH_3—CH_2—O—CH_3
CH_2N_2/BF_3
H_3C—CH_2—O—CH_2—CH_3
Cl_2
Dark
Cl
H_3C—CH—O—CH—CH_3
Cl
HCl
$\left[(C_2H_5)_2\overset{H}{O}\right]^+ Cl^-$
HI/cold
(NSR)
(HI > HBr > HCl)
CH_3—CH_2I + CH_3—CH_2—OH
(Ziesel Method)
HI/Δ
excess
CH_3—CH_2I + CH_3—CH_2—I

CHAPTER

8

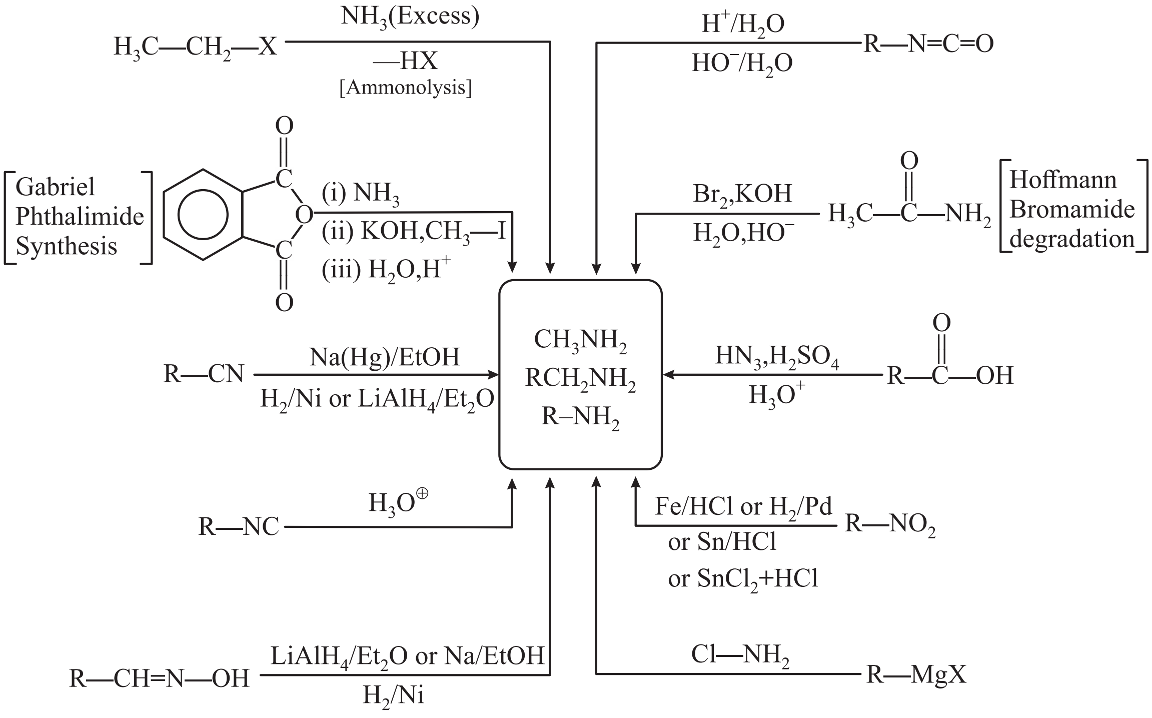
Aldehydes, Ketones and Carboxylic Acids

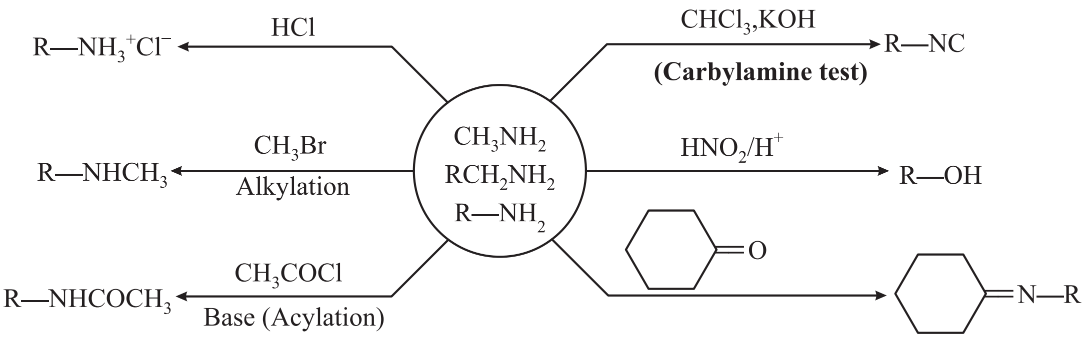
Name	Reagent	Function
Wolf Kishner Reduction	(i) N_2H_4/ (ii) KOH, Δ	
Clemmenson Reduction	Zn–Hg/HCl	
Mozingo Reduction	 Dry HCl, followed by Raney Ni	
Stephen's Reduction	$SnCl_2$/HCl followed by H_3O^+	$R–C\equiv N \longrightarrow R–CH=O$
Rosenmund Reduction	H_2, Pd–$BaSO_4$	 $R-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow R-\overset{\overset{O}{\|}}{C}-H$ $*-C\equiv C- \longrightarrow -\underset{H}{\underset{\|}{C}}=\underset{H}{\underset{\|}{C}}-$
DIBAL-H (–78°C)	 $H-Al\left(-CH_2-\underset{CH_3}{\underset{\|}{CH}}-CH_3\right)_2$ followed by $H_3O^{\oplus}$	 $\left.\begin{array}{l}-COOR\\-C\equiv N\\-COCl\\-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}\end{array}\right\}\longrightarrow -CHO$
MPV Reduction	 $Al\left(-O-CH\begin{matrix}CH_3\\CH_3\end{matrix}\right)_3 / HO-CH\begin{matrix}CH_3\\CH_3\end{matrix}$	
Red phosphorus in presence of HI	Red P + HI	 $R–CO_2H \longrightarrow RCH_3$ $R–CH=O \longrightarrow RCH_3$ $R-\underset{O}{\underset{\|}{C}}-R \longrightarrow RCH_2R$ $R-OH \longrightarrow R-H$

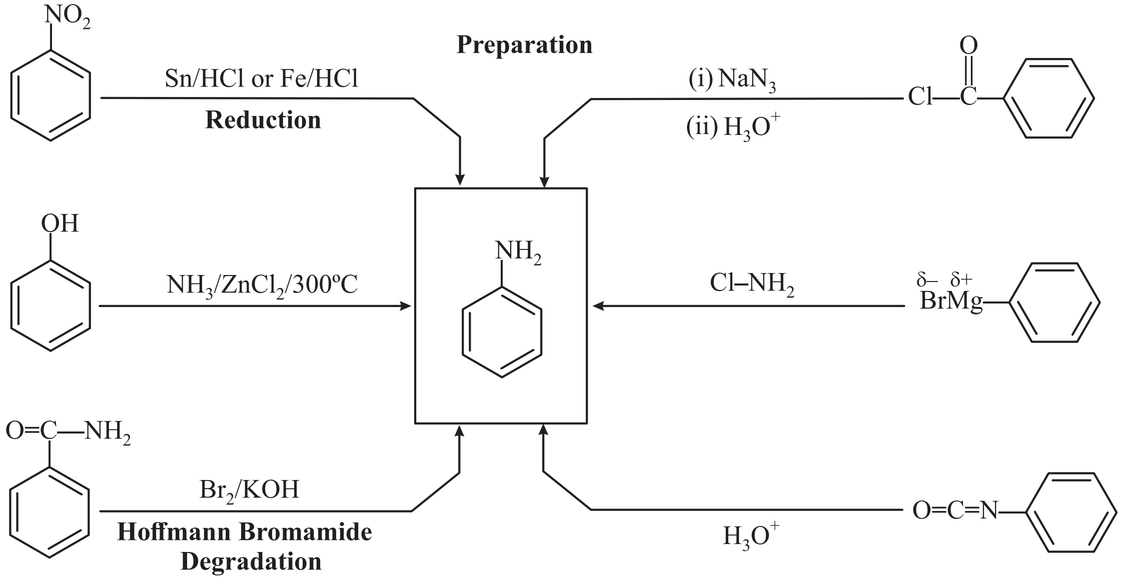
Hydroboration Reduction	B_2H_6/AcOH, H_2O	 
Bouveault–Blanc reduction	Na/EtOH	$R–COO–R \longrightarrow RCH_2OH + ROH$
Transfer Hydrogenation	N_2H_4/H_2O_2	

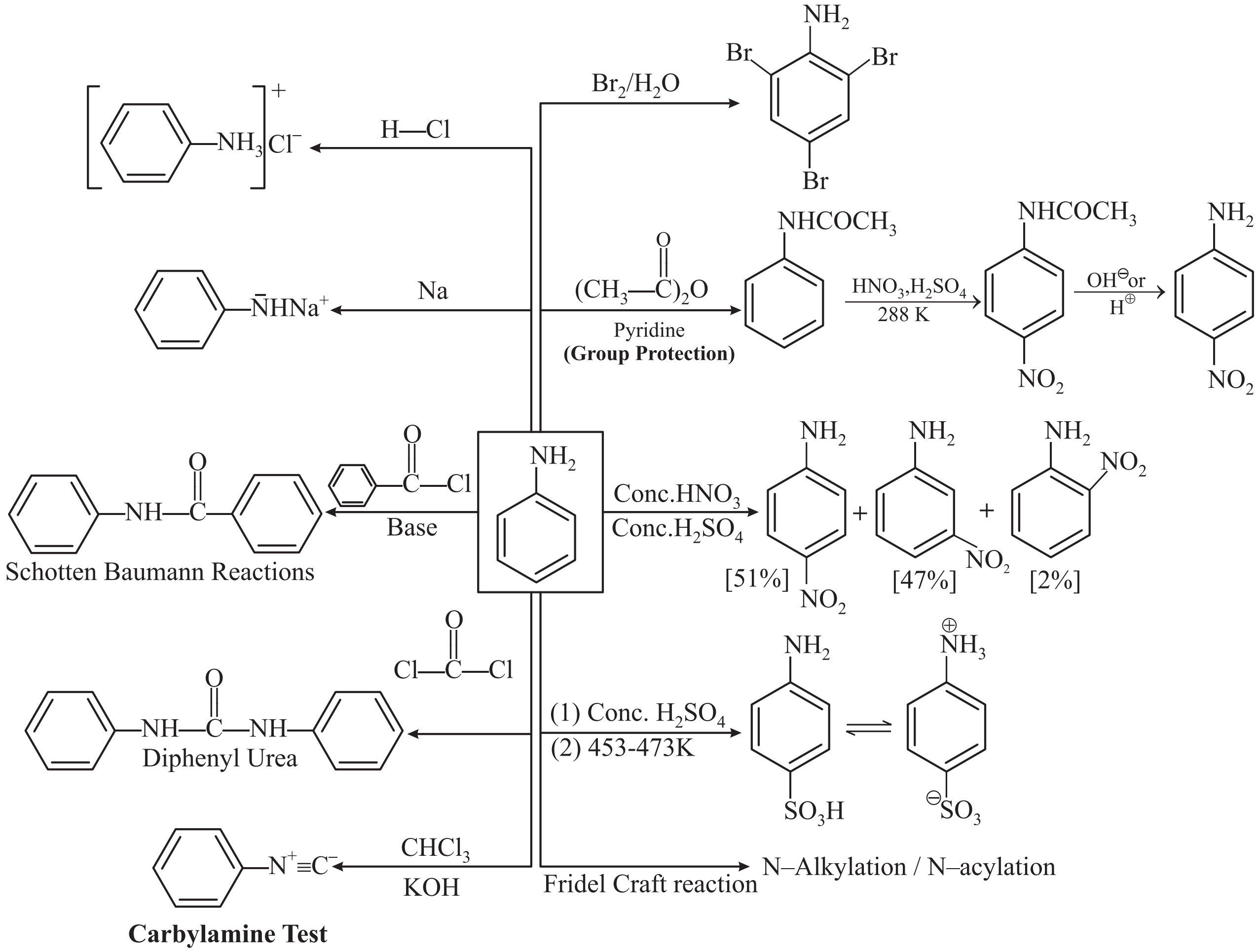
CHAPTER 9

Amines

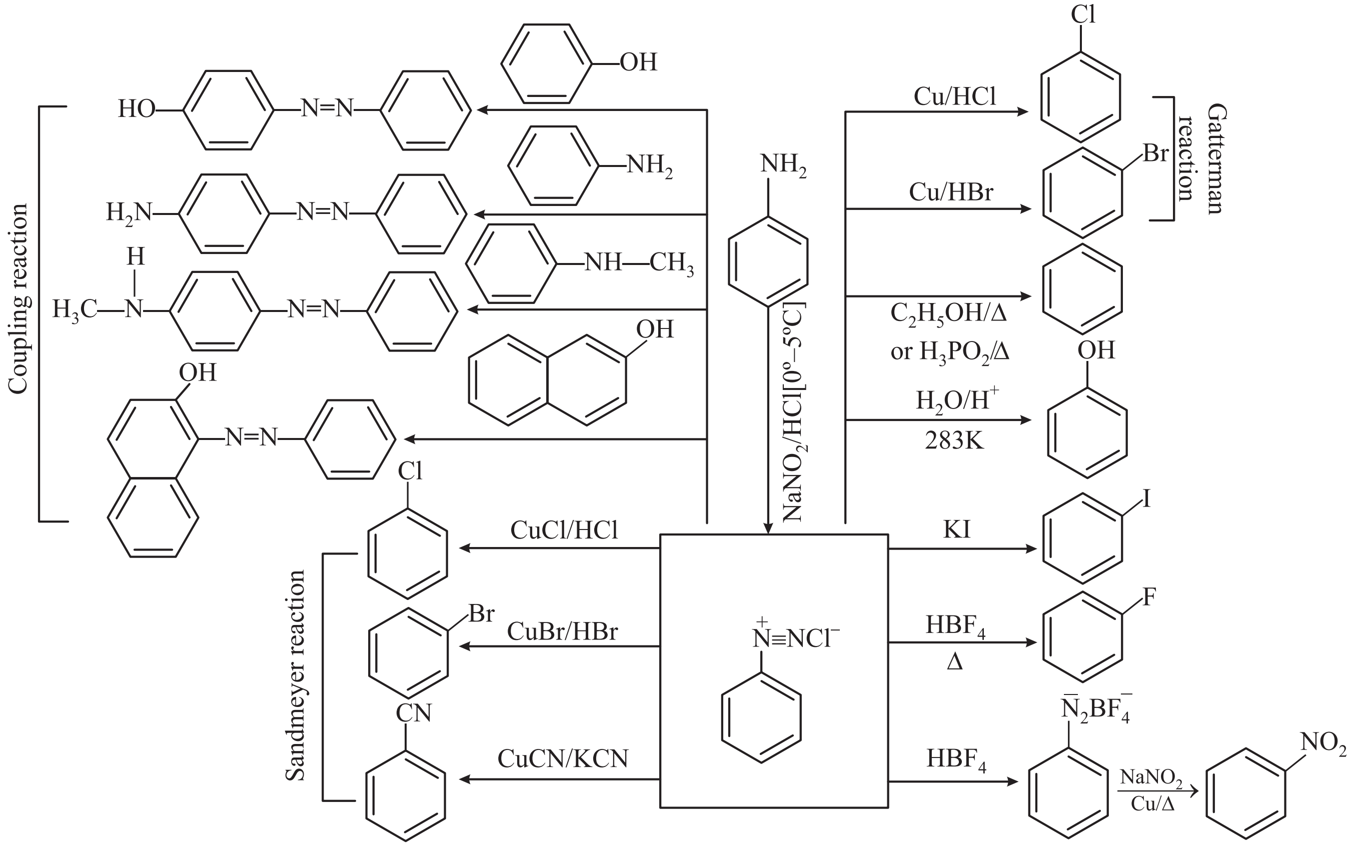





Preparation
NO_2
Sn/HCl or Fe/HCl
Reduction
(i) NaN_3
(ii) H_3O^+
Cl—C(=O)
OH
$NH_3/ZnCl_2/300°C$
NH_2
Cl–NH_2
δ– δ+
BrMg
O=C—NH_2
Br_2/KOH
Hoffmann Bromamide Degradation
O=C=N
H_3O^+


NH_2
Br
Br
Br_2/H_2O
Br
NH_3Cl^-
H—Cl
NHCOCH$_3$
NHCOCH$_3$
NH_2
$(CH_3—C(=O))_2O$
Pyridine
(Group Protection)
HNO_3,H_2SO_4
288 K
$OH^{\ominus}$ or $H^{\oplus}$
Na
$\bar{N}HNa^+$
NO_2
NO_2
NH_2
NH_2
NH_2
NH_2
NO_2
C(=O)—Cl
Base
NH—C(=O)
Schotten Baumann Reactions
Conc.HNO_3
Conc.H_2SO_4
[51%]
[47%]
[2%]
NO_2
NO_2
Cl—C(=O)—Cl
NH_2
$\overset{\oplus}{N}H_3$
NH—C(=O)—NH
Diphenyl Urea
(1) Conc. H_2SO_4
(2) 453-473K
SO_3H
$^{\ominus}SO_3$
$CHCl_3$
KOH
$N^+\equiv C^-$
Carbylamine Test
Fridel Craft reaction
N–Alkylation / N–acylation

Benzene Diazonium Chloride
Reaction



CHAPTER

10

The d & f-Block Elements

Definition

Transition elements are those d-block elements which have partially filled (n – 1)d subshell either in their ground state or in their stable oxidation states. Therefore, Zn, Cd & Hg are d-block elements and not transition elements.

General electronic configuration

$ns^{0-2} (n-1)d^{1-10}$

$$\text{Exceptions}\begin{cases} Cr = 3d^5 4s^1 \\ Cu = 3d^{10} 4s^1, Pd = 4d^{10} 5s^0 \end{cases}$$

Transition Series

1st	3d series	Sc_{21} — Zn_{30}	9 + 1 = 10
2nd	4d series	Y_{39} — Cd_{48}	9 + 1 = 10
3rd	5d series	La_{57}, Hf_{72} — Hg_{80}	9 + 1 = 10
4th	6d series	Ac_{89}, Unq_{104} — Uub_{112}	9 + 1 = 10

Atomic Radius

3d series: $Sc > Ti > V > Cr > Mn \geq Fe \simeq Co \simeq Ni \leq Cu < Zn$. In a group from 3d to 4d series, atomic radius increases but 4d and 5d series have nearly same atomic radius due to poor shielding of f electrons (Lanthanide contraction).

$$\boxed{3d < 4d \simeq 5d}$$

$$e.g: Ti < Zr \simeq Hf \left| \begin{array}{l} \text{Smallest radius} - Ni \\ \text{Largest radius} - La \end{array} \right.$$

$$\boxed{\textbf{Melting point}: \text{s-block metals} < \text{d-block metals}}$$

In a series, on increasing number of unpaired electrons, melting point increases upto Cr and then decreases.

$Sc < Ti < V < Cr > Mn < Fe > Co > Ni > Cu > Zn$

↓ ↓

Half filled d^5 Fully filled d^{10}

∴ weak metallic bond ∴ weak metallic bond

$$\text{Melting point} \left| \begin{array}{l} Zn > Cd > Hg \\ Cu > Ag \leq Au \end{array} \right. \text{(data based)}$$

E.N. Exception: $Zn < Cd < Hg$

$$\boxed{\textbf{Density}: \text{s – block metals} < \text{d – block metals.}}$$

3d series

$$\boxed{Sc < Ti < V < Cr < Mn < Fe < Co \leq Ni < Cu > Zn}$$

Density in a Group: $3d < 4d << 5d$

Metallic character: They are solid, hard, ductile, malleable, good conductor of heat and electricity and exhibit metallic lusture, high tensile strength. Hg is a liquid.

Electrical conductivity:-

$$\underbrace{Ag > Cu > Au >}_{d-block} \underset{p-block}{Al}$$

Oxidation State

Transition elements exhibit variable oxidation states due to small energy difference of ns and (n–1)d orbitals.

- Sc(+3) and Zn(+2) exhibit only one stable oxidation state in their compounds.
- Common oxidation state is +2 & +3.
- In 3d series, highest oxidation state is +7 (Mn).
- In d-block, highest oxidation state is +8 (Os, Ru).
- In carbonyl compounds, oxidation state of metals is zero due to synergic effects.
- Their higher oxidation states are more stable in fluorides and oxides.
- Higher oxidation states in oxides are normally more stable than fluorides due to capability of oxygen to form multiple bonds.

  Eg. stable fluoride in higher oxidation state of Mn is MnF_4 while oxide is Mn_2O_7.
- Mn shows maximum number of oxidation states (+2 to +7) among 3d series.
- Beyond Mn, trihalides are not observed except in FeX_3 (X = Cl/Br/I) & CoF_3.

⇒ V_2O_3	V_2O_4	V_2O_5
Basic	Basic	Amphoteric

⇒	CrO	Cr_2O_3	CrO_3
	Basic	Amphoteric	Acidic
⇒	MnO	MnO_2	Mn_2O_7
	Basic	Amphoteric	Acidic

⇒ CuI_2 does not exist as it decomposes to give CuI & I_2 at room temperature

$$CuI_2 \longrightarrow CuI + \frac{1}{2}I_2$$

⇒ In aqueous solution, Cu^+ disproportionates into Cu & Cu^{2+}. In p-block, lower oxidation states of heavier elements are more stable, while in d-block higher oxidation state of heavier elements are more stable.

Eg. In VIB group, Mo(+6) & W(+6) are more stable than Cr(+6).

Magnetic Property

All transition elements are paramagnetic due to the presence of unpaired electrons. Magnetic moment of unpaired electrons is due to spin and orbital angular momentum.

"Spin only" magnetic moment can be calculated by using the formula, $\mu = \sqrt{n(n+2)}$ Bohr magneton. (n is the number of unpaired e^-s)

If n is 1, $\mu = 1.73$ BM

n is 2, $\mu = 2.84$ BM

n is 3, $\mu = 3.87$ BM

n is 4, $\mu = 4.90$ BM

n is 5, $\mu = 5.92$ BM

Substances, that are not attracted by applied magnetic field are diamagnetic. They have all the electrons paired. d-block elements and ions, having d^0 and d^{10} configuration are diamagnetic.

Colour

Colour in transition metal ions is associated with d-d transitions of unpaired electrons from t_{2g} to e_g set of energies. This is achieved by absorption of light in the visible spectrum.

Colourless – Sc^{3+}, Ti^{4+}, Zn^{2+} etc.

Coloured – Fe^{3+} yellow, Fe^{2+} green, Cu^{2+} blue, Co^{3+} blue etc.

Alloys

Solid mixture of metals in a definite ratio (15% difference in metallic radius). They are hard and have high melting point.

Eg. Brass (Cu + Zn)

Bronze (Cu + Sn) etc.

Hg when mixed with other metals form semisolid amalgam except Fe, Co, Ni, Pt.

Interstitial compound

When less reactive non-metals of small atomic size eg. H, B, N, C are trapped in the interstitial space of transition metals, interstitial compounds are formed, like: TiC, Mn_4N, Fe_3H etc.

They are non-stoichiometric compounds.

They have high melting point than the metals from which they are formed.

They are chemically inert.

Catalytic Properties

Most of the d-block compounds act as catalyst due to their variable oxidation state, complex formation tendency and adsorption of gases on their surface.

Example:

Contact process = V_2O_5

Haber's process = $Fe_2O_3 + Al_2O_3 + K_2O$

Fenton's reagent = $FeSO_4 + H_2O_2$

Decomposition of $KClO_3 + MnO_2$

Ostwald's process = Pt/Rh

Zeigler-Natta = $TiCl_4 + (C_2H_5)_3$ Al

Hydrogenation of Alkene = Ni/Pd

Wilkinson's catalyst = RhCl + PPh_3

Important reactions of d-block elements

(*a*) $Cu^{2+} + 4I^- \rightarrow Cu_2I_2(s) + I_2$

(*b*) $CuSO_4 + \underset{\text{Excess}}{KCN} \rightarrow K_2SO_4 + \underset{\text{Unstable}}{Cu(CN)_2}$

$2Cu(CN)_2 \rightarrow 2CuCN + \underset{\text{Cyanogen}}{(CN)_2}$

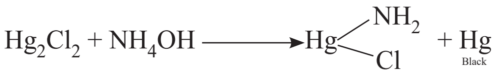
$CuCN + 3KCN \rightarrow K_3[Cu(CN)_4]$

(*c*) $Cu \xrightarrow[\text{moist air}]{H_2O + CO_2} \underset{\text{Green}}{CuCO_3.Cu(OH)_2}$

$Au \xrightarrow[(3HCl + HNO_3)]{\text{Aqua regia}} H[AuCl_4] + NOCl + H_2O$

(*d*) $AgNO_3(s) \xrightarrow{\text{Heating}} Ag + NO_2 + \frac{1}{2}O_2$

$Ag_2CO_3(s) \xrightarrow{\text{Heating}} Ag + CO_2 + \frac{1}{2}O_2$



(*e*) $Hg_2Cl_2 + NH_4OH \longrightarrow Hg\begin{smallmatrix}NH_2\\Cl\end{smallmatrix} + \underset{\text{Black}}{Hg}$

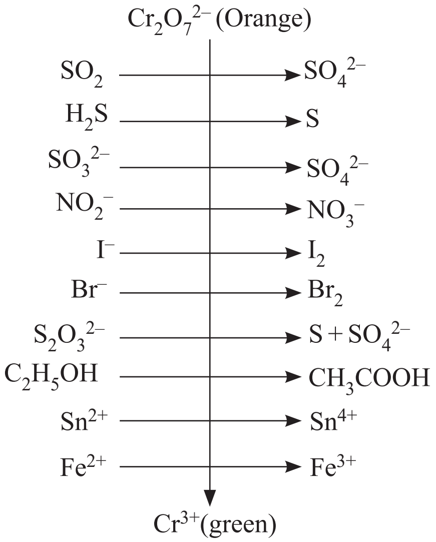
(*f*) $NO_3^-/NO_2^- \xrightarrow{FeSO_4 + H_2SO_4} \underset{\text{Brown ring complex}}{[Fe(H_2O)_5\ NO^+]SO_4}$

(*g*) $AgBr + 2Na_2S_2O_3 \longrightarrow \underset{\text{Photographic complex}}{Na_3[Ag(S_2O_3)_2]} + NaBr$

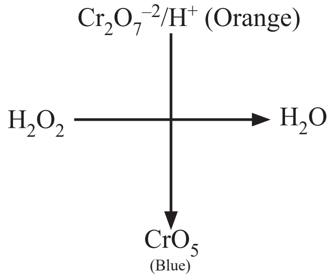
(*h*) Chemical volcano:

$\underset{\text{orange solid}}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} N_2 + 4H_2O + \underset{\text{Green residue}}{Cr_2O_3}$

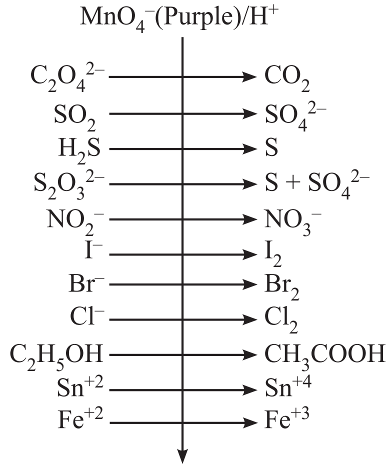
Reactions of $Cr_2O_7^{2-}$



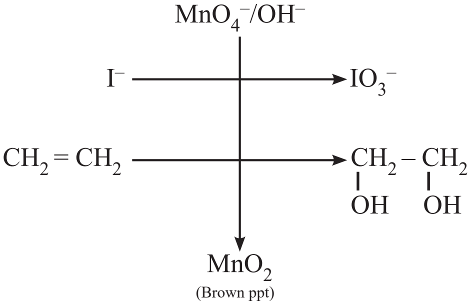
$$\underset{\text{Yellow}}{CrO_4^{2-}} \underset{^-OH}{\overset{H^+}{\rightleftharpoons}} \underset{\text{Orange}}{Cr_2O_7^{2-}}$$



Reaction of MnO_4^-



$$\underset{\text{Purple}}{MnO_4^-} \xrightarrow[\text{Basic Solution}]{\text{Strongly }\Delta} \underset{\text{Green}}{MnO_4^{2-}}$$



Some important d-Block metal compounds

Ferrous sulphate, $FeSO_4.7H_2O$ (Green Vitriol)

Heating effect:

$$FeSO_4.7H_2O \xrightarrow{140°C} FeSO_4.H_2O \xrightarrow{300°C} 2FeSO_4 \xrightarrow[\text{Temp.}]{\text{High}} Fe_2O_3 + SO_2\uparrow + SO_3\uparrow$$

$$\text{Fe (from iron scrap)} \xrightarrow[-H_2\uparrow]{H_2SO_4} FeSO_4$$

$$FeSO_4 \xrightarrow[-K_2SO_4]{KCN} K_4[Fe(CN)_6]$$

$$FeSO_4 \xrightarrow{\text{Hydrolysis}} Fe(OH)_2 + H_2SO_4$$

(Solution is acidic)

Uses : For making laboratory reagents, like Mohr's salt etc.

$$FeSO_4 + (NH_4)_2SO_4 + 6H_2O \longrightarrow FeSO_4.(NH_4)_2SO_4.6H_2O$$

(Mohr's salt)

2. **Zinc Sulphate, $ZnSO_4.7H_2O$ (White Vitriol)**

$$ZnSO_4 \xrightarrow[-Na_2SO_4]{NaOH} \underset{\text{White}}{Zn(OH)_2\downarrow} \xrightarrow[-H_2O]{NaOH} \underset{\text{Soluble Complex}}{Na_2ZnO_2}$$

$$ZnSO_4 \xrightarrow{100°} ZnSO_4\cdot 6H_2O \xrightarrow{200°} ZnSO_4 \xrightarrow{800°C} ZnO + SO_3\uparrow$$

3. **Copper sulphate, $CuSO_4.5H_2O$ (Blue vitriol)**

Physical Properties: Blue crystalline compound, soluble in water.

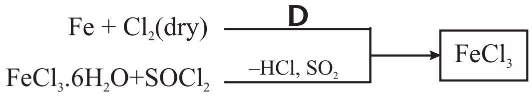
$$CuSO_4.5H_2O \xrightarrow[\text{effloresces}]{\text{air}} CuSO_4.4H_2O \xrightarrow{100°C} CuSO_4.H_2O \xrightarrow{250°C} CuSO_4 \xrightarrow{750°C} CuO + SO_2\uparrow + O_2\uparrow$$

$$Cu + H_2SO_4 + O_2 \xrightarrow[-H_2O]{} CuSO_4$$

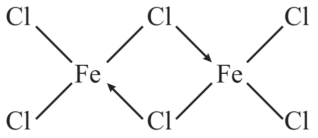
$$CuSO_4 \xrightarrow[-Na_2SO_4/-Na_2SO_4,\,CO_2]{NaOH/Na_2CO_3} \underset{\text{blue}}{Cu(OH)_2}\downarrow$$

$$CuSO_4 \xrightarrow{KSCN + SO_2 + H_2O} CuSCN\downarrow\text{(white)} + K_2SO_4 + H_2SO_4$$

4. **Ferric Chloride, $FeCl_3$**



It sublimes at 300°C giving a dimeric gas.



Two 3C-4e^- bond
Four 2C-2e^- bond

5. **Zinc Chloride**

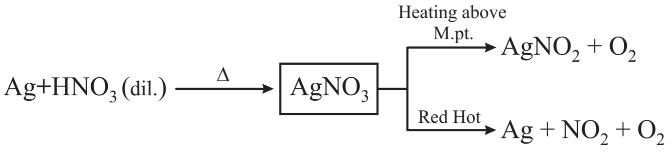
Prepration of hydrated $ZnCl_2(ZnCl_2.2H_2O)$

$$ZnO+HCl \longrightarrow ZnCl_2.2H_2O \xrightarrow[-HCl,\ H_2O]{\Delta} Zn(OH)Cl \xrightarrow{\Delta} ZnO+HCl$$

6. **Cupric chloride, $CuCl_2$, $2H_2O$**

Heating effect: $CuCl_2.2H_2O \xrightarrow[HCl\ gas]{150°C} CuCl_2 + 2H_2O$

7. **Silver nitrate, $AgNO_3$ (Lunar Caustic)**



Photography

(*i*) A photographic film consists of a light sensitive emulsion of fine particles (grains) of silver salts in gelatin, spread on a clear celluloid strip or a glass plate. AgBr is mainly used as the light sensitive material.

(*ii*) The film is placed in a camera. When the photograph is exposed, light from the subject enters the camera and is focussed by the lens to give a sharp image on the film. The light starts a photochemical reaction by exciting a halide ion, which loses an electron. The electron moves in a conduction band to the surface of the grain, where it reduces Ag^+ ion to metallic silver. To remove the excess of AgBr, hypo solution is used.

$$2AgBr(s) \xrightarrow{light} 2Ag + Br_2$$

$$AgBr + 2Na_2S_2O_3(aq.) \xrightarrow{light} Na_3[Ag\,(S_2O_3)_2] + NaBr$$

f-block elements

Lanthanoids are a series of elements that involve the filling of 4f- subshell. These are fourteen elements, following lanthanum, from Cerium to Lutetium. Actinoids are a series of elements that involve filling of 5f-subshell. These are fourteen elements following Actinium from Thorium to Lawrencium. The common oxidation state of lanthanoids and actinoids is +3.

Some Applications of d- and f-Block Elements

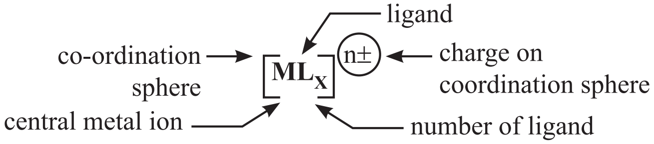
Iron and steels are the most important construction materials. Their production is based on the reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals, such as Cr, Mn and Ni. TiO is used in pigment industry and MnO_2 in dry battery cells. The battery industry also requires Zn and Ni/Cd. The 'silver' UK coins are Cu/Ni alloy.

CHAPTER

11

Coordination Compounds

Representation of Complex Compound



Co-ordination number = Number of atoms surrounded to central metal ion.

Notes:

Bidentate and Polydentate ligands are also called chelating ligand.

Bonding in Coordination Compound

Effective Atomic Number & Sidgwick Rule

Total number of electrons present around central metal atom or ion after accepting the electron pair from ligand.

VBT

- Metal provide hybridised vacant orbital for the acceptance of lone pair from ligand.
- Hybridisation, shape and magnetic behaviour of complex depends upon the nature of ligand.
- Strong field ligand pair up the unpaired e^- of central metal atom where as weak field ligand does not.
- If unpaired e^- is present in complex then complex is paramagnetic. If unpaired e^- is absent then diamagnetic.
  eg. C.N. = 4; $[NiCl_4]^{2-}$

Spectrochemical Series

I^- (weakest) $< Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- <$ edta$^{4-} < NH_3 <$ en $< CN^- <$ CO(strongest)

Exception

$[Co(OX)_3]^{3-}$	d^2sp^3	diamagnetic
$[Co(H_2O)_6]^{3+}$	d^2sp^3	diamagnetic
$[NiF_6]^{2-}$	d^2sp^3	diamagnetic
$[Cr(NH_3)_6]^{2+}$	sp^3d^2	paramagnetic
$[Mn(NH_3)_6]^{2+}$	sp^3d^2	paramagnetic
$[Fe(NH_3)_6]^{2+}$	sp^3d^2	paramagnetic
$[CoL_6]^{4-}$ ($L = NO_2^-/CN^-$)	d^2sp^3	paramagnetic

Exception

- d^3s hybridisation, Td, diamagnetic, inner orbital complex eg.
  $MnO_4^-, CrO_4^{2-}, Cr_2O_7^{2-}, CrO_2Cl_2, CrO_2F_2, VO_4^{3-}$
- Transference of electron
  eg. Cu^{+2} in C.N. → 4 with L
  (where L = NO_2^- / CN^- / NH_3 etc.)

Organometallic Compounds

Compounds in which the less E.N. (Ge, Sb, B, Si, P, As) central metal atoms are bonded directly to carbon atoms are called organometallic compounds.

- σ-bonded compounds formed by non-transition elements.
  R-Mg-X, $(CH_3–CH_2)_2$ Zn, Ziegler natta catalyst, etc.
- π-bonded organometallic compounds are generally formed by transition elements e.g. Zeise's salt, ferrocene, dibenzene chromium, etc.
- σ-and π-bonded organometallic compounds: Metal carbonyl compounds formed between metal and carbon monoxide belong to this class. $Ni(CO)_4$, $Fe(CO)_5$ etc.

Stereo Isomerism

Stereo Isomerism in Co-ordination Compound

CN-4

- Square planar complex does not show optical isomerism.
- Square planar complex show optical activity if the co-ordinated ligand have chiral center.
- Square planar complexes: $[Ma_2b_2]^{n\pm}$, $[Ma_2bc]^{n\pm}$, $[Mabcd]^{n\pm}$, $[M(AB)cd]^{n\pm}$, $[M(AB)(CD)]^{n\pm}$ show geometrical isomerism
- Tetrahedral complex: $[Mabcd]^{n\pm}$, $[M(AB)cd]^{n\pm}$ $[M(AB)(CD)]^{n\pm}$ show optical isomerism
- Tetrahedral complex does not show geometrical isomerism.

CHAPTER

12

The p-Block Elements-II

15th–Group Elements

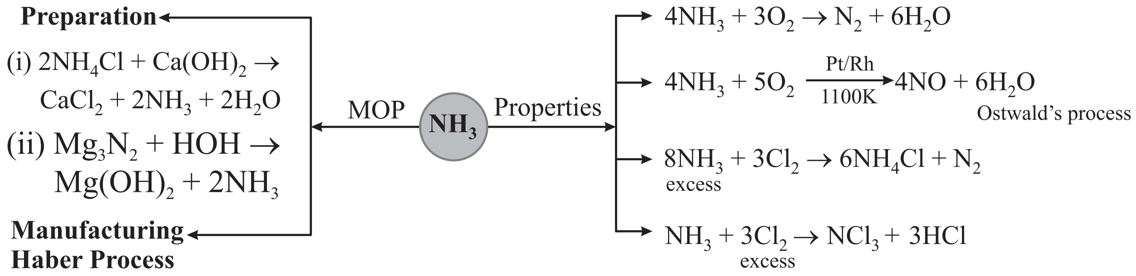
Nitrogen Family

1. In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. for example,
   (i) $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$
2. In case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid.

Compounds of Nitrogen Family

Ammonia (NH_3)

Colorless, Pungent Smell, basic in nature, liquified easily, used as coolant



Preparation

(i) $2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$

(ii) $Mg_3N_2 + HOH \rightarrow Mg(OH)_2 + 2NH_3$

Manufacturing
Haber Process

Properties

$4NH_3 + 3O_2 \rightarrow N_2 + 6H_2O$

$4NH_3 + 5O_2 \xrightarrow[1100K]{Pt/Rh} 4NO + 6H_2O$ Ostwald's process

$\underset{\text{excess}}{8NH_3} + 3Cl_2 \rightarrow 6NH_4Cl + N_2$

$NH_3 + \underset{\text{excess}}{3Cl_2} \rightarrow NCl_3 + 3HCl$

$$N_2 + 3H_2 \underset{\substack{750\text{ K}\\200\text{-}300\text{ atm}}}{\overset{\text{Fe + Mo}}{\rightleftharpoons}} 2NH_3 + 24\text{KCal/mol}$$

Nitric Acid (HNO_3)

Preparation

Ostwald's process

(i) $4NH_3(g) \xrightarrow[\text{500 K . 9 bar}]{\text{Pt / Rh – guage catalyst}} 4NO(g) + 6H_2O(g)$

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

(iii) $3NO_2(g) + H_2O(\ell) \rightarrow 2HNO_3(aq) + NO(g)$

Properties

HNO_3, nitric acid was earlier called as aqua fortis (meaning strong water).

It usually acquires yellow colour. Due to its decomposition by sunlight into NO_2.

It acts as a strong oxidising agent.

Reaction with $FeSO_4$

$FeSO_4 + 8HNO_3 \rightarrow Fe_2(SO_4)_3 + 2NO + 4H_2O$

Reaction with non-metals

Non-metals are converted into highest oxyacids by hot and conc.

$HNO_3 \cdot NO_2$ gas is evolved (S to H_2SO_4 ; P to H_3PO_4; C to H_2CO_3; I_2 to HIO_3; As to H_3AsO_4; Sb to H_3SbO_4 and Sn to H_2SnO_3). Most of the metals except noble metals are attacked by HNO_3. It plays double role in action on metals, i.e., it acts as an acids as well as an oxidising agent.

Reaction with Metals

$3Cu + 8\ HNO_3\ (\text{dilute}) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

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

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

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

Concentration of nitric acid	Metal	Main products
Very Dilute HNO_3	Mg, Mn	H_2+ metal nitrate
	Fe, Zn, Sn	NH_4NO_3 + metal nitrate
	Cu, Ag, Hg	No reaction
Dilute HNO_3	Fe, Zn	N_2O + metal nitrate
	Pb, Cu, Ag	NO + metal nitrate
Conc. HNO_3	Sn	$NO_2 + H_2SnO_3$ (Metastannic acid)
Conc. HNO_3	Fe, Co, Ni, Cr, Al	rendered passive

Phosphine (PH_3)

Preparation

(i) $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

(ii) $PH_4I + NaOH \rightarrow NaI + H_2O + PH_3$

Physical Properties

Colourless gas having smell of garlic or rotten fish, slightly soluble in water and slightly heavier than air.

Chemical Properties

(i) $2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O$

(ii) $4PH_3 \xrightarrow{713\text{ K}} P_4 + 6H_2$

(iii) $PH_3 + 4Cl_2 \rightarrow PCl_5 + 3HCl$

- On heating, phosphorus acid, H_3PO_3 decomposes into phosphine (PH_3) and phosphoric acid (H_3PO_4).

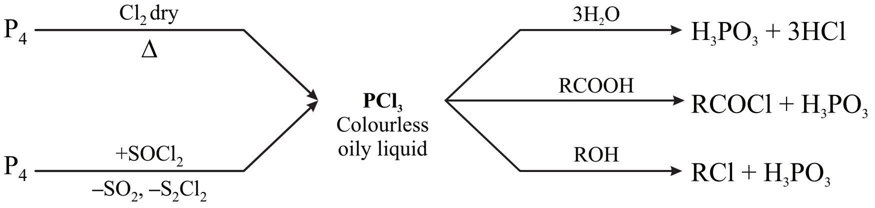
  $4H_3PO_3 \xrightarrow{\text{Heat}} 3H_3PO_4 + PH_3$

  $2H_3PO_2 \xrightarrow{\text{Heat}} H_3PO_4 + PH_3$
- **Holme's signals:** A mixture of Ca_3P_2 and CaC_2 on treatment with H_2O forms PH_3 and P_2H_4 along with C_2H_2. The mixture burns with a bright light

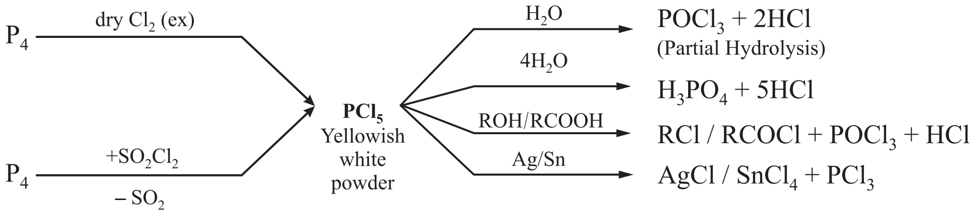
  $Ca_3P_2 + 6H_2O + 3Ca(OH)_2 + 2PH_3$

  $CaC_2 + H_2O \rightarrow Ca(OH)_2 + C_2H_2$
- Smoke screens, involve the use of calcium phosphide, Ca_3P_2. The PH_3 gas obtained from Ca_3P_2 catches fire to give the needed smoke.

PCl_3



PCl_5



16th–Group Elements

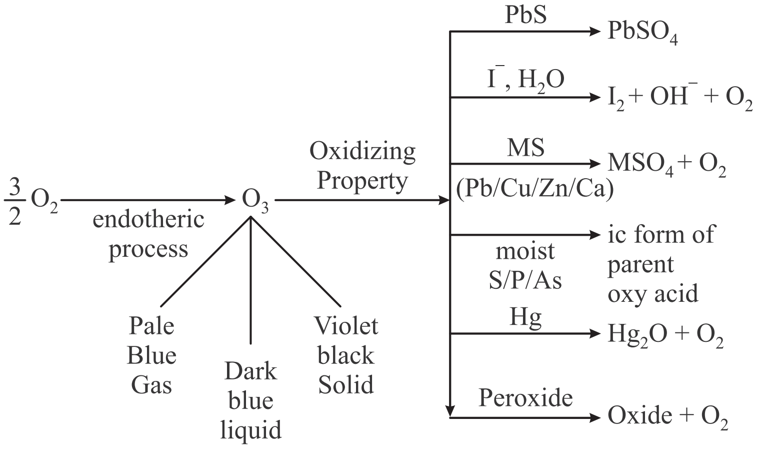
- Sulphur trioxide (SO_3) is a white crystalline solid with melting point 290 K and boiling point 318 K.
- SO_3 is prepared by the direct oxidation of SO_2 with atmospheric oxygen in presence of finally divided Pt or V_2O_5 at a pressure of 2 bar and temperature 720 K.
- SO_3 reacts with water to produce H_2SO_4 and large amount of heat is evolved.

  $SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

  SO_3 reacts with water to produce H_2SO_4 and large amount of heat is evolved.

  $SO_3 + H_2O \rightarrow H_2SO_4 + \text{heat}$

Ozone



Gases	Absorbent
O_3	Turpentine Oil/Oil of cinnamon.
NO	$FeSO_4$
SO_2	NaOH
CO	Cu_2Cl_2
O_2	Pyrogallol

Sulphuric Acid (H_2SO_4)

It is also known as oil of vitriol and king of chemicals.

Manufacture of Sulphuric Acid

Lead chamber process

The various steps involved are :

(a) Production of SO_2 : By burning S or iron pyrites.

$S + O_2 \xrightarrow{\Delta} SO_2$

$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

(b) Production of catalyst : Oxides of nitrogen.

$2NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_3$

$2HNO_3 \xrightarrow{\Delta} H_2O + NO + NO_2 + O_2$

(c) Reaction in lead chamber

$SO_2 + NO_2 \longrightarrow SO_3 + NO$

$SO_3 + H_2O \longrightarrow H_2SO_4$

$2NO + O_2 \longrightarrow 2NO_2$ (used again)

Contact Process

The steps involved are:

(a) **Production of SO_2:** It is produced by burning sulphur or iron pyrites and purified by treating with steam to remove dust particles.

(b) **Conversion of SO_2 to SO_3 :** It is done in container or catalyst chamber after being pre-heated to 450°C.

$2SO_2 + O_2 \rightleftharpoons 2SO_3 + x$ cal

Catalyst : Formerly, platinised asbestos was used which is costly and easily poisoned. These days V_2O_5 is used.

(c) SO_3 is absorbed by conc. H_2SO_4 and then water is added to produce the acid of desired concentration.

$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$

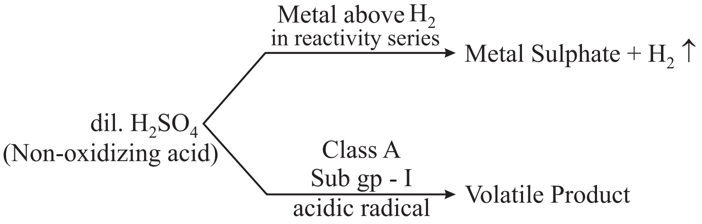
$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

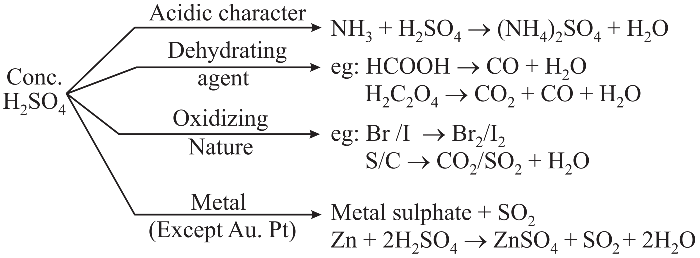
Properties

Its specific gravity is 1.8 and it is 98% by weight.

It is strong dibasic acid.

$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$





Uses

In lead storage batteries.

In manufacture of paints and pigments.

In metallurgy for electrolytic refining of metals.

17th–Group Elements

1. All halogens are coloured. For example, F_2 has yellow gas, Cl_2 greenish yellow gas, Br_2 red liquid and I_2 violet coloured solid.
2. They react with metals and non-metals to form halides and the reactivity of the halogens decreases down the group. i.e. the order is $F_2 > Cl_2 > Br_2 > I_2$.
3. In general, a halogen oxidises halide ions of higher atomic number.

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

   $Cl_2 + 2X^- \rightarrow 2Cl^- + X_2$ (X = Br or I)

   $Br_2 + 2I^- \rightarrow 2Br^- + I_2$
4. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from spent nuclear fuel.
5. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

Interhalogen Compounds

These compounds are regarded as halides of more electropositive (i.e. less electronegative) halogens.

Types of interhalogen compound:

AB type : ClF, BrF, BrCl, ICl, IBr

AB_3 type : ClF_3, BrF_3, ICl_3

AB_5 type : BrF_5, IF_5

AB_7 type : IF_7

Hydrochloric Acid, (HCl)

Preparation: By dissolving hydrogen chloride gas in water. Hydrogen chloride gas required in turn can be prepared by the following methods:

By the direct combination of hydrogen and chlorine.

$$H_2(g) + Cl_2(g) \xrightarrow{\text{Sunlight}} 2HCl(g)$$

Hydrogen chloride gas can also be obtained by burning hydrogen in chlorine.

Properties: Hydrogen chloride is a covalent compound but when dissolved in water it ionizes to form hydrogen ions and chloride ions.

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

Thus, anhydrous HCl does not show acidic properties. Only aqueous HCl or in pressure of moisture, HCl behaves as an acid.

Metal + Hydrochloric acid ⟶ Metal chloride + Hydrogen

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2\uparrow$$

It react with bases and basic oxides or hydroxides to form their respective chlorides and water.

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

It reacts with metal carbonates, bicarbonates, sulphides, sulphites, thiosulphates and nitrites,etc, to form their respective chlorides.

$$AgNO_3 + HCl \longrightarrow HNO_3 + AgCl\downarrow$$

Reducing property: HCl is a strong reducing agent.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2\uparrow$$

Uses

In the production of dyes, paints, photographic chemicals, etc.

Used in the preparation of chlorides, chlorine, aquaregia, etc.

Used as a laboratory reagent.

Pseudo Halides

Pseudo halides are uninegative groups which show certain characteristics of halide ions. For example Cyanide (CN^-), Cyanate (OCN^-), Thiocyanate (SCN^-), Selenocyanate ($SeCN^-$), Azide (N_3^-), and isocyanate (ONC^-).

Chlorine (Cl_2)

Preparation: By oxidation of conc. HCl.

$$PbO_2 + 4HCl \rightarrow PbCl_2 + 2H_2O + Cl_2\uparrow$$

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2\uparrow$$

Manufacture: By heating pyrolusite with conc. HCl.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2\uparrow$$

Deacon process: $2HCl + O_2 \xrightarrow{CuCl_2} Cl_2\uparrow + H_2O$

Properties: It is a yellowish green gas, poisonous in nature, soluble in water. Its aqueous solution is known as chlorine water which on careful cooling gives chlorine hydrate $Cl_2\cdot 8H_2O$.

Bleaching action and oxidising property:

(*i*) $Cl_2 + H_2O \rightarrow HOCl + HCl$

$HOCl \rightarrow HCl + [O]$

Coloured matter + nascent [O] → Colourless matter

The bleacing action of chlorine is permanent and is due to its oxidising nature.

(*ii*) $SO_2 + Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$

Action of hydrogen:

$$H_2 + Cl_2 \xrightarrow[\text{Charcoal catalyst}]{\text{U.V. light}} 2HCl$$

Displacement reactions :

$2KBr + Cl_2 \rightarrow 2KCl + Br_2$

$2KI + Cl_2 \rightarrow 2KCl + I_2$

Action of NaOH :

$$\underset{\text{(cold \& dil.)}}{2NaOH} + \underset{\text{dry}}{\overset{0}{Cl_2}} \rightarrow \overset{-1}{NaCl} + \underset{\text{sodium hypochloride}}{\overset{+1}{NaOCl}} + H_2O$$

$$\underset{\text{(hot \& conc.)}}{6NaOH} + 3\underset{\text{dry}}{\overset{0}{Cl_2}} \rightarrow 5\overset{-1}{NaCl} + \underset{\text{sodium chlorate}}{\overset{+5}{NaClO_3}} + 3H_2O$$

Addition reactions:

$SO_2 + Cl_2 \rightarrow SO_2Cl_2$

$CO + Cl_2 \rightarrow COCl_2$

- **Test for chlorine:**
  - (a) It is a greenish yellow gas with irritating smell.
  - (b) It turns starch iodide paper blue.
  - (c) It bleaches litmus paper and indigo solution.

Key Note

- **Action of silica and glass :** Strong solution of HF attacks readily forming silicon fluoride which gives complex fluorosilicic acid, H_2SiF_6 with excess HF.

  $SiO_2 + 2H_2F_2 \rightarrow SiF_4 + 2H_2O$

  $SiF_4 + H_2F_2 \rightarrow H_2SiF_6$

  This is called etching of glass.
- Iodine is slightly soluble in water but much more soluble in KI due to the formation of KI_3.

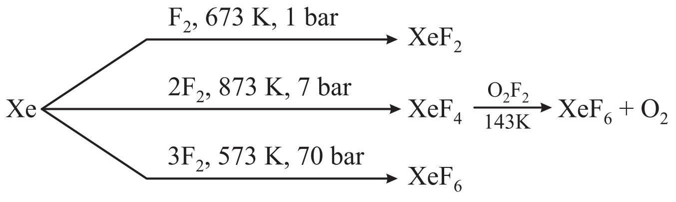
  $KI + I_2 \rightarrow KI_3$

  The solution behaves as a simple mixture of KI and I_2.

18th–Group Elements

1. Relative Abundance:
   Ar > Ne > Kr > He > Xe > Rn
2. Melting and Boiling point:
   Rn > Xe > Kr > Ar > Ne > He
3. He has the lowest boiling point among all elements.
5. $O_2[PtF_6]$ is the first noble gas compound.
6. Ar, Kr and Xe from clathrate compounds. e.g.,
   $A\cdot 6H_2O$ (A = Ar/Kr/Xe)

Preparation of Xe-Fluoride



Properties

Fluoride donor : Eg. $XeF_2 + \underset{(M=As/Sb/P)}{MF_5} \longrightarrow [XeF]^+[MF_6]^-$

Fluoride acceptor : Eg. $XeF_6 + \underset{(M=Na/K/Rb/Cs)}{MF} \longrightarrow M^+[XeF_7]^-$

Fluoride agents : Eg. $XeF_4 \xrightarrow{SF_4/Pt} PtF_4/SF_6 + Xe$

Reaction with SiO_2 : Eg. $2XeF_6 + SiO_2 \rightarrow SiF_4 + XeOF_4$

Hydrolysis

$$XeF_2 \begin{cases} \xrightarrow{H_2O} Xe + 2HF + \frac{1}{2}O_2 \\ \xrightarrow[2OH^-]{+\,SOCl_2} Xe + 2F^- + H_2O + \frac{1}{2}O_2 \end{cases}$$

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

CHAPTER

13

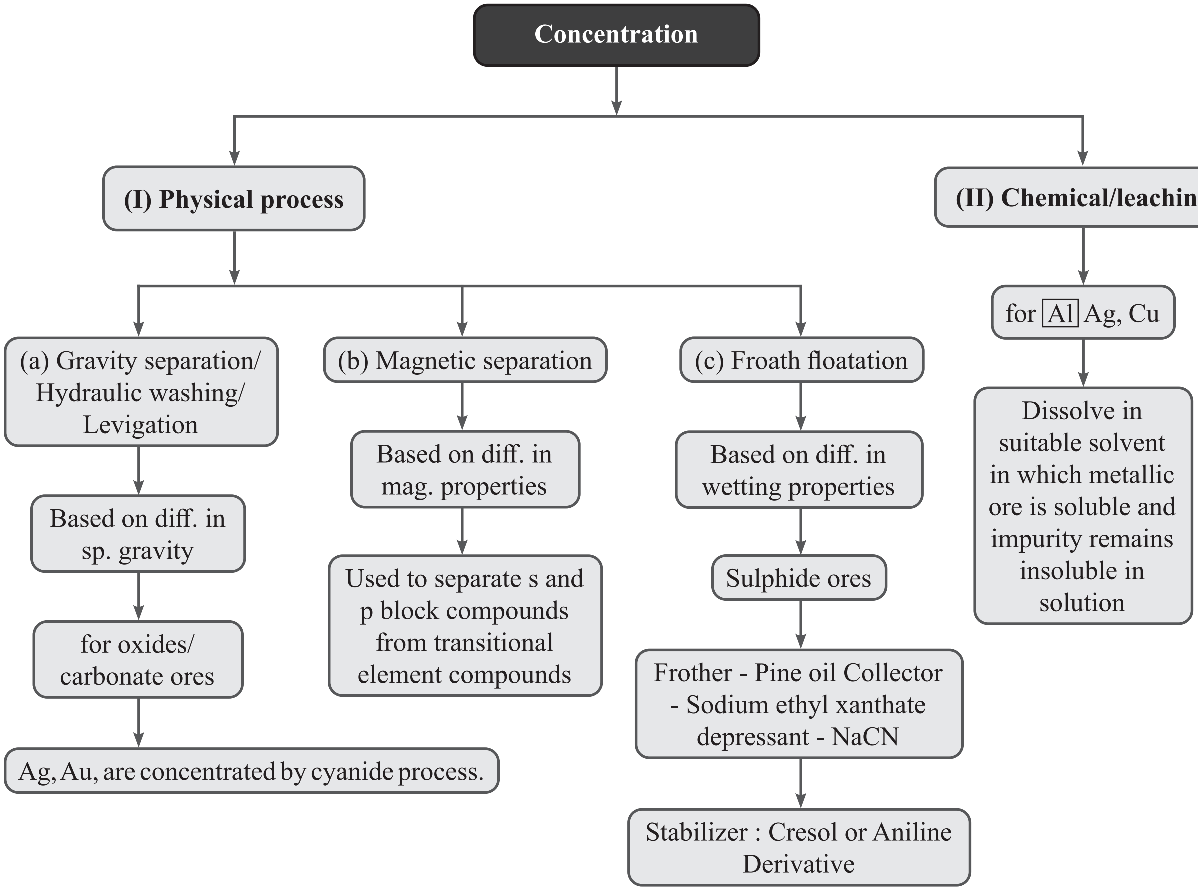
General Principles and Process of Isolation of Elements

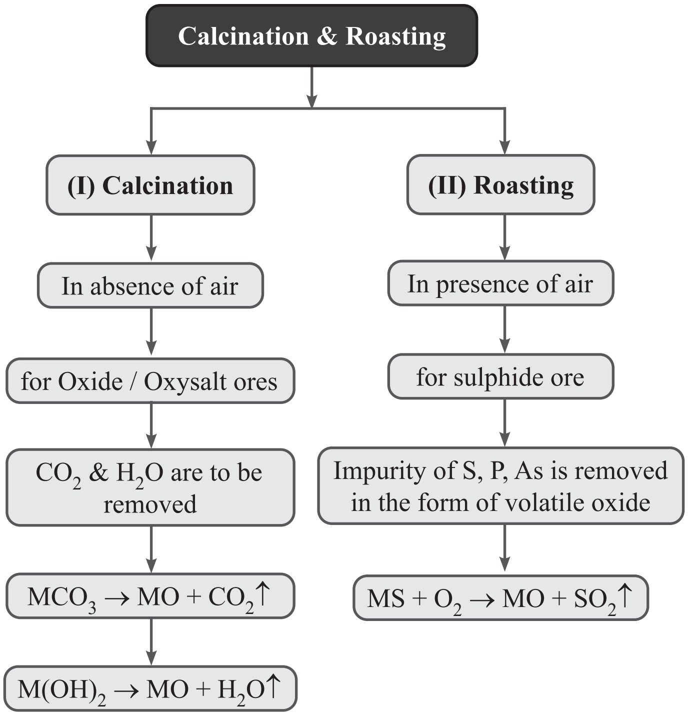
Ore: Minerals from which metal can be extracted economically :

Metallurgical Process

1. Mining : Ore obtained in big lumps (less reactive)
2. Crushing/grinding/pulverization : Big lumps convert into powder (more reactive)
3. Concentration : To remove matrix/gangue from ore

   To increase the concentration of ore particle in ore sample.





Reduction

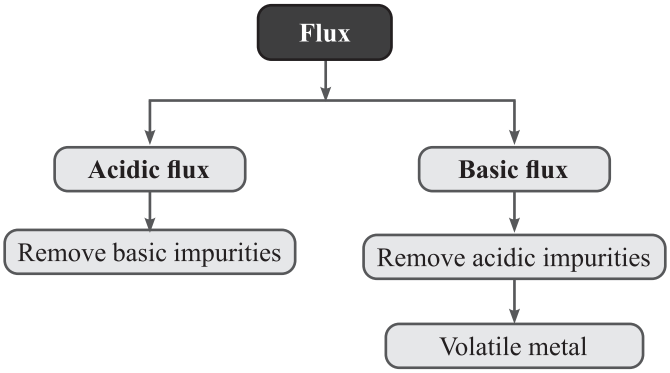
To obtain metal (95 to 98%) from metal oxide.

Self Reduction

- Sulphide ore itself act as reducing agent.
  eg. $PbS + 2PbO \xrightarrow{\Delta} 3Pb + SO_2$
- Thermal decomposition
  eg. $HgO \xrightarrow{\Delta} Hg + \frac{1}{2}O_2$

Carbon Reduction (Smelting)

- Reducing agent C/CO
- eg. $Fe_2O_3 + 3CO \xrightarrow{250^{\circ} - 700^{\circ}C} 2Fe + 3CO_2$
  $ZnO + C \xrightarrow{\approx 1200^{\circ}C} Zn + CO$
  Flux - substance to convert non-fusible impurities to fusible one.



Imp. point – Above 710º C, C is better reducing agent.

– Below 710ºC, CO is better reducing agent.

Aluminum reduction method

(Thermite process)

- Al act as reducing agent
  eg. $Cr_2O_3 + 2Al \xrightarrow{\Delta} Al_2O_3 + 2Cr$
  Thermite mixture mass ratio : $Cr_2O_3 : Al = 3 : 1$

Extraction of Silver/gold

(*i*) Cyanidation (Leaching Process)

$Ag_2S + 2NaCN \xrightarrow{O_2} 2Na[Ag(CN)_2] + Na_2SO_4$

$Au + 2KCN + H_2O \longrightarrow K[Au(CN)_2]$

(*ii*) Recovery of Ag/Au (Metal displacement Reactions)

$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN_4)] + 2Ag\downarrow$

$2K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN_4)] + 2Au\downarrow$

Electrolytic Reduction

- For IA, IIA, Al
- Electrolysis of molten solution

Example

(*i*) Extraction of Al(Hall-Heroult)

Al can be extracted from Al_2O_3

To decrease fusion temp. of Al_2O_3, $Na_3\,AlF_6$ & CaF_2 is to be added as auxiliary electrolytes.

Na_3AlF_6 & CaF_2 increase the conductivity & reduce the fusion temp.

At cathode, impure Al is collected and at anode O_2, CO, CO_2 is released.

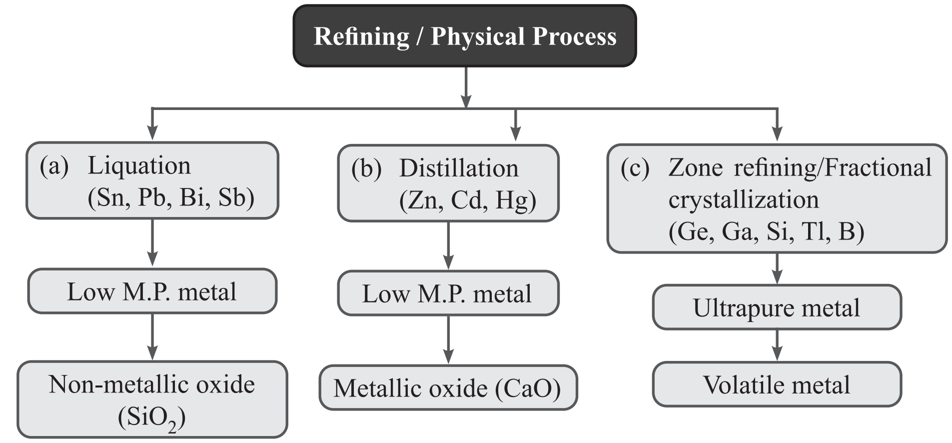
(*ii*) Extraction of Na (Down cell process)

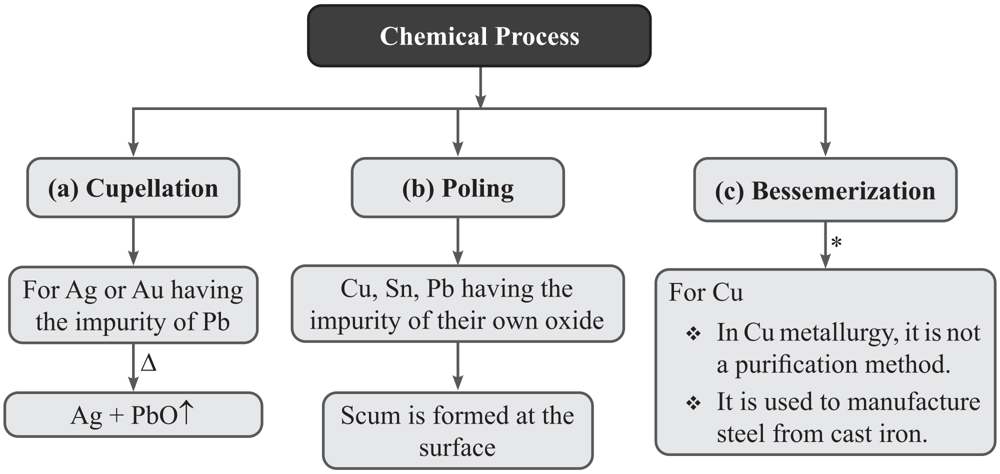
Na can be extracted from NaCl

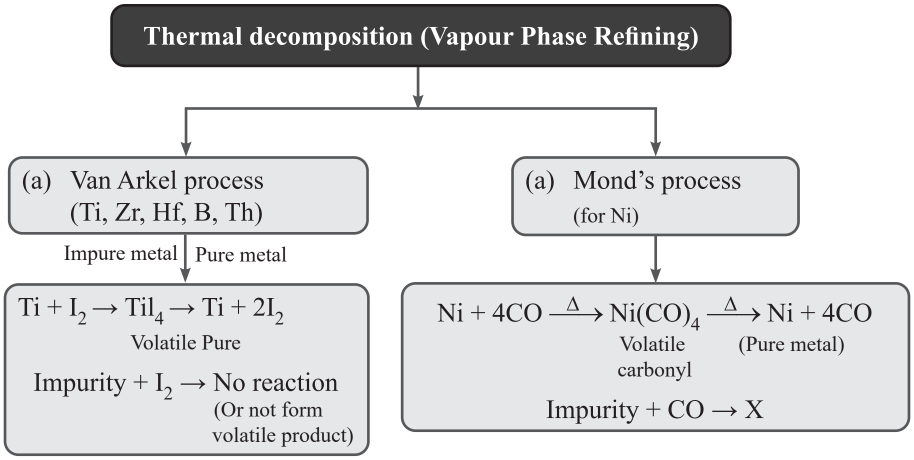
Down Process, neutral flux ($CaCl_2$) is to be added to decrease the fusion temp. of NaCl

Neutral flux - substance used to increase the conductivity of NaCl

Auxiliary Electrolyte – decrease the fusion temp. of ionic compounds of (IA, IIA, Al) which is more than the melting point of metal. To obtain metal (99.98%)







(*i*) Electrolytic refining

Anode–made up of impure metal

Cathode–pure metal

impurity deposited below anode as anode mud or goes to electrolytic solution, pure metal is deposited at cathode.

Thermodynamics Principle of Metallurgy

- The graphical representation of Gibbs energy was first used by H.I.T. Ellingham. This provide a sound basis for considering the choice of reducing agent in the reduction of oxides. This is known as Ellingham diagram Such diagram help us in predicting the feasibility of thermal reduction of an ore.
- The Criteria of feasibility is that at a given temperature, Gibbs energy of reaction must be negative.
- In blast furnace, reduction takes place at low temperature i.e. why CO is the reducing agent (For Fe).

A summary of the occurence and Extraction of some Metals is presented in the following table:

Metal	Occurrence	Common method of extraction	Refining	Remarks
Aluminium Eº = –1.66	1. Bauxite, $Al_2O_3.xH_2O$ 2. Cryolite, Na_3AlF_6	Electrolysis of Al_2O_3 dissolved in molten $Na_3AlF_6 + CaF_2$	Electrolytic refining by Hoop's cell	For the extraction, a good source of electricity is required
Iron Eº = –0.44	1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4 3. Limonite, $Fe_2O_3.3H_2O$ 4. Siderite, $FeCO_3$	Reduction of the oxide with CO and coke in blast furnace	Bessemerization (impurites has more affinity for O_2 as compared to Fe)	Temperature approaching 2170K is required
Copper Eº = –0.34	1. Copper pyrites, $CuFeS_2$ 2. Copper glance, Cu_2S 3. Malachite, $CuCO_3.Cu(OH)_2$ 4. Cuprite, Cu_2O 5. Azurite, $2CuCO_3. Cu(OH)_2$	Partial roasting of sulphide and reduction	(i) Poling (ii) Electrolytic method	It is self reduction in a specially designed convertor. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy from low grade ores.
Zinc Eº = –0.76	1. Zinc blende or Sphalerite, ZnS 2. Calamine, $ZnCO_3$ 3. Zincite, ZnO	Roasting of sulphide ore or calcination of $ZnCO_3$ followed by reduction with coke	The metal may be purifed by fractional distillation	For ZnO, carbon is better reducing agent, then CO and Zn is obtained in vapours form. $ZnO + C \xrightarrow{1673K} Zn + CO$
Mg Eº = –2.36	1. Carnallite, $KCl.Mg\ Cl_2.6H_2O$ 2. Magnesite, $MgCO_3$	Electrolysis of fused $MgCl_2$ with KCl		$MgCl_2.6H_2O$ is heated in the excess current of dry HCl gas to produce anhydrous $MgCl_2$
Sn Eº = –0.14	1. Cassiterite, SnO_2 (Tin stone)	Reduction of the SnO_2 with carbon. $SnO_2 + 2C \rightarrow Sn + 2CO$	Poling and Liquation	Ore contain impurity of wolframite, $FeWO_4 + MnWO_4$ (magnetic separation)

Metal	Occurrence	Common method of extraction	Refining	Remarks
Pb $E^o = -0.13$	1. Galena, Pbs	Roasting, then self reduction or Reduction of PbO (Roasted ore) with carbon $PbS + 2PbO \rightarrow 3Pb + SO_2$ $PbO + C \rightarrow Pb + CO$	Liquation & electrolytic method	
Ag $E^o = 0.80$	1. Argentite- Ag_2S, native Silver	Hydro metallurgy $Ag_2S + 4NaCN$ $2Na[Ag(CN)_2] + Na_2S$ $2Na[Ag(CN)_2] + Zn \rightarrow Na_{2[}Zn(CN)_4] + 2Ag$	Cupelation & electrolytic method	In hydro metallurgy, Ag is obtained in the form of dark amorphous ppt.
Au $E^o = 1.40$	Native ore	1. Amalgamation 2. Cynide process	Cupelation & electrolysis method	In hydro metallurgy Au is obtained in the form of dark amorphous ppt.

CHAPTER 14

Biomolecules

Biomolecules are the organic compounds which form the basis of life.

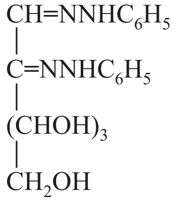
Carbohydrates

Optically active polyhydroxy aldehydes (aldoses) or ketones (ketoses) or the compounds which produce these units on hydrolysis are known as carbohydrates.

- The monosaccharides and oligosaccharides having sweet taste are collectively known as sugars. Polysaccharides which are insoluble in water and not sweet in taste, are known as non-sugars.
- All monosaccharides and disaccharides (except sucrose) are reducing sugars. Polysaccharides are non-reducing sugars.
- All naturally occurring monosaccharides belong to D-series.
- Kiliani synthesis is used to convert an aldose into next higher aldose.
- **Glucose:** It is also known as Dextrose. It is present in grape sugar, corn sugar and blood sugar ($C_6H_{12}O_6$).
- **Anomers:** Anomers are cyclic monosaccharides differing from each other in the configuration at C–1 if they are aldoses or in the configuration at C–2 if they are ketoses.
- **Mutarotation:** The change in optical rotation on standing is called mutarotation.

$$\underset{+111.5^\circ}{\alpha\text{-D-(+) Glucose}} \rightleftharpoons \underset{+52.5^\circ}{\text{Open chain form}} \rightleftharpoons \underset{+19.5^\circ}{\beta\text{-D-(+) Glucose}}$$

- **Epimers:** Monosaccharides differing in configuration at a carbon other than anomeric carbon are called epimers, e.g. glucose and galactose differ in configuration at C_4, hence are called epimers.
- **Osazones:** Monosaccharides and reducing disaccharides react with excess of phenyl hydrazine to form crystalline substances of the structure.



$$\begin{array}{l} CH{=}NNHC_6H_5 \\ | \\ C{=}NNHC_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}$$

It is known as osazone. Glucose, fructose and mannose give same osazone.

- **Sucrose ($C_{12}H_{22}O_{11}$):** Sucrose is most abundant in plants and known as cane sugar or table sugar or invert sugar.
- **Lactose or milk sugar:** It is present in milk of mammals and made up of one glucose and one galactose units. It is a reducing sugar.
- **Maltose or Malt sugar:** It is named because of its occurrence in malted grain of Barley. It is a reducing sugar.
- **Starch ($(C_6H_{10}O_5)_n$):** It is a polymer of α-glucose and a major reserve food in plants. It turns blue with iodine. It is a mixture of two components:

(i) Amylose (20%), an unbranched water soluble polymer.
(ii) Amylopectin (80%), a branched water insoluble polymer. Sources of starch are potatoes, wheat, rice, maize, etc.

- **Cellulose ($(C_6H_{10}O_5)_n$):** It is the most abundant and structural polysaccharide of plants. It is important food source of some animals. It is a polymer of β–D-(+) -glucose.
- **Glycogen:** It is found in animal body (mainly in liver and muscles) as reserve food and is called animal starch. Like starch, it is a polymer of α-D-glucose.

Test for Carbohydrates

- Molisch's test, it is positive for all carbohydrates.
- Iodine test, it is specific for starch and glycogen.
- Benedict's test, it is positive for reducing sugars.
- Barfoed's test, it differentiates between monosaccharides and disaccharides.
- Seliwanoff's test, it is positive for monosaccharides with ketonic group.
- Osazone test, it is the confirmatory test in which shape of crystals tell the type of sugar present in the solution.

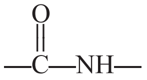
Amino Acids

The compounds containing amino group ($-NH_2$) and carboxylic group (–COOH) are called amino acids.

(*a*) **Neutral amino acids:** Having one $-NH_2$ and one –COOH group. E.g. glycine.
(*b*) **Acidic amino acids:** Having one $-NH_2$ and two –COOH groups. E.g. aspartic acid.
(*c*) **Basic amino acids:** Having two or more $-NH_2$ and one –COOH group. E.g. lysine.

- **Essential and Non-essential amino acids:** Amino acids synthesised in body are called non-essential amino acids and that are not synthesised in body are called essential amino acids.
- **Nomenclature:** They are known by their common names and abbreviated by first three letters of their common names e.g. glycine as 'gly' and alanine as 'ala'. Naturally occurring α-amino acids are L-amino acids.

Peptides

Peptides are condensation products of two or more amino acids,  $-\overset{\overset{\Large O}{\|}}{C}-NH-$ is known as peptide linkage. A polypeptide made up of n-amino acids has (n –1) peptide bonds.

- **Fibrous proteins:** Polypeptide chains are held together by hydrogen and disulphide bonds. Such proteins are insoluble in water. E.g. Keratin (present in hair, wool) etc.
- **Globular proteins:** These are usually soluble in water. E.g. Insulin, albumins.
- **Simple proteins:** These yield only α-amino acids upon hydrolysis. E.g. Albumin.
- **Conjugated proteins:** These yield α-amino acids and non-protein part, called prosthetic group.
- **Derived proteins:** These are obtained by partial hydrolysis of simple or conjugated proteins.

Denaturation of Proteins: The process that changes the three dimensional structure of native proteins is called denaturation of proteins.

Tests of Proteins

(*i*) Biuret Test: Protein solution + NaOH + dil. $CuSO_4 \rightarrow$ pink or violet colour.

(*ii*) Millon's Test: Protein solution + Millon's reagent → red colour.

Millon's reagent is a solution of mercuric nitrate and traces of sodium nitrate solution.

(*iii*) Iodine reaction: Protein solution + iodine in potassium iodide solution → yellow colour.

(*iv*) Xanthoproteic test: Protein solution + conc. $HNO_3 \rightarrow$ yellow colour $\xrightarrow{NaOH}$ orange colour.

Enzymes: Serve as biological catalyst e.g., pepsin, trypsin etc.

Vitamins: Vitamins are required by body to maintain normal health, growth and nutrition.

- Vitamins A, D, E and K are fat soluble whereas vitamins B and C are water soluble.
- Vitamin H is neither fat soluble nor water soluble.

Nucleic Acid: DNA and RNA

(*i*) DNA (Deoxyribonucleic acid).

$DNA + H_2O \rightarrow$ Phosphoric acid + deoxyribose + A, G, C, T

(*ii*) RNA (Ribonucleic acid).

$RNA + H_2O \rightarrow$ Phosphoric acid + Ribose + A, G, C, U

- In both DNA and RNA, heterocyclic base and phosphate ester linkages are at C_1 and C_5 respectively of the sugar molecule.

Hormones

These are the chemical substances which are produced by endocrine (ductless) glands in the body. Hormones acts as chemical messengers.

Insulin is a protein hormone. Its deficiency leads to diabetes mellitus.

CHAPTER

15

Polymers

- **Polymers:** Polymers are high molecular mass macro molecules.
- **Polymerisation:** The process by which the monomers (simple molecules) combine with each other and transform into polymers, is known as polymerisation.
- **Natural polymers:** Those polymers which occur in nature, i.e., in plants or animals, are called natural polymers, e.g. starch, cellulose, proteins, natural rubber.
- **Synthetic polymers:** The polymers which are prepared in the laboratory are known as synthetic polymers or man-made polymers, e.g. polythene, synthetic rubber, PVC, nylon 6,6, teflon, orlon etc.
- **Semi-synthetic polymers:** Polymers obtained by making some modification in natural polymers by artificial means, are known as semisynthetic polymers, e.g. cellulose acetate (rayon), vulcanised rubber etc.
- **Linear polymers:** These are the polymers in which the monomer units are linked to one another to form long linear chains, e.g., high density polyethene, nylon and polyesters are linear polymers.
- **Branched chain polymers:** In such polymers, the monomer units are linked to form long chains with some branched chains of different lengths attached to the main linear chain. Some common examples of such polymers are low density polyethene, starch, glycogen etc.
- **Cross-linked polymers or network polymers:** These are formed from bi-functional and tri-functional monomers. Examples of cross linked polymers are bakelite, glyptal, melamine-formaldehyde polymer etc.
- **Addition polymers:** The polymers formed by the polymerisation of monomers containing double or triple bonds (unsaturated compounds) are called addition polymers. e.g. polythene, orlon, PVC, Buna-S, etc.
- **Condensation polymers:** The polymers which are formed by the combination of monomers with the elimination of small molecules such as water, alcohol, hydrogen chloride etc., are known as condensation polymers, e.g. nylon 6,6, Dacron, Bakelite etc.
- **Elastomers:** These are rubber like solid polymers in which the polymer chains are held together by weakest intermolecular forces, e.g. natural rubber, Buna-S, Buna-N etc.
- **Fibres:** Fibres belong to a class of polymers which are thread-like and can be woven into fabrics. A few examples of this class are nylon 6,6, terylene and polyacrylonitrile (PAN).
- **Thermoplastics:** These are linear polymers and have weak van der Waals' forces acting in the various chains, e.g. polyethene and polystyrene.
- **Plasticizers** are high boiling esters or haloalkanes. These are added to plastics to make them soft like rubber.
- **Thermosetting plastics:** These are normally semifluid substances with low molecular masses. e.g., Bakelite, melamine-formaldehyde resin and urea-formaldehyde resin.
- **Free radical addition polymerisation:** The monomers used are generally monosubstituted alkenes.
- **Cationic polymerisation:** It involves formation of carbocation
- **Anionic polymerisation:** It involves formation of a carbanion.
- **Polyamides:** The polymers which contain amide linkages in chain are known as polyamide, e.g. nylon 6,6.
- **Natural Rubber:** Natural rubber is a coiled linear 1,4-polymer of isoprene.
- The process of introducing –S–S– crosslinks in the structure of rubber by heating with sulphur at 110°C is called **vulcanisation of rubber**.
- **Polyesters:** The polymers which contain ester linkages are known as polyester, e.g. dacron.
- **Biopolymers and Biodegradable Polymers:** Synthetic polymers are mostly non-biodegradable. Natural polymers are called biopolymers, e.g. polysaccharides, proteins, nucleic acids, etc. Biodegradable polymers can be easily degraded by microorganism in a reasonable period. Aliphatic polyesters are the common examples of biodegradable polymers.

Important Polymers

- Saran is a copolymer of vinylidene chloride and Vinyl chloride and is used for wrapping food materials.
- ABS rubber is a copolymer of acrylonitrile, buta-1,3-diene and styrene.
- Bubble gum contains styrene butadiene (Buna-S) rubber.
- Dynel is a copolymer of vinyl chloride and acrylonitrile and is used for making human hair wigs.
- Silk is a thread like natural polymer which is obtained from cocoons of silk worms. It is a natural polyamide fibre.
- Thermocol is a foamed plastic obtained by blowing air through molten polystyrene or polyurethane.

CHAPTER

16

Salt Analysis

INTRODUCTION

Qualitative analysis involves the detection of cation(s) and anion(s) of a salt or a mixture of salts.

Preliminary Test

1. **Physical appearance (smell):**

Table: 1

Take a pinch of the salt between your fingers and rub with a drop of water	
Smell	**Inference**
Ammoniacal smell	NH_4^+
Vinegar like smell	CH_3COO^-
Smell like that of rotten eggs	S^{2-}

2. **Flame test:**

Table: 2

Colour of Flame	Inference
Crimson Red	Lithium
Golden yellow	Sodium
Violet/Lilac	Potassium
Brick red	Calcium
Crimson	Strontium
Apple Green/Yellowish Green	Barium
Green with a Blue centre/Greenish Blue	Copper

3. **Borax Bead test:**

On heating, borax forms a colourless glassy bead of $NaBO_2$ and B_2O_3 .

$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$

On heating with a coloured salt , the glassy bead forms a coloured metaborate in oxidising flame.

For example, In oxidising flame, copper salts give blue bead.

$CuSO_4 \longrightarrow CuO + SO_3$; $CuO + B_2O_3 \longrightarrow Cu(BO_2)_2$ (blue bead)

4. Solubility Chart:

Table: 3

S. No.	Anion	Solubility / Exception
1.	CO_3^{2-}	Except carbonates of alkali metals and of ammonium, all other normal carbonates are insoluble.
2.	SO_3^{2-}	Only the sulphites of the alkali metals and of ammonium are water soluble. The sulphite of other metals are either sparingly soluble or insoluble.
3.	S^{2-}	The normal sulphide and polysulphide of alkali metals are soluble in water. The normal sulphides of most other metals are insoluble, those of the alkaline earths are sparingly soluble, but are gradually changed by contact with water into soluble hydrogen sulphides.
4.	NO_2^- , NO_3^-	Almost all nitrites and nitrates are soluble in water. $AgNO_2$ is sparingly soluble. Nitrates of mercury and bismuth give basic salts on treatment with water. These are soluble in dilute nitric acid.
5.	CH_3COO^-	Acetates are water soluble except Ag(I) and Hg(II) acetates which are sparingly soluble.
6.	Cl^-	Most chlorides are soluble in water. $PbCl_2$ (sparingly soluble in cold but readily soluble in boiling water), Hg_2Cl_2, AgCl, CuCl, BiOCl, SbOCl and Hg_2OCl_2 are insoluble in water.
7.	Br^-	Silver, mercury(I) and copper(I), bromides are insoluble. Lead bromide is sparingly soluble in cold but more soluble in boiling water. All other bromides are soluble in water.
8.	I^-	Silver, mercury(I), mercury(II), copper(I), lead and bismuth(III) iodides are the least soluble in water.
9.	SO_4^{2-}	The sulphates of barium, silver, lead are insoluble in water, those of calcium and mercury(II) are slightly soluble. Some basic sulphates of mercury, bismuth and chromium are also insoluble, but these dissolve in dilute hydrochloric or nitric acid.
10.	PO_4^{3-}	The phosphate of the alkali metals, with the exception of lithium and ammonium, are soluble in water ; the primary phosphate of the alkaline earth metals are soluble. All the phosphates of the other metals and also the secondary and tertiary phosphate of the alkaline earth metals are sparingly soluble or insoluble in water.

Analysis of ANIONS (Acidic Radicals)

Analysis of anions (acidic radicals) can be broadly divided into two groups.

(A) GROUP 'A' RADICALS: It involves those anions which are characterised by volatile products by reaction with HCl/ H_2SO_4. It is further subdivided into two groups as given below.

(a) Dilute Sulphuric acid/Dilute Hydrochloric acid: The anions of this group liberate gases or acid vapours with dilute sulphuric acid/hydrochloric acid.

Table: 4

Observation	Inference	
	Gas	Radical
Effervescence with the evolution of a colourless and odourless gas which turns lime water milky	CO_2	CO_3^{2-}
Evolution of colourless gas having smell of rotten egg which turns lead acetate paper black.	H_2S	S^{2-}
Colourless gas having suffocating odour (like burning sulphur) which turns acidified $K_2Cr_2O_7$ paper green.	SO_2	SO_3^{2-}
Evolution of reddish brown pungent smelling gas which turns **(i)** $FeSO_4$ solution brownish-black and **(ii)** wet starch –iodide paper blue.	NO_2	NO_2^-
Colourless gas having smell of vinegar.	HAc(g)	CH_3COO^-
No peculiar gas is evolved.	–	All above are absent

(b) Concentrated Sulphuric acid group: The anions of this group liberate acid vapours or gases with conc. H_2SO_4.

Table: 5

Observation	Inference	
	Gas	Radical
Colourless gas with pungent smell which gives dense white fumes with a glass rod dipped in NH_4OH.	HCl	Cl^-
Reddish brown gas with pungent smell, intensity of reddish brown fumes increases on addition of a pinch of solid MnO_2. Also, it turns starch paper, orange red.	Br_2	Br^-
Evolution of violet vapours which turns starch paper, blue.	I_2	I^-
Evolution of reddish brown fumes which intensifies on addition of copper turnings or bits of filter paper. Starch iodide paper develops a blue–black spot due to the formation of a I_2–starch complex. (NO_2 liberated acts as oxidising agent).	NO_2	NO_3^-

(B) GROUP 'B' RADICALS: Anions of this group do not give acid vapours or gases with dilute as well as concentrated H_2SO_4 but are characterised by their specific reactions in solutions. This group is further sub divided into two groups based on the type of the reactions.

(a) Oxidation and reduction in solutions: CrO_4^{2-}, $Cr_2O_7^{2-}$ etc.

(b) Precipitation reactions: These are given by SO_4^{2-}, PO_4^{3-} etc.

Observation	Inference
W.E. or S.E. + $BaCl_2(aq) \longrightarrow$ White precipitate, insoluble in dil. HCl and HNO_3	SO_4^{2-}
W.E or S.E + conc. HNO_3 (1–2 mL) + ammonium molybdate and boil $\rightarrow$ Canary yellow precipitate	PO_4^{3-}

Classification of Cations

Cations are classified into five groups on the basis of their behaviour with some reagents.

Table: 6

Group	Group Reagent	Ions	Colour and Ppt.
Group I	dil. HCl	Pb^{2+} , Hg^+, Ag^+	$PbCl_2$, Hg_2Cl_2, AgCl-White CdS, As_2S_3, As_2S_5, SnS_2 -Yellow
Group II A Group II B	H_2S in dil. HCl	Hg^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+} As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+}, Sn^{4+}	Sb_2S_3, Sb_2S_5 - Orange SnS - Brown HgS, CuS, PbS, Bi_2S_3 - Black
Group III	NH_4OH in presence of NH_4Cl	Fe^{3+}, Al^{3+}, Cr^{3+}	$Fe(OH)_3$ - Brown; $Al(OH)_3$ - White; $Cr(OH)_3$ - Green
Group IV	H_2S in presence of NH_3 and NH_4Cl or $(NH_4)S$	Ni^{2+}, Co^{+2}, Mn^{+2}, Zn^{+2}	ZnS - White or grey; CoS, NiS - Black; MnS - Buff (light pink)
Group V	$(NH_4)_2CO_3$ in presence of NH_4Cl and NH_4OH	Ba^{+2}, Sr^{+2}, Ca^{+2}	$BaCO_3$, $SrCO_3$, $CaCO_3$ - White
Group VI	No common group reagent	Mg^{2+}, Na^+, K^+	$Mg(NH_4)PO_4$ - White

CHAPTER

17

Chemistry in Everyday Life

- Medicine which promotes secretion of urine in order to get rid of your body from sodium salt and water is called diuretic.
- Antibiotic with broad spectrum acts on different types of antigen.
- Streptomycin ⟶ Antibiotic

  Novalgin ⟶ Analgesic

  Chloromycetin ⟶ Antibiotic

  Penicillin ⟶ Antibiotic
- Morphine belongs to a class of drugs known as **opioid** analgesics.
- Antiseptic action to dettol is due to chloroxylenol.
- **Diclofenac** sodium injection is not a narcotic.
- Paracetamol is antipyretic as well as analgesic.
- Chloroquine is required for malaria.
- Glycogenolysis occurs primarily in liver and is stimulated by the hormone adrenaline.
- Cocaine in early days of USA was used as antidepressant.
- Chloromycetin can be used for treatment of typhoid.
- Ampicillin is beta-lactum antibiotic. It is not a natural antibiotic.
- Tranquilizer is used for calmness and reduces anxiety.
- 2-acetoxybenzoic acid also called aspirin is used to treat pain, fever and inflammation. It is a class of antipyretic drug.
- Aspartame is only artificial sweetener that is stable at low temperatrure.